COHERERS, A REVIEW

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ABSTRACT

The first known radio frequency detector was the coherer, and even though this device has been around for over a century there is still no generally accepted explanation of how it works. A historical review of the different realizations of the coherer together with any investigations that might help illuminate its inner workings was under taken. As a result of the historical review, it became clear that the coherer evolved directly into the MOM (Metal-Oxide-Metal) 'diode' and, by only a slightly more circuitous route, it appeared as the forerunner to the STM (Scanning Tunneling Microscope). The MOM 'diode', besides being a progeny of the coherer, has something else in common with the coherer, no generally accepted explanation of how it works. Examining the history of the STM, from its nascent form (circa 1901) to its present day configuration, revealed along the way an explanation for bridge formation, i.e. cohering of coherers. In addition, in the course of reviewing some of the work done in the mid 1920s on coherer behavior, information surfaced that helps shed some light on the so-called positive and negative coherer behavior.

Lastly, the approach taken in this thesis, wherein the coherer was related to the MOM ‘diode’ and the STM, was found to have been completely anticipated by three papers (circa 1918-1924) written by Angelika Maria Josefa Székely de Doba.

ACKNOWLEDGEMENTS

No effort is ever truly an individual one. Even Sir Isaac Newton admitted as to how he had stood "…upon the shoulders of Giants." If I have managed to accomplish anything intellectually worthwhile in this thesis, it was only because of my clambering onto various shoulders. I should now like to thank those who helped me. First, my mother and father, Camille and Howard Cuff, for their encouragement, support and for their providing a quiet place for me to study and write. Second, my advisor, Dr. Thomas E. Sullivan, who allowed me to choose 'coherers' as my thesis topic and who then suggested that there might be useful and revealing links between coherers and MOM (Metal-Oxide-Metal) 'diodes' and STMs (Scanning Tunneling Microscopes) - there indeed were. I also wish to thank him for the innumerable hours he spent listening to my verbal discourses on the subject of this thesis, and for providing me with much needed pep talks when I became discouraged. Third, I wish to thank the other members of my thesis committee, Dr. Vallorie Peridier and Dr. Richard D. Klafter, for having read the various drafts of my thesis - a not inconsiderable task considering its size - and for their comments and especially their criticisms; their criticisms improved the readability, organization and grammar of my thesis, but all the remaining deficiencies in these three areas clearly are my own doing. A penultimate thanks must also go out to the W. W. Smith Charitable Foundation for their funding of my Future Faculty Fellowship. And lastly, I must express my appreciation to Dr. Vivian J. Phillips, whose book, Early Radio Wave Detectors, provided me with the inspiration to choose the subject of coherers for my thesis - thanks for the memories.

TABLE OF CONTENTS

LIST OF FIGURES

CHAPTER 1 - INTRODUCTION

“The most beautiful thing in the world is, of course, the world itself.”
- Wallace Stevens

“The universe is not only queerer than we imagine, but it is queerer than we can imagine.”
- J. B. S. Haldane

“God is in the details.”
-Ludwig Mies van der Rohe

Electrical engineers, physicists and material scientists have spent a considerable amount of time studying and characterizing the bulk properties of certain industrially important materials. The fact that materials are so important not just for technology but human affairs in general is perhaps best acknowledged by the temporal classifications of Stone Age, Bronze Age, Iron Age and currently the Silicon Age. In tandem with the search for new materials or, what sometimes amounts to the same thing, better purification of preexisting materials, there is also the inexorable trend towards miniaturization. Because the surface-to-volume ratio goes as 1/L, where L is the characteristic length of a body, as electronic or for that matter mechanical devices become smaller, this ratio gets larger and larger. As the surface-to-volume ratio increases, the surface begins to exercise a more dominant *rôle* on the electrical and mechanical behavior of the device. An example of these so-called size effects is the increase in electrical and thermal resistance of very thin wires. [1]

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[1] Kasturi L. Chopra; Thin Film Phenomena; McGraw-Hill; 1968; see the chapter entitled, Electron-Transport Phenomena in Metal Films.

It should be noted that while miniaturization implies that surface effects will be important, the converse is not true, i.e., significant surface effects do occur in macroscopic devices. Many times all it takes is for the macroscopic device to rely on current flow though an interface. Many macroscopic electrical devices are composed of mechanical junctions, e.g., mechanical switches, and in these devices, the surface takes on the *rôle* of an interface through which the electrons must pass, and so the condition of the surface is critical to the functioning of the device. This is especially true when the impressed voltage is small. In fact, coherer behavior is to Electrical Engineering what friction is to Mechanical Engineering, i.e., it is ubiquitous, confounding and fundamental. Thus, the subject of this thesis is the electrical attributes of mechanical junctions, either macroscopic or microscopic, under the influence of direct current, alternating current and the superposition of the two.

The first practical radio frequency detector was the coherer, which was composed of mechanical junctions. In its most basic realization, the so-called ‘single contact’ coherer consisted of two metal electrodes, whose surfaces had been slightly oxidized, lightly pressed against one another and biased with DC (Direct Current) voltage of usually <1.0 V. The coherer will be my starting point for an examination of the influence of the state of the surface of a metal on the conduction of electrons through this same surface. From its *début* in 1878, the exact mechanism by which it functions has been the subject of much experimentation and speculation, though substantive elucidation has not been forthcoming. Although the coherer ceased to be a commercially viable competitor for RF detection by 1905-1910, it had nevertheless spawned <u>two</u> offshoots which, while structurally and even sometimes functionally similar, are not usually thought of a having anything to do with coherers. These are the

MOM (Metal-Oxide-Metal) ‘diode’ and the STM (Scanning Tunneling Microscope).

It is the purpose of this thesis to examine the evolution of the coherer from its 19th century realizations to its current form as MOM ‘diodes’ and STMs. The main body of this thesis is concerned with the history of the coherer and its direct metamorphosis into the MOM ‘diode’. The MOM ‘diode’ never was much more than a laboratory curiosity from 1900 to 1930, after which time it effectively disappeared from view even from this cloistered venue. Starting in the late 1960s and going on to the present day, MOM ‘diodes’ have enjoyed a miraculously seeming resurrection as detectors and mixers of submillimeter microwave and later lasers. The history behind the rebirth of the MOM ‘diode’ is complicated enough that it has been relegated to APPENDIX A.

At the same time as the coherer was undergoing its transformation into the MOM ‘diode’ (circa 1900), the coherer was undergoing a somewhat more indirect reconfiguration into the STM. As will be shown in APPENDIX E, the STM arose in a very natural way from the efforts of researchers to extend the envelope of applicability of Paschen’s law to extremely small electrode separations. During this process, researchers, who were familiar with coherer behavior, noticed some striking similarities between the device used to check Paschen’s law at small interelectrode distances (the nascent STM) and coherers. One of the striking similarities was the ability of the nascent STM to cohere, under certain conditions, just like the coherer. An explanation of this cohering behavior had to wait until the 1950s and 1960s, when workers, studying the erosion of telephone switching relay contacts on closure, discovered a crucial set of conditions which gave rise to coherer-like behavior; this exhaustive research is documented in APPENDIX F.

By tracing the linkages, both historical and behavioral, among coherers, MOM 'diodes' and STMs, a group of mechanisms relating to coherer behavior has been brought to light. These mechanisms are not only applicable to coherers, but are equally adept at explaining some intrinsic limitations and some counterintuitive loopholes in the operation of vacuum microelectronic devices of today.

Lastly, I make no apologies for devoting the majority of this thesis to historical technical considerations. I realize that this approach to a technical problem is nonstandard, but I believe it to be just as informative if not more so than the current approach of burying the reader in mathematical models and computer simulations. As I have become more acquainted with early scientific writers, I have come to appreciate and hopefully have incorporated their tutorial style which allowed the subject under discussion to be understood by a wide audience of technically informed readers and not just a select few of the initiated. And besides which, to paraphrase someone famous, who was speaking about a more dire human enterprise, "History is much too serious a thing to be left to the historians."

CHAPTER 2 - HISTORY

“Of late it has been rather the custom to question the utility of history with reference to engineering in its various aspects; but those who are inclined that way should remember that it is only by a study of what has been done before that the repetition of failures and wrong methods can be avoided.”
- Sir Charles T. Bright, circa 1880s

Disregarding the ingenious but distinctly quaint and somewhat impractical coherer, the cat’s whisker semiconductor detector was the only useful device for the detection of signals in the early days of radio.
- Ernest Braun, circa 1992 [2]

Many technological solutions are discovered by serendipitous means or many times just by plain ‘dumb’ luck [3] without any true understanding of the physics behind the solution. If the solution has longevity, either because it is the most economical of the cadre of solutions to a given problem or simply because regardless of its cost it outperforms everything else, then by virtue of it being in the public eye, scientists will attempt and sometimes succeed in incorporating it into the current body of scientific knowledge by explaining the microscopic mechanism of its macroscopic behavior. But the catch is that the technological solution must hang around long enough to evince some interest by the scientific community.

During the early days of radio, there arose the need to have a way of detecting the incoming radio frequency excitations picked up by the receiving

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[2] Ernest Braun; Selected Topics from the History of Semiconductor Physics and Its Applications; in Lillian Hoddeson, Ernest Braun, Jürgen Teichmann, Spencer Weart (Eds.); Out of the Crystal Maze, Chapters from the History of Solid-State Physics; Oxford University Press; 1992; p. 445.

[3] According to Louis Pasteur, ‘dumb’ luck is a rare phenomenon, since according to him, “Chance favors the prepared mind.” A slightly different view was taken by Pailleron, “Have success and there will always be fools to say that you have talent.”

antenna. Heinrich Hertz, in his classic set of experiments, used an air spark gap to detect the presence of radio frequency energy. This was a great example of reciprocity since a spark gap was also employed to create the radio frequency energy at the transmitter. [4] We note in passing that the amount of serendipity accompanying Hertz's experiments is more than is fair for one person to have: the amplification of the effect of the receiving spark gap due to the light falling on it from the transmitting gap was noted by Hertz and generated enough interest in other researchers to be given a name and explanation, the photoelectric effect. However, the spark gap as a detector was nothing to write home about. Subsequent experiments carried out by J. J. Thomson and a Mr. J. B. Peace revealed that approximately 300 V was required to produce a visible spark between the two balls employed in Hertz's spark gap receiver. [5] 275 V represents pretty much the absolute minimum voltage which will cause an electrical discharge to occur in a air regardless of its pressure, the electrode separation or the electrode material. [6] As we will see later, this result explains

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[4] The oscillatory nature of the discharges from an underdamped RLC circuit made up of Leyden jars, wires and a spark gap (a crude spark gap transmitter) were known as far back as ~1825. Today if called upon to prove this fact experimentally, we would most likely employ a digital storage oscilloscope to capture the discharge waveform. Around the mid-1800s there were two ways of demonstrating this fact: i) if the LC product was large enough so that the circuit's resonant frequency was in the audio range, the resulting spark could be heard to sing briefly at this frequency; ii) for RLC circuits oscillating at RF frequencies of a couple of megahertz, the oscillatory nature of the discharge could be deduced by photographing the oscillating light from the spark gap using a rotating mirror which swept the image of the spark across a piece of film [today this is called a streak camera and it was invented by Sir Charles Wheatstone in 1834]; the image on the film is a series of equally spaced and slightly elongated bright spots. The first person to utilize the rotating mirror technique to photograph sparks was Berend Feddersen in 1858. Feddersen's method was improved upon by J. Jamin & Rogers (1868), C.V. Boys (1890), L. Décombe (1898) and C. Tissot (1901) to name a few; Décombe and Tissot refined this approach to the point where they could show that not only was the discharge oscillatory, but also damped - the intensity of the elongated bright dots on the film diminished with time. Also see the following reference,

Vivian J. Phillips; Waveforms, A History of Early Oscillography; Adam Hilger; 1987; chap. 1.

[5] Joseph John Thomson; Notes on Recent Researches in Electricity and Magnetism; Clarendon Press; 1893; pp. 84-90.

[6] Leonard B. Loeb; Fundamental Processes of Electrical Discharge in Gases; John Wiley & Sons, Inc.; 1939; p. 413ff.

why STMs (Scanning Tunneling Microscopes) can function in air (see APPENDIX E). As far as its commercial use in the then nascent field of radio communication was concerned, prospects for this type of detector did not look good. Quite simply, the spark gap detector - no matter what form it took - lacked sensitivity and a better detector was needed. A solution to this technological problem manifested itself in the form of the Branly filings coherer, 'invented' by Édouard Branly.

The construction of the Branly coherer is simplicity itself: take a glass tube open at both ends, partially fill it will metal filings (e.g., nickel & iron or silver & nickel, etc.), insert a silver plug in each end of the tube to allow electrical contact to made with the filings and prevent them falling out, wait a few hours for an oxide film to form on the filings, and you are finished.[7] The coherer has two terminals: A & B. Terminal A is connected to the antenna; terminal B is connected to the ground (earth); the series circuit of a radio frequency choke (RFC), telephone receiver, low voltage battery, current limiting resistor and another radio frequency choke has one end connected to terminal A and the other to terminal B (see Fig. 1). The chokes are necessary to prevent the RF energy from being shunted by the series circuit containing the telephone receiver, current limiting resistor and battery.

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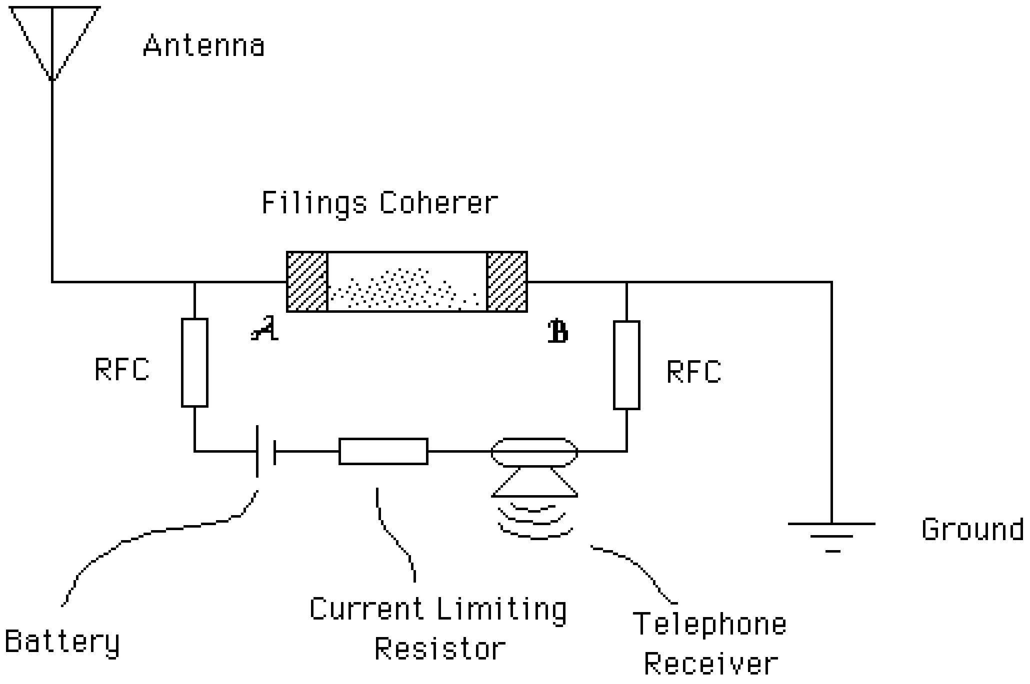
[7] Donald McNicol; Radio's Conquest of Space; Murray Hill;1946. [An even better and more recent source of information on the early days of radio is,
Hugh Aitken; Syntony and Spark; John Wiley & Sons, Inc.; 1976.
where 'syntony' is an archaic synonym for resonance.]

FIGURE 1- Marconi Type Radio Receiver (circa 1900)



The operation of the Branly filings coherer is rather simple. Initially, the resistance of the coherer is very high and so no DC current passes through it, but as soon as it senses the radio frequency (RF) energy coming down the antenna its resistance drops dramatically, and DC current flows through it thus completing the circuit containing the telephone receiver, which produces a sound. Note, once the filings coherer is in its conducting state it does not usually spontaneously revert to the nonconducting state, but must be coaxed with a sharp rap. The technical term for this process of hitting the detector to restore its high resistance state is decohering.

This basic design of the Branly coherer was improved upon by numerous workers including Guglielmo Marconi who used it in his earlier commercial radio sets. It should be mentioned for completeness that Branly also invented a somewhat more reliable version of his coherer called the Branly tripod detector. The tripod detector consists of three vertical steel pins, connected together at their tops as if to form an all metal three legged stool; the ends of the three legs, sharpened and slightly oxidized by heating, rested on a polished steel base, the counterelectrode. Thus, instead of relying on the multitudinous contacts between the filings, the tripod version of the coherer has only three contacts. As with all other coherers, the tripod detector is biased with a small DC voltage, and when an RF signal is impressed across it, something happens to the oxide layer to cause its DC resistance to drop; as was the case with the filings coherer, the tripod coherer must be decohered by a sharp mechanical shock - usually administered to the base.

Once the world was made aware of the existence of the coherer, quite naturally people attempted - and in some cases succeeded - in improving on its initial design, fabrication and use. The list of persons who were associated with some phase of coherer development includes such heavy-hitters as O. J. Lodge, G. Marconi, A. Popov, A. Blondel, E. Dorn, W. H. Eccles, J. Stone Stone, [8] and legions of lesser known scientists, engineers and inventors. The intense search for newer and better coherers led to the discovery of, for example, self-restoring coherers, i.e., coherers which spontaneously returned to the sensitive or high resistance state.

The exact mechanism of the coherer behavior was and still is not known. One idea, that was proposed by a number of people, was that the

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[8] John Stone Stone - two Stone's - was his name.

incoming RF energy caused the individual particles making up the coherer to weld or fuse together forming a conductive path between the electrodes, thus requiring a mechanical shock to sever the conductive link. "This has been shown by producing coherence in a coherer of iron filings and subsequently removing the loose filings with a magnet, leaving the chains of particles; also, by producing coherence in a tube of brass filings, and observing that the resistance lengthwise of the tube was very much lower than that transversely." [9] This quote, from a paper by Robert H. Goddard - the 'Father' of rocketry, indicated that welding or fusion of some type can take place, but the question was whether it was <u>necessary</u> for coherer action?

The main problem with this welding and/or fusion scenario is the existence of what Jagadis Chandra [Chunder] Bose [10] called negative coherers, i.e., coherers whose resistance <u>increased</u> upon exposure to RF energy; according to Bose's nomenclature a coherer whose resistance decreases [increases] upon exposure to RF energy is a positive [negative] coherer. [11] Bose had undertaken

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[9] R.H. Goddard; On Some Peculiarities of Electrical Conductivity Exhibited by Powders and a Few Solid Substances; Physical Review; Vol. 28; 1909; pp. 403-428.

[10] **Note**, do not confuse - as I did - Jagadis C. Bose with Satiendranath N. Bose, who is most famous for his part in formulating Bose-Einstein statistics. J.C. Bose led an eclectic intellectual life being equally at home in both the physical and life sciences. See,

S.N. Bose; <u>Jagadis Chandra Bose</u>; National Book Trust, India; 1970. [This is a rather difficult book to locate, but I was able to find it in the Van Pelt library of the University of Pennsylvania under the Library of Congress Call Number, Q 143 B36B3.]

[11] J.C. Bose; On a Self-Recovering Coherer and the Study of the Cohering Action of Different Metals; Proceedings of the Royal Society (London); Vol. 65; 1899; pp. 166-172. [J.C. Bose was not the first person to notice negative coherer behavior, that honor falls to one A. Neugschwender,

A. Neugschwender; Eine neue Methode, elektrische Wellen nachzuweisen [A New Method of Detecting Electrical Waves]; Annalen der Physik und Chemie [Annals of Physics and Chemistry]; Vol. 67; 1899; pp. 430-432.

Idem; Eine neue Methode, elektrische Wellen nachzuweisen [A New Method of Detecting Electrical Waves]; Annalen der Physik und Chemie; Vol. 68; 1899; p. 92-98.

Other researchers who contributed to knowledge regarding negative coherer behavior included,

E. Aschkinass; Theoretisches und Experimentelles über den Cohärer [On the Coherer]; Annalen der Physik und Chemie; Vol. 66; No. 2; 1898; pp. 284-307.

the task of trying out most of the metallic elements of the periodic chart as coherer material, when he chanced upon the anomalous, i.e., negative, behavior of potassium and arsenic, among others. [12] The potassium coherer, which in construction consisted of lumps of potassium under kerosene between two electrodes, besides exhibiting negative behavior was also self-restoring. And, yes, he did check the behavior of other alkali metals (specifically sodium and lithium), and found that they too exhibited negative behavior, although they were not as sensitive as potassium. As if things were not complicated enough, Bose also showed that positive coherers could, with the judicious application of pressure and/or applied DC bias, be made to act in the manner of a negative coherer. And just so that there was no dearth of confusion, the potassium coherer, for example, was shown to go reversibly from negative to positive behavior by changing the intensity of the incident RF radiation, all other conditions such as DC bias and pressure were kept constant constant. It should also be noted that there are certain positive coherers where welding and/or fusion can't take place. The carbon-on-shiny-steel coherers of David E. Hughes (see next paragraph), which were also self-restoring, cannot weld since carbon does not weld with itself or steel; in fact, carbon does not even melt, it sublimes. Another positive, self-restoring coherer that can't undergo welding was the tantalum-in-mercury coherer of Mr. L. H. Walter. [13] And finally there were the negative coherers formed using lead peroxide, PbO_2, and cupric sulfide, CuS.

E. Branly; Accroissements de Résistance des Radioconducteurs [Increase of Resistance of Radioconductors]; Comptes Rendus Hebdomadaries des Seances de l'Acadamie des Science (Paris) [The Weekly Review Session of the Academy of Science (Paris)]; Vol. 130; April 17,1900; pp. 1068-1071. Note, at the time Branly wrote this article, the term 'coherers' was not yet in wide use and hence Branly referred to them as 'radioconductors'.]

[12] J.C. Bose; On the Periodicity in the Electric Touch of Chemical Elements (Preliminary Notice); Proceedings of the Royal Society (London); Vol. 66; 1899/1900; pp. 450-474.

[13] L.H. Walter; A Tantalum Wave-Detector, and its Application in Wireless Telegraphy and Telephony; Proceedings of the Royal Society (London); Vol. 81 (Series A); 1908; pp. 1-8. [Note, after 1905 the Proceedings of the Royal Society were split into a Series A and B.]

No theory of coherers can be considered complete without the incorporation of negative coherer behavior.

As we shall see later on in case of the carbon microphone, determining who actually invented a particular device can lead the searcher down the path to madness due to the extraordinary number of persons claiming to be the legitimate 'Father' of the device. This is the situation in the case of the coherer also. Most books on the history of radio credit Oliver J. Lodge with coming up with the name 'coherer', and with fielding his own version of the device; Branly's coherer was apparently conceived and built independently and without knowledge of Lodge's ideas. However, the first known single contact coherer, though it wasn't called that by its inventor, was discovered by David E. Hughes in 1879 with many other versions being constructed between 1879 and 1886. What might you ask was Hughes doing with a coherer before the 'official' discovery of electromagnetic waves by Heinrich Hertz in 1888? The rather surprising answer is that he was employing his coherer to detect radio waves generated by his transmitter; Hughes was transmitting and receiving radio waves approximately ten years before Hertz! Not only was Hughes doing some of the things which Hertz would later become famous for, but he did it with better equipment, e.g., Hughes detected the RF energy using a coherer, which was much more sensitive than the crude spark gaps ultimately employed by Hertz. The reason Hertz and not Hughes was considered to be the one who confirmed James Clerk Maxwell's theory about the existence of electromagnetic radiation was that Hughes never published his findings in a journal, scientific or otherwise.

Hughes' exploits are known to us today through a curious set of circumstances. Some time around 1899, J. J. Fahie [pronounced 'Fay' [14]] set out to write a popular account of the history of wireless telegraphy between the years 1838 and 1899. [15] In the course of his writing, Fahie happened upon an article which quoted William Crookes as having personally witnessed and participated in a demonstration of wireless transmission and reception around 1879. When Fahie requested more details from Crookes about this experience, he was informed by Crookes that the events, alluded to in the article, had taken place at the residence of David E. Hughes on Dec. 1879. At this point Fahie sent Hughes a letter asking him for details of his experiments and any subsequent conclusions. At first Hughes refused, saying, "At this later date I do not wish to set up any claim to priority, as I have never published a word on the subject…". Later, Hughes changed his mind and sent a brief but lucid description of what had transpired between 1879 and 1886. Note, this account by Hughes is not very detailed, the actual nuts-and-bolts of what he did can only be found in his laboratory notebooks; Hughes' letter to Fahie was also published, in full, in the *The Electrician*. [16] The gist of the story was that Hughes discovered that the making and/or breaking of a contact, which allowed current to flow through his induction balance, produced a sensible effect in a separate and distant circuit containing a carbon microphone and telephone receiver; the microphone apparently rectified the RF signal which was then heard over the receiver. It is important to note that Hughes initially ascribed this behavior to nothing more complicated than magnetic coupling between the two separate circuits - the

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[14] Charles Süsskind; Observations of Electromagnetic-Wave Radiation Before Hertz; Isis; Vol. 55; 1964; pp. 32-42.

[15] J.J. Fahie; A History of Wireless Telegraphy (1838-1899); Dodd, Mead, and Co.; 1899.

[16] D.E. Hughes; Prof. D. E. Hughes's Researches in Wireless Telegraphy; The Electrician (London); Vol. 43; 1899; pp. 40-41.

same principle explicitly used in his induction balance.[17] However, further experimentation convinced him that magnetic induction could not possibly account for the observed effect. In particular, he noted that the effect persisted even when the coils in the transmitting circuit were removed, and the orientation of the two circuits arranged so as to minimize their mutual inductance. Hughes was particularly suited to the task of eliminating the possibility of magnetic induction as the causative agency, since he was one of the foremost authorities in the field of magnetism and magnetic induction at the time.[18]

In an attempt to optimize the behavior of the detector, Hughes tried a different approach. He installed a small voltage source in series with the detector and telephone receiver so that when the resistance of the detector fell, due to the incident pulse of RF energy, the detector now acted like a switch, allowing the current from the voltage source to flow through the receiver causing an audible click to be heard. This latter approach to detecting the incident RF energy presages the way coherers were to be employed by Marconi in his commercial radio sets (circa 1895-6). However, unlike Marconi's version of the coherer, Hughes' coherer was not bistable, i.e., it spontaneously decohered and so did not require any mechanical shock to return it to the high resistance state as would be the case with Marconi's coherer 15 years later. Hughes' coherer was in fact a carbon microphone. "I found that all microphonic contacts or joints were

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[17] D.E. Hughes; On an Induction-Currents Balance, and Experimental Researches made therewith.; Proceedings of the Royal Society (London); vol. 29; May 15, 1879; pp. 56-65.

[18] Of the ten papers credited to David E. Hughes in the *Proceedings of the Royal Society (London)*, eight of them were on the subject of magnetism or magnetic induction, see,

Anon.; Index to the Proceedings of the Royal Society of London (Old Series), Vols. 1-75, 1800-1905; 1913; p. 113.

For an even more interesting and in depth discussion of Hughes' process of elimination of the known causes of electrical coupling between separate circuits see,

J.O. Marsh, R.G. Roberts; David Edward Hughes: inventor, engineer and scientist; Proceedings of the IEE; Vol. 126 (Series A); No. 9; September 1979; pp. 929-935.

extremely sensitive. Those formed of a hard carbon such as coke, or a combination of a piece of coke resting upon a bright steel contact, were very sensitive and self-restoring; whilst a loose contact between metals was equally sensitive, but would cohere, or remain in full contact, after the passage of an electric wave." [19]

Considering all the ahead-of-his-time things that Hughes did, why didn't he publish his findings? Naturally Hughes was both excited and puzzled by the results of his experiments, excited by the novelty of the results and puzzled by what they meant - not being familiar with Maxwell's highly mathematical treatise on the subject of electromagnetism. So he did what any scientist in his position might have done, and invited various experts to examine his apparatus and participate in a demonstration of the wireless telegraphy. The experts included,

> Dec. 1879. - Mr. W. H. Preece, F.R.S.; Sir William Crookes, F.R.S.; Sir W. Robert[s]-Austin, F.R.S.; Prof. W. Grylls Adams, F.R.S.; Mr. W. Grove.
>
> Feb. 20, 1880. - Mr. Spottiswoode, Pres. R.S. [Royal Society]; Prof. [Thomas] Huxley, F.R.S.; Sir George Gabriel Stokes, F.R.S.
>
> Nov. 7, 1888. - Prof. [James] Dewar, F.R.S.; Mr. Lennox, Royal Institute. [20]

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[19] J. J. Fahie; Ibid.; pp. 290-291 [Appendix D.].

[20] Ibid.; p. 293.

This partial guest list provided by Hughes was indeed impressive. In fact, with only one exception, all its members were and, in some cases, still are famous.

William Grylls Adams did work on the action of light on selenium. Sir William Crookes discovered thallium, invented the vane radiometer, and spinthariscope. Sir James Dewar invented the insulating flask that bears his name, demonstrated the paramagnetic properties of liquid oxygen and ozone, produced and studied the physical properties of liquid and solid hydrogen, [21] and co-invented cordite with F. A. Abel. Sir William Robert Grove was famous for the Grove battery, which had a high voltage per cell and low internal resistance making it able to deliver large currents. [22] Thomas Henry Huxley named the phylum coelenterata, and popularized Darwin's evolutionary theories. Sir William Henry Preece sponsored G. Marconi in his bid to produce the first commercial wireless telegraphy set, and served as a intellectual scratching post and punching bag for Oliver Heaviside. [23] Sir William Chandler Roberts-Austin invented an automatic pyrometer for high temperature work, and showed that diffusion in solids was possible by pressing together gold sheet and a lead block. William Spottiswoode did extensive work extending and standardizing the

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[21] It is not generally appreciated today that James Dewar succeeded in producing solid hydrogen as far back as 1899, see,

J. Dewar; Solid Hydrogen; Nature; Vol. 6; May-October 1899; p. 514. [An essentially word-for-word translation of this article into French can be found in the following citation,

J. Dewar; Sur la solidification de l'hydrogène [On the solidification of hydrogen]; Comptes Rendus Hebdomadaries des Seances de l'Academie des Sciences (Paris); Vol. 129; July-December 1899; pp. 451-454.]

[22] According to,

Allen G. Debus (Ed.); <u>World Who's Who in Science</u>; A. N. Marquis Co.; 1968; p. 713.

Grove also did, "Research on electrolytic decompositions, including 1st demonstration of dissociation of water;..." This appears to be <u>in</u>correct. According to a number of sources (see below), the first persons who demonstrated decomposition of water were William Nicholson and Sir Anthony Carlisle on May 2, 1800 - eleven years before Grove was born. See,

Malcolm Dole; <u>Principles of Experimental and Theoretical Electrochemistry</u>; McGraw-Hill Co., Inc.; 1935; p. 5.

Floyd L. Darrow; <u>The New World of Physical Discovery</u>; The Bobbs-Merrill Co.; 1930; p. 149.

[23] Paul J. Nahin; <u>Oliver Heaviside: Sage in Solitude</u>; IEEE Press; 1987; chap. 5.

subject of determinants. Sir George Gabriel Stokes laid the foundation for the field of hydrodynamics and did an enormous amount of original work in mathematical physics. [24]

The demonstration all these learned gentlemen witnessed included reception of the signal from as far away as 500 yards and they were suitably impressed and no doubt mystified. Now for the strange part. Stokes allegedly told Hughes that the phenomenon although occurring over large distances was due solely to induction and was not anything new! Hughes claims he was so disheartened by this pronouncement by Stokes that he decided not to publish his experiments and their results. That Hughes should give in to Stokes so easily is understandable given Stokes' acknowledged expertise in all things having to do with physics, and the fact that Hughes was only a professor of music. [25] Hughes' pre-Hertzian exploits are today almost completely forgotten, but this was not always so. Most books on the history of wireless telegraphy published before about 1930 do credit Hughes with having been the first to transmit and detect radio waves, [26] it is the later histories, after approximately 1930, which have

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[24] Allen G. Debus (Ed.); World Who's Who in Science; A. N. Marquis Co.; 1968; p. 1, 389, 454, 713, 850, 1372, 1431, 1589, 1616.

[25] I wish to thank Elliot Sivowitch, Division of Electricity and Modern Physics, Smithsonian Institute for pointing out to me the peripatetic nature of Hughes' life. Although David Edwards Hughes was born in London (May 16, 1830), his parents moved to Virginia in 1837 and Hughes attended St. Joseph's College, Bardstown, Kentucky where he became a professor of music. His interest in experimental science, especially having to do with electricity, caused him to teach both music and physical science courses at St. Joseph's. In a bid to win recognition for his invention of a typeprinting telegraph he eventually moved back to England, then to the Continent, and finally back to England. A more detailed description of Hughes' life can be found in,

Sir Leslie Stephen, Sir Sidney Lee (Eds.); The Dictionary of National Biography, Vol. XXII, Supplement; Oxford University Press; 1937-38; pp. 877-879.

[26] G.G. Blake; History of Radio Telegraphy and Telephony; Chapman & Hall Ltd.; 1928; pp. 38-46. [Reprinted in 1974 by the Arno Press.]

Charles R. Gibson, William B. Cole; Wireless of To-Day; Seeley, Service & Co. Ltd.; 1924; pp. 55-57.

gradually downplayed Hughes' contribution and in some instance even his very existence. [27]

Once coherers had been firmly ensconced in the minds of scientists and engineers, there were many review papers and books written on the subject. A number of these reviews attempted to trace the origins of the coherer as far back in time as was possible. Some of these historical postmortems managed to locate the first known description on coherence in metal and/or carbon particles to 1835 and one Munk of Rosenschöld.

In 1904, K. E. Guthe wrote a coherer review article in *The Electrician* in which he mentioned Munk of Rosenschöld's discovery in 1835, but, in an infuriating lapse of regard for future readers, provided no reference to the original source. [28] Fortunately, a footnote to this article indicated that it was actually an abstract of a talk presented at the 1904 International Electrical Congress, St. Louis, Missouri. [29] Upon examination of the Transactions of the Congress, it was found that Guthe's paper did indeed have a bibliography. The bibliography, however, did <u>not</u> reveal any articles or books authored by Munk of Rosenschöld, but, according to the annotations accompanying the first two citations: a paper by G. Schlabach and a book by Augusto Righi and Bernhard Dessau contained

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[27] It would be interesting to hear Stokes' own version of these events and this may indeed be possible, since just recently, a compendium of Stokes' correspondence with Lord Kelvin and vice versa has been published,

David B. Wilson; <u>The Correspondence Between Sir George Gabriel Stokes and Sir William Thomson, Baron Kelvin of Largs, Vols. 1 & 2</u>; Cambridge University Press; 1990.

Perhaps somewhere in these two massive tomes, there is a letter from Stokes to Lord Kelvin discussing the events that transpired at Hughes' lab and his [Stokes'] reaction to them.

[28] K.E. Guthe; Coherer Action; The Electrician (London); Vol. 54; November 4, 1904; pp. 92-94.

[29] K.E. Guthe; Coherer Action; in A.E. Kennelly, W.D. Weaver (Eds.); <u>Transactions of the International Congress, St. Louis, 1904, Vol. 1</u>; J.B. Lyon Co.; 1905; pp. 242-255.

bibliographies going well back into the 1800s.[30] Perusal of the *Physikalische Zeitschrift* article written by Schlabach did uncover the exact venue of Munk of Rosenschöld's original work: an 1835 article in the journal *Annalen der Physik und Chemie*, followed in 1838 by another article in the same journal.[31] Examination of these *Annalen der Physik und Chemie* articles revealed that Guthe's and Schlabach's Munk of Rosenschöld was actually P. S. Munck of Rosenschöld in Lund, hereafter referred to as P. S. Munck or simply Munck. Note, this corruption of Munck's name continues unabated into modern times, e.g., see the book on early transistors by Thomas R. Scott.[32] Guthe's synopsis of this research was that Munck unequivocally demonstrated that a tube, which contained metal or carbon particles, suffered a reduction in resistance due to the discharge of a Leyden (Leiden) jar, which could only be reversed by shaking the tube.

Guthe next traced the coherer phenomenon to "…Varley…" circa 1870 - another terse and inchoate reference. Again, going to the first two citations in Guthe's bibliography yielded a more substantial fund of information. To wit, Samuel Alfred Varley and his brother Cromwell Fleetwood Varley, while investigating the 'critical voltage' required to cause a tube of powdered lead or

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[30] G. Schlabach; Der heutige Standpunkt der Kohärerfrage [The Current Thinking on the Coherer Question]; Physikalische Zeitschrift; Vol. 2; No. 26; 1901; pp. 383-387.

Augusto Righi, Bernard Dessau; Die Telegraphie ohne Draht [Wireless Telegraphy]; Druck und Verlag von Friedrich Vieweg und Sohn; 1907; pp. 228-274. [Note, Righi and Dessau correctly identify Munck, unlike Guthe and Schlabach.]

[31] P.S. Munck; Versuche über die Fähigkeit starrer Körper zur Leitung der Elektrizität [Experiments on the Ability of Solid Bodies to Conduct Electricity]; Annalen der Physik und Chemie; Vol. 34 (2nd Series); 1835; pp. 437-463.

Idem; Untersuchungen über Elektriztät, mit besonderer Rücksicht auf die Theorie der galvanischen Kette [Investigation of Electricity, with special Consideration of the Theory of the Galvanic Series]; Annalen der Physik und Chemie; Vol. 43 (2nd Series); 1838; pp. 193-227.

[32] Thomas R. Scott; Transistors and Other Crystal Valves; MacDonald & Evans, Ltd.; 1955; pp. 1 & 237.

carbon to cohere, hit upon the idea of using this as a lightning arrester for telegraph systems, and presented their ideas and results at the British Association [for the Advancement of Science] meeting held in Liverpool in 1870. [33] To be exact, Samuel Alfred Varley noticed in 1852 the high resistance of finely powdered blacklead [?] and wood charcoal, and in 1856 the surprising decrease on this resistance in the presence of a thunderstorm. These observations incited Samuel and Cromwell Varley to harness this effect for the purpose of protecting overland telegraph systems. [34] Both brothers were familiar with such systems. In fact, Cromwell F. Varley was a member of the Electric and International Telegraph Co. from 1846 to 1868 when it was nationalized and so was well versed in land lines used for this purpose; in addition, he was also directly involved with the Atlantic submarine telegraph cable. [35] The first two citations in Guthe's bibliography also reveal that between

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[33] S.A. Varley; On the Mode of Action of Lightning on Telegraphs, and on a New Method of constructing Telegraph-coils.; in Anon.; Report of the Fortieth Meeting of the British Association for the Advancement of Science held at Liverpool in September 1870; John Murray; 1871; pp. 28-30. [**Warning**, some books incorrectly identify S.A. Varley as Stephen A. Varley. See, for example,

Donald McNicol; Radio's Conquest of Space; Murray Hill Books, Inc.; 1946; p. 108.]

[34] See British Patent Specification No. 165 of 1866 in which the Varleys discussed their lightning arrester. It consisted of two metal points (electrodes) about 1/18 inch apart in a box of powdered carbon mixed with a nonconducting substance and was dubbed the 'lightning bridge'. Also see,

[Sir] John Ambrose Fleming; The Principles of Electric Wave Telegraphy and Telephony; Longmans, Green, and Co.; 1919; p. 366.

Note, lightning protectors or arrestors had been in use with telegraph systems for years, before S.A. Varley invented his so-called 'lightning bridge'. These earlier protectors usually consisted of a small spark gap, one end of which went to ground (earth) while the other end was collected to the equipment requiring protection. But as Varley, who had extensive practical experience with telegraph system of the day, noted, these spark gap protectors many times failed to protect the equipment they were connected across. Even today, modern lightning protectors are not all they are cracked up to be. See,

L. Dayton; Pendulum swings into action against lightning; New Scientist; Vol. 133; No. 1803; January 11, 1992; p. 23.

[35] Cromwell Fleetwood Varley is today more famous than his brothers Samuel Alfred Varley and Frederick Henry Varley. His fame rests mainly and justifiably on his accomplishments in the field of submarine telegraphy. One invention to his credit - or more to his brother Samuel, by some accounts - was the development of a simulacrum (model) of the submarine telegraph cable. This functioning model, composed of n RC sections in cascade, allowed telegraph stations to test their sending and receiving equipment with a known 'good' cable - the model. This was very

P. S. Munck (1835) and the Varley brothers (1852, 1856, 1866 & 1870), a number of other researchers investigated the behavior of finely divided conducting substances, but Munck and the Varleys are good milestones: Munck because he appears to be the first to have researched the phenomenon and the Varleys because they appear to have been the first to have applied this research to a commercially important technology.

Before continuing it should be noted that the Hertzian spark gap and Branly coherer were not the only detectors vying for a place in the sun. It seems that everyone was trying to build a better mousetrap as far as detecting radio waves was concerned. The list of detector inventors included such luminaries as Lord Rutherford, who while still a student at the Canterbury College in New Zealand constructed and elucidated the mechanism of a magnetic radio wave

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important for troubleshooting since it allowed the operators to unequivocally ascertain whether it was the sending and receiving equipment or the cable that was the problem. The model also served well as an pedagogical and promotional tool. See,

C.F. Varley; On the Atlantic Telegraph; Notices of the Proceedings at the Meetings of the Members of the Royal Institution of Great Britain; Vol. 5; 1866-1869 (February 8, 1867); pp. 45-59. [**Warning**, do not confuse this journal, which after 1928 was called the *Proceedings of the Royal Institution of Great Britain*, with the *Proceedings of the Royal Society (London)*. The Royal Institution was founded in 1799 by Benjamin Thompson (a.k.a. Count Rumford); the Royal Society of London was founded in 1660. In addition, this is not an easy journal to locate, but I was able to located it at the library of The Academy of Natural Sciences of Philadelphia, a member of the Philadelphia Area Consortium of Special Collections Libraries.]

Besides the model cable, C.F. Varley was responsible for the invention, by himself or in collaboration with S.A. Varley, of numerous other devices and systems used in undersea telegraphy. For example, the use of capacitors, at both ends of the cable to 'curb' the signal and by doing so increase the signaling rate, was one of the innovations pioneered by him. In the field of overland telegraphy, he instituted the process of 'killing' the wire, which involved stretching the freshly drawn wire past its elastic limit. This process improved the mechanical properties of the wire by reducing the objectionable springiness induced by drawing and also broke out the bad spots. Varley's interests were not restricted to the field of telegraphy. Witness his invention of the cymaphen (telephone), an instrument presaging the Bell telephone, in August 1877; his observations of electrocapillary phenomenon in 1870; and he proposed the idea that cathode rays were made of material particles. **Note**, the entry for C.F. Varley in

Sir Leslie Stephen, Sir Sidney Lee (Eds.); The Dictionary of National Biography, Vol. 20; Oxford University Press; 1937-38; pp. 149-150

is incorrect in stating that the date of public exhibition of Varley's cymaphen was 1870. See the August 1877 announcement in,

Anon.; Notes; The Telegraphic Journal; Vol. 5; August 1, 1877; p. 178.

detector. Rutherford's magnetic detector utilized the ability of high frequency discharges to magnetize the surface of an iron wire. That the magnetization occurred only on the surface of the iron wire was shown conclusively by first magnetizing the wire with a high frequency discharge, then removing the outer layer of the wire with nitric acid and, finally, noting that the magnetization of the wire had subsequently vanished. [36] It must be noted that Rutherford did not discover the magnetic RF detector. That honor actually goes to Joseph Henry who, on or about 1842, discovered that violent electrical discharges could magnetize iron needles situated far away from the spark or arc. [37] Because of his desire to pursue this line of inquiry and the rather recalcitrant nature of lightning discharges - never around when you need them, and always around when you don't - Henry tried to see if the same phenomenon occurred with artificial sparks, such as those generated by a Leyden jar. It turned out that man made sparks also could magnetize steel needles at large distances. The resulting magnetization of the needles was sometimes in one direction and sometimes in the opposite direction. As a direct result of this observation, Henry postulated that the discharge of the Leyden jar [38] was oscillatory - he was right, but confirmation had to wait for the spinning mirrors of Décombe and Tissot.

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[36] Emilio Segrè; From X-Rays to Quarks; Freeman;1980; pp. 48-49. [For the original paper see Ernest Rutherford; The Collected Papers of Lord Rutherford of Nelson, under the Scientific Direction of Sir James Chadwick; Interscience; 1962-1965; Vol. 1.]

[37] Vivian J. Phillips; Early Radio Wave Detectors; Peter Peregrinus Ltd.; 1980; p. 1. [This is a truly wonderful book that devotes a whole chapter, 47 pages, just to coherers, not to mention his equally detailed chapters on spark gap, electrolytic, magnetic, thin film & capillary, thermal, tickers and miscellaneous detectors.

According to David E. Hughes, Professor Joseph Henry had this work published by the Smithsonian Institute; Wash., D. C.; Vol. 1; around 1850; p. 203. Hughes states this in his previously cited 1899 article in *The Electrician*.]

[38] The Leyden jar, in its modern form, was reinvented in 1746 by Sir William Watson and John Bevis [or Bevans], an English astronomer and physician. The modern form of the Leyden jar employed a tin foil covering on the inside and outside of the glass jar to substantially increase its capacitance, this arrangement was, of course, the same configuration used in all modern day capacitors of which the Leyden jar was the progenitor. As to the question of who first discovered the Leyden jar, I offer up the following three candidates: Peter [Pieter] Van Musschenbroeck of Leyden, Dean [Ewald Georg] Von Kleist of Camin in Pomerania, and Cunœus of Leyden; the

Unfortunately for the coherer, more reliable, cheaper and sensitive detectors came on the scene: the galena (PbS) [pyrites (iron sulfide, a.k.a. fool's gold), perikon (zinc oxide), etc.] catwhisker crystal detector, the carborundum crystal detector, the Fleming vacuum rectifier (vacuum diode), the De Forest Audion tube (vacuum triode), the germanium crystal detector, and finally the silicon crystal detector (a.k.a. the silicon diode). This was not to say that these other detectors were initially so great themselves. They weren't. For example, the galena detector, which consisted of a hunk of galena crystal mounted in a metal base and probed by a springy metal point contact - the so-called catwhisker - was notoriously unreliable. Given two pieces of galena from the

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general scientific community appears to have been informed about this discovery early in 1746. I have offered only this brief history knowing full well that it is infinitely disputable, every book or article mentioning this device accredits its discovery and evolution to a different person or persons. See,

Park Benjamin; <u>The Intellectual Rise in Electricity</u>; D. Appleton and Co.; 1895; pp. 510-523.

As if the confusion regarding its discovery weren't enough, consider the following conundrum resulting from an experiment performed around 1748. Benjamin Franklin, after hearing about the wondrous properties of the Leyden jar, decided to try and find out on which part of the jar the electricity resided. The Leyden jar he employed was simply a bottle filled partly with water; a cork with a wire through it was inserted in the neck of the bottle so that one end of the wire dipped in the water. To charge this Leyden jar, one held the bottle in one hand - to provide a ground connection - and applied the charge to the wire sticking up out of the cork. After first charging up the jar, Franklin removed the cork with its wire electrode and while holding the jar with one hand, he touched the surface of the water inside the jar, and received a very strong shock for his trouble. This result forced him to conclude that the electricity resided, not on the wire or cork, but in either the water or the glass. He was able to eliminate the water as the repository of the electricity by showing that if one charged up Leyden jar #1, removed its cork and wire, and transferred the water to another Leyden jar #2, which initially was both uncharged and contained no water, jar #2 <u>still</u> had no charge. However, if the Leyden jar #1 was partially refilled with water from a grounded teakettle, it was then found capable of imparting a significant shock. From these simple experiments Franklin was able to surmise that the electricity resided on the glass. Note, the same result is had even using a more modern form of the Leyden jar, i.e., one with a metal electrode on the outside as well as the inside. See,

I. Bernard Cohen; <u>Benjamin Franklin Experiments</u>; Harvard University Press; 1941; pp. 191-194.

The answer to why the charge was on the glass, instead of on the metal electrode(s), where we would expect it to be, had to wait for its resolution until the year 1922, when G.L. Addenbrooke solved the riddle,

G.L. Addenbrooke; A Study of Franklin's Experiment on the Leyden Jar with Movable Coatings; Philosophical Magazine [and Journal of Science]; Vol. 43 (6th Series); January-June 1922; pp. 489-493.

same source one might work, i.e., rectify, and the other might not no matter how long or assiduously it was probed with the catwhisker contact. Nevertheless, these other detectors had the potential to be improved and eventually were. The coherer resisted further improvement, and since no one back then - or now - understood why they worked in the first place, there was no way of systematically improving its performance - all improvements were strictly by luck. And since the coherer did not stay around very long (1894-1905), [39] no explanation was ever forthcoming as to why they worked, and to add insult to injury, its very existence was almost - see below - forgotten by everyone including the scientific community.

So, in the end, we are still left with the original question about how coherers work, since even today there is no explanation backed with experimental proof of what happens to the coherer when it is exposed to radio frequency energy. Why should we care about the mechanism behind the success of the coherer's operation, such as it was? Well for one thing the coherer exhibits bistable behavior, i.e., it could be used as a memory device. Just think of it, a tiny coherer which goes into the "1" or conducting state when exposed to RF energy and can be returned to the "0" or nonconducting state by a mechanical jostle - perhaps we can enlist Maxwell's Demon to do the bumping! As we shall see later in the section WHAT IS KNOWN (pre-1970), a serious attempt was made during the early 1950s to study the feasibility of coherer-based computer memories and/or logic gates.

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[39] Vivian J. Phillips; Early Radio Waves Detectors; Peter Peregrinus Ltd.; 1980; p. 113.

The other funny thing about the coherer is that it keeps turning up in modern technical literature. I mean, it's gone but yet not forgotten. How else would you explain an article in the May 1967 issue of Popular Electronics [40] which describes how to build and test a coherer, or the offhand mention of it and the lack of any good explanation of its behavior in the 1990 revised retrospective [41] of the semiconductor industry written by the Director of the Max Planck Institute for Solid State Research in Stuttgart, Germany? My contribution to the subject of coherers will be to keep the subject alive so that, hopefully, someone might eventually divine the true nature of the mechanism behind this deceptively simple device.

Unlike modern solid state devices, which must be constructed out of materials that are both structurally perfect (in the crystallographic sense) and chemically pure (so that they may be doped to carefully controlled levels employing chemically pure 'impurities'), coherers and their descendants, MOM 'diodes' and STMs, do not need these utopian-like conditions. In fact, most electronic components, whether of today or yesteryear, are realized out of materials whose morphology and pedigree are distinctly nonutopian. It is with these thoughts in mind that we now consider briefly the stuff from which coherers were constructed.

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[40] H.B. Davis; The Coherer; Popular Electronics; May 1967; pp. 47-50. [Davis builds his version of the coherer using a mixture of 5% silver and 95% nickel filings - the same combination used by Marconi.]

[41] Hans Queisser; The Conquest of the Microchip; Harvard University Press; 1990; pp. 8-9.

CHAPTER 3 - AMORPHOUS MATERIALS

> "It is and it must in the long run be better for man to see things as they are than to be ignorant of them."
> - A. E. Houseman

> "And I am living in a material world, and I am a Material Girl."
> - song, Material Girl, by Madonna

"The existence of a periodic lattice of ions lies at the heart of modern solid state physics. It provides the basis for the entire analytical framework of the subject, and without it comparatively little progress would have been made." [42] As the previous quote indicates physicists have a real tough time with anything other than an infinitely large single perfect crystal. Unfortunately, there are many useful materials - probably most - which do not fit into the category of an infinitely large single perfect crystal. The coherer is obviously not constructed of a single perfect crystal, but there are also many other examples of things both commonplace and esoteric which operate using so-called disordered/amorphous materials or materials exhibiting extremely fine polycrystalline structure which, in the limit as the size of the individual crystallites decreases, approaches the amorphous state:

1) Every time you use a telephone manufactured by Western Electric, you make use of a carbon button microphone. No big deal, you say. Wrong! This simple device not only is a transducer, converting acoustic energy into electrical signals, it is also an amplifier. The amplification factor is on the order of +40 dB [43] (100X), this is definitely not a passive device. [44] One can build an oscillator

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[42] N.W. Ashcroft, N.D. Mermin; Solid State Physics; Holt, Rinehart & Winston; 1976; p 62.

[43] Bruce E. Briley; Introduction to Telephone Switching; Addison Wesley; 1983; pp. 1-2 & 10-11. [This book also contains the bizarre story of how in 1889 an embalmer named Almon Brown Strowger invented the first automatic telephone switching system, after he found out he was

using just a DC power source, a speaker or receiver from a phone and a carbon button microphone. In fact, a gentleman named Alfred Graham invented, on or about 1890, an audio oscillator consisting of a series electrical circuit of a carbon microphone, electromagnetic telephone receiver, battery and switch with the positive feedback provided by acoustically coupling the microphone and receiver to one another via a length of corrugated tube.[45] As Briley states, "Even experienced electrical engineers [and I suppose physicists, also] are sometimes taken aback by the claim that the carbon microphone is an active device." It is no exaggeration to say that without the inherent amplification provided by the carbon button microphone, the pre-vacuum tube telephone system would not have been possible; the condenser and electromagnetic microphones have better fidelity but they are passive devices and so require electronic amplification using either tube or transistor circuits. Alexander Graham Bell's original demonstration of the telephone employed a single electromagnetic receiver/transmitter at both ends of his system; the reciprocal nature of the

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losing business to a competitor because the competitor's sister-in-law was the local exchange's switchboard operator and was directing all requests for embalming services to her brother-in-law's establishment! See also,

W.A. Atherton; Pioneers 19; Electronics & Wireless World; Vol. 94; No. 1629; July 1988; pp. 677-678.

We will revisit Strowger's SXS (Step-by-Step) switching mechanism later on as an example of a system loaded with coherer-like junctions.]

[44] Electrical engineers divide the menagerie of electric components they employ into two general categories: passive and active devices. Passive components, examples of which include resistors, capacitors and inductors, are usually - but not always - two-terminal devices, which have no ability to produce a power gain. Active components, examples of which include vacuum tubes and transistors, are usually - but not always - devices with three or more terminals, which do have the ability to produce a power gain, i.e., amplify, by means of a control terminal such as the control grid of a vacuum tube or the base terminal of an injection transistor. Note, a step-up transformer is a four-terminal device in which the output voltage is larger than the input voltage, but it is still classified as a passive device. The reason is that there is no power gain. Even though the output voltage is higher than the input voltage, the input current is higher than the output current and so the output power (output voltage times output current) equals the input power. Actually, the output power is slightly less - by anywhere from 1to 4% - than the input power due to the inevitable dissipative losses within the transformer, itself.

[45] J.G. McKendrick; Note on Mr. Alfred Graham's Method of Producing Sound by an Electrical Arrangement; Proceedings of the Royal Society (Edinburgh); Vol. 21; 1895-96; pp. 46-48.

electromagnetic transducer allows it to function as both a transmitter and a receiver. Of course, Bell's original system [46] only went between two rooms. This system with its electromagnetic transducer was impractical for long distance communications due to the attenuation introduced by just the transducers themselves, ignoring the line losses: "…an electromagnetic receiver would roughly convert one thousandth of the applied electrical power into acoustic power in the ear canal. The efficiency of a similar device used as a transmitter would not be identical but would be of the same order of magnitude. Thus the dual conversion from acoustic to electric waves and back to acoustic would provide the listener with about one millionth of the voice power at the transmitting end, i.e., it would suffer a "loss" of -60 dB." [47] To appreciate just how good carbon microphones are, consider this fact. "One of the longest unrepeatered [not amplified by tube, transistor or auxiliary circuits] telephone routes used in this country [United Kingdom] was that from London to Glasgow, a distance of about 400 miles [line losses were ~-16 dB]." [48]

Today, the carbon button microphone has two major competitors, the electret and electromagnetic microphone, both of which require external

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[46] Actually, the electromagnetic transmitter came later. The transmitter used by Bell on March 10, 1876 to utter the immortal words, "Mr. Watson, come here; I want you!", was a liquid rheostat type of transmitter in which a metal needle attached to the back of the diaphragm was submerged in a high resistance liquid; the movement of the needle to different depths within the liquid, in response to the sound pressure on the diaphragm, caused the current flowing through the transmitter to change. Note, Bell got the idea for the liquid rheostat from a transmitter invented by Philip Reis in Germany. In Reis' liquid transmitter, the needle attached to the diaphragm, made and broke contact with the surface of the conducting liquid due to sound waves impinging on the diaphragm. As was mentioned earlier Cromwell Fleetwood Varley had perfected his cymaphen in 1877, and succeeded that same year in transmitting music via a normal telegraph line from Canterbury Music Hall in Westminster Bridge Rd. to the Queen's Theatre in Long Acre.

[47] M.D. Fagen (Ed.); A History of Engineering and Science in the Bell System, The Early Years (1875-1925); Bell Telephone Labs, Inc.; 1975; pp. 63-64.

[48] George Shiers (Ed.); The Telephone, An Historical Anthology; Arno Press; 1977; p 270.

amplification.[49] The dielectric materials that can form electrets are, like the carbon aggregates used in the carbon microphone, microcrystalline substances such as hard waxes (e.g., carnauba and candelilla) and amorphous materials such as plastics which have completely superseded waxes in this *rôle*.

Ferreting out the inventor of the carbon microphone - it was not Mr. Bell - is a rather frustrating task since many references appear to give priority to different people. The list of candidates for the coveted position of carbon microphone inventor include: David E. Hughes, Franz Hermann Robert [?] Lüdtge,[50] Thomas Alva Edison, Emile Berliner, Henry Hunnings,... If

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[49] Most technical people are, no doubt, familiar with some type of electromagnetic sound transducer (speakers, microphones, telephone receivers, etc.), but the term 'electret microphone' probably does not have as wide an acquaintance. Briefly, an electret is a dielectric able to exhibit a permanent external macroscopic electric field. The constituent molecules of most normal dielectrics, while they may have, individually, a significant dipole moment, do not produce collectively any macroscopic electric fields because the dipole moments are oriented randomly to one another. In an electret, the individual molecules with their dipole moments can be made to exhibit large scale organization, i.e., all the molecule can be made to line up facing the same direction (homocharge). In addition, the conducted charge can be frozen in place temporarily (heterocharge); it is this heterocharge which is responsible for the short term transient variations in the sign of the electret field. Consider carnauba wax, if it is brought to the melting point, then placed in an electric field - say, between the plates of an air capacitor - and then allowed to cool and solidify in the presence of the imposed field, the constituent dipole molecules will be oriented and frozen in position. A similar process is used to create magnets. In fact, the name 'electret' was originally chosen by Oliver Heaviside to suggest the idea of an ELECTRical magnET. Note, at the time Heaviside conjured up this name, electrets were just an idea as no one had actually made any. It was not until 1919, that the Japanese physicist, Mototarô Eguchi, while investigating electrical conduction in waxes, had the idea of trying to freeze these charges in place. Although he first published in 1919 in the *Proceedings of the Physico-Mathematical Society of Japan*, this journal is not generally available so the following citation is offered,

M. Eguchi; On the Permanent Electret; Philosophical Magazine [and Journal of Science]; Vol. 49 (6th Series); January-June 1925; pp. 178-192.

A good review article on the subject is,

A. Gemant; Recent Investigations on Electrets; Philosophical Magazine [and Journal of Science]; Vol. 20 (7th Series); November 1935; pp. 929-952.

[50] [F.H.R.] Lüdtge; title unknown; Dinglers Polytechnisches Journal; Vol. ???; 1878; pp. 220-???.

Idem; Das Universaltelephon [Universal Telephone]; Polytechnisches Notizblatt für chemiker, gewerbtreibende, fabrikanten und Künstler; Vol. 34; 1878; pp. 97-??. [**Warning**, I have been unable to locate these articles or find correct citations to them. Note, Lüdtge was granted a German patent on his Universal Telephone on January 12, 1878. See,

Silvanus P. Thompson; Philipp Reis Inventor of the Telephone, Biographical Sketch; E. & F.N. Spon; 1883; p. 152.]

"…success has many fathers, but failure is an orphan…", then the carbon microphone, its technical merits notwithstanding, is definitely a success on this account. Although it probably will never be known with any certainty, it is a good bet that Hughes [51] and Lüdtge were the simultaneous and independent inventors of the carbon microphone in 1878. One thing that most sources do agree upon is that Edison was the one who did the most exhaustive search for alternate materials for the carbon microphone and ultimately settled on lampblack.

As was his style, Edison utilized the shotgun approach to finding the best material for the job. A partial list of the most efficacious materials he found includes: lampblack, [52] hyperoxide of lead [lead peroxide], iodide of copper, plumbago (graphite), gas carbon & platinum black. Other candidates included, "Finely divided materials which do not oxidize in the air, such as osmium, ruthenium, silicon, boron, iridium and platinum…". [53] It should also be mentioned that Edison designed and built a commercial receiver which worked like a carbon microphone but in the reverse sense. This receiver was called the chalk drum receiver. [54] In this receiver, a rotating drum of chalk, saturated with a solution of potash (a mixture of potassium hydroxide and potassium carbonate) and mercuric acetate, made a mechanical contact with a flat metal spring

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[51] D.E. Hughes; On the Action of Sonorous Vibrations in varying the Force of an Electric Current; Proceedings of the Royal Society (London); Vol. 27; May 9, 1878; pp. 362-369.

[52] Edison produced lampblack by the expedient of using kerosene lamps, whose wicks had been adjusted to produce a smoky flame. The lampblack accumulated on the glass mantle where it was removed by gentle scrapping. See,

William S. Pretzer (Ed.); Working at Inventing: Thomas A. Edison and the Menlo Park Experience; Henry Ford Museum & Greenfield Village; 1989; p. 93.

[53] Ibid.; pp. 122-123. [Whether, in fact, osmium, ruthenium, iridium and platinum are not oxidized in air is and has been the subject much controversy. The resolution of this controversy is important to an understanding of the mechanism of the coherer, and will be dealt with in APPENDIX B.]

[54] I Ibid.; pp. 96-97.

attached to a thin metal diaphragm; the attractive force between the metal spring and the rotating chalk drum was modulated by the voltage or current impressed across the receiver, and this time varying normal force produced a time varying tangential force on the metal spring strip which, in turn, caused the diaphragm to move thus reproducing the sound (see Fig. 2). The normal force generated at the interface between a metal and a poor conductor (e.g., marble, agate, etc.) when a voltage difference is applied is known as the Johnsen-Rahbek effect, after the two Danish telephone engineers who rediscovered it around 1923, this effect is not named after Edison, who patented his chalk drum telephone in 1877, because as Johnsen and Rahbek point out, the first person to patent a device based on this effect was actually Elisha Gray around 1875.[55] Johnsen and Rahbek were well acquainted with Edison's chalk receiver, which they referred to by its original name: the Edison Electromotograph, but they did not believe that it functioned by the Johnsen-Rahbek effect. They maintained that Edison's apparatus worked by modulating the coefficient of friction between the parts in

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[55] According to,

Ragnar Holm, Else Holm; Electric Contacts, Theory and Application, 4th Ed.; Springer-Verlag; 1967; p. 60.

Edison was issued an English patent (No. 2909) for his chalk drum telephone receiver on July 30, 1877 with an addition in 1878. The following references give more insight into the Johnsen-Rahbek effect,

A. Johnsen, K. Rahbek; A Physical Phenomenon and its Application to Telegraphy; Journal of the Institution of Electrical Engineers (London); Vol. 61; No. 320; July 1923; pp. 713-725.

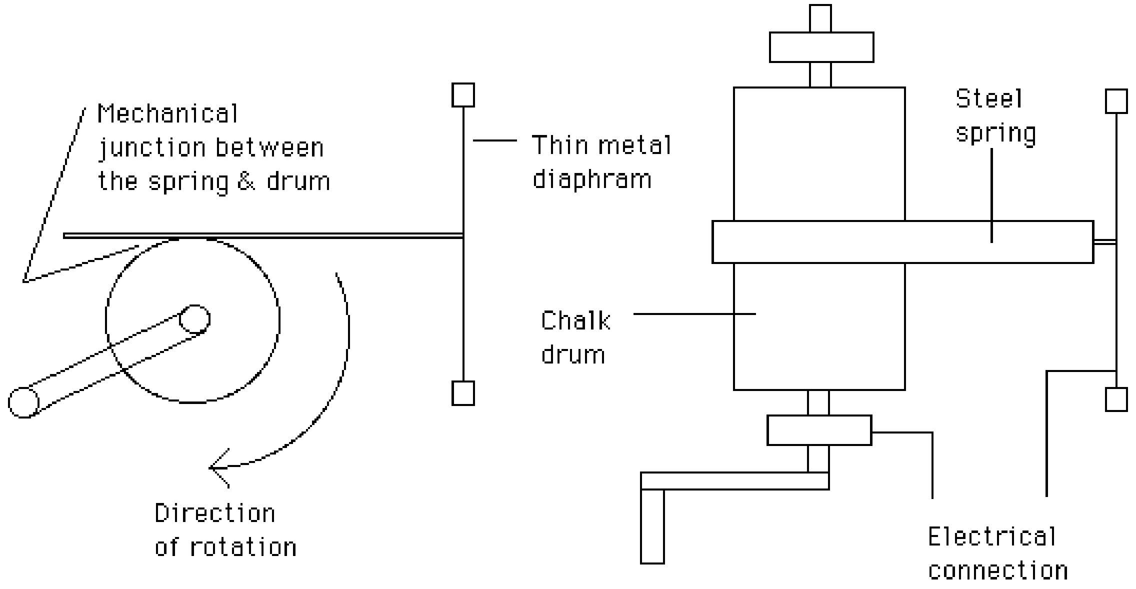
A.D. Stuckes; Some Theoretical and Practical Considerations of the Johnsen-Rahbek Effect; Proceedings of the Institution of Electrical Engineers (London); Vol. 103 (Pt. B); 1956; pp. 125-131.

It should be noted that the formation of a capacitor using a slab of polished stone and a metal plate did not start with Johnsen and Rahbek, but can be traced all the way back to the work of Alessandro Volta in 1782. Volta was looking for a way to 'amplify' small amounts of charge, quantities so small that they would not register even on an electroscope. His solution was to bring the charged object in contact with the metal plate of a metal-stone 'multiplier'. Since the capacitance of the multiplier was very large, most of the charge was transferred to it. The contact between the charged object and the multiplier was then broken and the metal was lifted off of the stone by means of an insulated handle causing the voltage of the metal stone capacitor to increase enormously. This voltage could then be easily detected by an electroscope. For more details see,

A. Volta; Of the Method of rendering very sensible the weakest Natural or Artificial Electricity.; Philosophical Transactions of the Royal Society (London); Vol. 72; 1782; pp. vii-xxxiii + xxxv.

contact mostly likely by the generation of gas between these parts, while the Johnsen-Rahbek effect occurs through modulating the normal force of attraction between the parts in contact.

FIGURE 2 - Edison's Chalk Receiver (Two Views)



Note, lampblack is not so much a material as a process, the same thing being true of charcoal, activated charcoal, coke, etc. These carbonaceous materials are not 100% carbon, they are instead mixtures of hydrocarbons and other 'stuff' with carbon being the principle constituent by weight. Subsequent research discovered that a far better material - pressed lampblack being among other things very friable - was anthracite coal from a <u>particular</u> mine in Pennsylvania. Better processing eventually vitiated the need to sole source the coal - a good thing too since this mine did ultimately run out.[56] The processing of the anthracite was as follows. "This coal was crushed in a specified manner, sifted, purified in a stream of air, and roasted according to a procedure that had been carefully studied by H. H. Lowery and his colleagues. This procedure produced particles of nearly uniform size and spherical shape and reduced the hydrogen content of the carbon without leaving pores that would have absorbed atmospheric gases and impair performance. A deposit of pyrolytic carbon, formed from the decomposition of methane gas, smoothed the surface of the granules further and increased their elastic modulus."[57] [58]

Except for its lack of bistability, the carbon microphone with its ability to convert sound waves to electrical energy appears very similar to the Branly coherer with its ability to transform RF energy to AF (Audio Frequency) electrical energy, and, as we have seen, David Hughes used it to do just that in his early

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[56] S. Millman (Ed.); A History of Engineering and Science in the Bell System, Physical Sciences (1925-1980); AT&T Bell Labs; 1983; pp. 555-561.

More details about the locations and characteristics of the particular types of anthracite coal utilized in the telephone transmitter can be found in the following references,

J.R. Fisher; Coal for Transmitters; Bell Laboratories Record; Vol. 10; September 1931 - August 1932; pp. 150-154.

W.E. Orvis; Coal Talks; Bell Laboratories Record; Vol. 10; September 1931 - August 1932; pp. 200-204.

[57] S. Millman (Ed.); Ibid.; p 555.

[58] Recently, there has been great interest in the newly discovered allotropic form of carbon called buckminsterfullerene (a.k.a. buckyballs), which in its most stable form is designated C_{60} and is arranged in the form of a soccer ball or closed geodesic dome, i.e., truncated icosahedron popularized by R. Buckminster Fuller, with the carbons at the vertices. Buckyballs are produced in quantity by vaporizing graphite in a 100 torr (760 torr = 1 atmosphere) helium atmosphere; gently scrapping the resulting soot off the glass walls of the vacuum chamber; dissolving the soot, which is only made up a few percent by weight of buckyballs, in benzene or some other nonpolar solvent, thus bringing only the buckyballs into solution; and finally evaporating away the benzene carrier to obtain pure buckyballs. See,

W. Krätschmer, L.D. Lamb, K. Fostiropoulos, D.R. Huffman; Solid C_{60}: a new form of carbon; Nature; Vol. 347; September 27, 1990; pp. 354-358.

There is some evidence that buckyballs may experience an electrical conductivity change in response to mechanical pressure. Perhaps this new allotrope of carbon can be used as the active ingredient in future carbon microphones and perhaps also in carbon coherers - it's an idea worth thinking about.

experiments on the transmission of radio waves. The reversible [nonbistable] behavior of the carbon aggregate used in the microphone is a very desirable quality from the point-of-view of a transducer; the Branly coherer's commercial lifespan probably would have been much longer had it possessed reversible behavior, i.e., if you didn't have to jar it to return it to the high resistance state. This last statement may appear contradictory, given what we said earlier about there being self-restoring coherers. However, it is not. The self-restoring type of coherer was not considered to be reliable enough for widespread day-to-day commercial applications, although it was employed successfully by both the military and commercial sector in a number of countries on a limited basis. As far as whether the Branly coherer is a passive or active device, I do not know nor have I seen anything in the literature which unequivocally answers this question, although, as we shall later, W. H. Eccles obtained some experimental results which had a bearing on this question.

2) While we are on the subject of carbon, let us not forget one of the most basic applications of amorphous carbon to the electronics industry, the carbon composition and the carbon film resistor. Carbon composition resistors are the workhorse resistors of the electronics industry. They are easy to make, cheap, reliable, have a wide range of resistances [1.0 - ~22 MΩ], [59] exhibit only a small voltage coefficient [-0.5 V/VDC] and moderate temperature coefficient [±1200 ppm/C], are relatively immune to radiation damage, and are ideal for use in high frequency applications due to their low self-inductance and capacitance. Their

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[59] It is not generally appreciated that the lower limit of the resistance range of carbon composition resistor is 1 Ω (actually 2.7 Ω). That this is indeed the case is documented in the following references,

Thomas H. Jones; Electronic Components Handbook; Reston Publishing Co., Inc.; 1978; p. 106.

Bruce D. Wedlock, James K. Roberge; Electronic Components and Measurements; Prentice-Hall, Inc.; 1969; p. 77.

disadvantages: lack of stable resistance value, thermally generated and current generated [60] electrical noise [especially above 1 MΩ] and mediocre tolerance [±5% min.] are more than made up for by their already mentioned advantages.

The 'carbon' slug that is the heart of the carbon composition resistor is a slurry of "… finely ground carbon or graphite, an inert nonconducting filler, usually silica, and a synthetic resin binder…" which is then sintered in a furnace.

3) Another ubiquitous circuit component which owes its existence to amorphous materials is the capacitor. No matter whether we are talking about plastic, ceramic, aluminum electrolytics or tantalum electrolytics they all depend on some type of amorphous material for their dielectric. [61]

4) Although the original silicon solar cells were constructed from single crystal silicon wafers, this proved to be too expensive for anything other than communication satellites or other similarly high-priced/high-tech ventures. Large area silicon solar cells, for earthbound uses in sunracers, solar houses, etc., only became commercially viable with the advent of amorphous silicon solar cells. [62]

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[60] This current generated noise is the effect utilized in the carbon button microphone. [For more information and references on resistors in general see,

Thomas H. Jones; Electronic Components Handbook; Reston;1978; Chapters 4 & 5.]

[61] D.M. Trotter; Capacitors; Scientific American; Vol. 259; No. 1; July 1988; pp. 86-90B. See also,

W.J. Bernard; Developments in Electrolytic Capacitors; Journal of the Electrochemical Society; Vol. 124; No. 12; 1977; pp. 403C-409C.

[62] D. Adler, S.R. Ovshinsky; Amorphous Photovoltaics; CHEMTECH; September 1985; pp. 538-546.

5) Where would we be without the xerox machine? But the xerographic process could not exist without the amorphous chalcogenous materials used in its toners.

6) Coal. It is not only the raw material for carbon button microphones, carbon composite resistors, etc., but it was used in World War II by the Germans as a source of synthetic fuel since Germany had no oil fields of its own.

Considering how useful a material coal was, it was surprising to find that no systematic investigation was undertaken of is composition and properties until World War II, when Rosalind Franklin [63] began an exhaustive and in-depth inquiry into the chemical, physio-chemical and crystallographic make-up of this rather neglected natural wonder. The crystallographic analysis must have been rather daunting given the amorphous nature of this class of materials. Franklin's research led her to divide hydrocarbon materials into two distinct groups depending on whether or not pyrolysis in an inert atmosphere yielded graphite or not; the end result of the pyrolysis of nongraphitizing hydrocarbons were known as amorphous, vitreous or glassy carbons to differentiate them from graphite. [64]

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[63] Rosalind Franklin is probably worst known as "Rosy" in,

James Watson; The Double Helix; Atheneum; 1968.

where she has her character assassinated by Watson's poisoned pen. People who have read Watson's account of the elucidation of the structure of DNA owe it to themselves - if not to Franklin - to read about this discovery from another point-of-view, e.g.,

Anne Sayre; Rosalind Franklin & DNA; Norton; 1975.

[64] The citations of Rosalind Franklin's work are too numerous to list in this thesis, but a good number of them can be found on pp. 204-206 of Anne Sayre's book (see previous footnote), also see,

Ragnar Holm, Else Holm; Electric Contacts, Theory and Application, 4th Ed.; Springer-Verlag; 1967; Appendix 5: Structure, electrical and thermal conductivity of carbon, pp. 404-412.

Briefly, Franklin would take a nongraphitizing hydrocarbon such as polyvinylidenechloride (a.k.a. Saran, as in Saran Wrap) and heat it to 1000°C in an oxygen-free nitrogen atmosphere until it stopped giving off HCl gas. The resulting material, which resembled coke, was >99.4% carbon and had a distinct metallic luster. Besides its characteristic x-ray diffraction patterns of

These amorphous carbons, turned out to have wide ranging commercial applications, and are used today to make tubing, crucibles, re-entry vehicle ablation shields, etc.

Note, most of Franklin's work on coal and nongraphitizing carbon was done in Paris between 1947 and the end of 1950, with a few retrospective papers on the subject published between 1950 and 1956. In 1951 Franklin was offered a post at King's College, London, the responsibilities of the position included setting up a x-ray crystallographic lab to do work on biological macromolecules, something she was imminently qualified to do given her experience with amorphous materials. It is at this point in time that the controversy about the discovery of the structure of DNA began.

7) The vacuum tube industry owes its existence to a phenomenon it cannot completely explain, namely thermionic emission from oxide coated filaments and indirectly heated cathodes. The amorphous alkaline oxide coating significantly increases the production of thermionic electrons over what can be achieved with a clean bare tungsten filament. However, just coating the filament cathode or indirectly heated cathode with the oxide mixture (barium and strontium or calcium oxide) is not enough. The coating must be activated by a combination of higher than average filament temperature and plate-to-cathode (or filament in the case of a filament cathode) voltage. The best explanation to

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diffuse bands superimposed on sharp lines, these amorphous carbons could also be differentiated from pure graphite by their almost complete resistance to chemical attack by Brodie's reagent (concentrated nitric acid + potassium chlorate).

date of what happens during the activation process is that electrolysis takes place in this coating resulting in the reduction of, e.g., barium ions to metallic barium at the interface between the coating and the cathode, and then the subsequent diffusion of some of this metallic barium to surface of the oxide coating facing the vacuum, where this metallic barium can aid in the production of thermionic electrons. Support for this theory comes from the following experimental result. The electron emission properties of a inactivated oxide coated cathode can be raised to activated levels by simply ‘flashing’ a exceedingly thin layer of barium metal onto its outer surface. [65]

Another electron emitting surface, whose structure parallels that of the oxide coated thermionic emitter, is the oxide or salt coated photoelectric tube. Most introductory quantum physics books and a surprising number of advanced ones restrictively describe the photoelectric cell as consisting of a clean alkali cathode and a clean metal anode separated by a ‘hard’ vacuum. Light enters the cell through a window, and strikes the cathode releasing photoelectrons which travel, under the influence of the applied electric field to the anode where they are collected. The rationale given for using alkali metal for the cathode is that their work function is small enough to allow visible light to produce significant amounts of photoelectrons; the more common, but less reactive metals will only produce photoelectrons under irradiation by ultraviolet light. While the preceding description is correct, it is also incomplete. In the 1930s, it was discovered that one way to both increase the efficiency of photoelectron emission and lower the threshold (into the red or even infrared) was to construct ‘contaminated’

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[65] J.A. Becker, R.W. Sears; Phenomena in Oxide Coated Filaments II. Origin of Enhanced Emission; Physical Review; Vol. 38; December 15, 1931; pp. 2193-2213.

photoelectric cathodes. [66] In this procedure, the clean alkali cathode, for example, had an oxide grown on it by backfilling with oxygen; salts of the alkali metals could also be employed, for example, potassium hydride could be formed by backfilling the cell with hydrogen gas plus a trace of water vapor and then striking a glow discharge. The alkali oxide or salt layers actually consisted of matrix of metal atoms and oxide or salt molecules. This so-called metal-oxide or salt 'colloidal' suspension confers the desired efficiency and lower threshold by the presence of the metal atoms sitting on and/or in the oxide or salt layer. Note, an oxide or salt layer on top of the base metal will not, by itself, improve the performance of the photoelectric cell, and, in fact, will degrade it.

8) The Ovonic switch is as fast as a Josephson junction, can have bistable behavior or not, but doesn't require all the exotic materials and cryogenic temperatures necessary with the Josephson junction. These devices, popularly referred to as amorphous semiconductor switches, were discovered by an autodidact and onetime machinist named Stanford Ovshinsky, who for his

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[66] Vladimir Kosma Zworykin, Edward Granville Ramberg; Photoelectricity and its Applications; John Wiley and Sons, Inc.; 1949; chapters 1-3.

trouble was booed when he presented his discovery at a meeting sponsored by the U.S. Army's research office in 1969. [67] Physically, an ovonic switch is usually composed of a thin layer of amorphous material between and in intimate contact with two conducting electrodes. The thin amorphous film is normally produced by evaporation in a vacuum. The actual active material "…include oxide- and boron-based glasses and materials which contain the elements tellurium and/or arsenic combined with other elements such as those of groups III, IV and VI." This quote, which is taken from the Physical Review Letters article, is very vague, and more detailed documents need to be consulted such as Ovshinsky's U.S. patent #3,271,591, entitled: Symmetrical Current Controlling Device, and granted on 9/6/66. This patent is quite expansive, being made up of 33 figures and 23 pages of text. [68]

The exact mechanism by which these switches function is still not understood, and there is considerable debate as to whether the underlying mechanism is electrical or thermal (i.e., driven by I^2R heating). [69]

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[67] Kenneth A. Brown; Inventors at Work; Tempus; 1988; pp. 147-165.
S.R. Ovshinsky; Reversible Electrical Switching Phenomena in Disordered Structures; Physical Review Letters; Vol. 21; No. 20; November 1968; pp. 1450-1453.

[68] Copies of U.S. patents (~1928 or ~1,839,190 [Patent No.]) on microfilm together with bound copies of the Index of Patents can be found in the Government Publications Department of the main branch of the Free Library of Philadelphia (FLP). Note, each year the Government Publications Department of the FLP attempts to extend its collection of patents on microfilm further backwards in time, e.g., in 1991 it used some excess book money to extend back the starting point of its collection from 1932 to 1928. Copies of pre-1928 patents can be obtained from: U.S. Department of Commerce, Patent & Trademark Office, Washington, D.C. 20231, (703)557-7800, @ $1.50 each. In addition, copies of International Patent Applications, which are normally filed with the World Intellectual Property Organization (WIPO) in Geneva, Switzerland can be obtained in this country from: U.S. Department of Commerce, Foreign Patent Branch, Crystal Plaza, Bldg. 34, STIC Rm. 2C01, Washington, DC 20231, (703)308-1077 or 603-0465, @ $10.00 each; to order a International Patent Application one must specify its Patent Cooperation Treaty (PCT) number, such as WO 90/12345, where '90' is the year it was filed and '12345' is the ID number.

[69] Nevill F. Mott, E.A. Davis; Electronic Processes in Non-Crystalline Materials; Clarendon Press; 1979; pp. 507-512.

While the original ovonic switches were reversible, i.e., nonbistable, more recent ovonic devices have been created which exhibit bistability. Such bistable ovonic memories require the light from a laser to switch them between states, and are the basis for the so-called optical memories or mass storage devices used by IBM.

9) High temperature superconductors, many of which are ceramics, e.g., those found by Paul Chu and coworkers in the mid ‘80s, are amorphous materials.

10) One of the latest high tech materials to emerge from the research laboratories and take industry by storm are the amorphous metal alloys, sometimes called glassy metals. [70] Glassy metals are formed by taking the molten alloy and cooling them very, very rapidly (sometimes as fast as a couple of million degrees per second) so that they do not have a chance to crystallize. These amorphous alloys can be thought of as a macroscopic version of the Beilby layer (see discussion in APPENDIX D). Originally, these glassy metals were valued for their extremely high strength, but later their superior magnetic properties almost eclipsed their structural advantages.

11) Finally, let’s not forget one of the most complex computers known to man, the brain [human or otherwise]. This magnificent device is built up of what Erwin Schrödinger called aperiodic crystals [71] , i.e., biological macromolecules. Its construction requires no exotic materials; it weighs about 1.5 kg [3.31

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[70] M. Hunt; Amorphous Metal Alloys; Materials Engineering; November 1990; pp. 35-38.

[71] Erwin Schrödinger; What is Life? & Mind and Matter; Cambridge Univ. Press; 1967; p 5. [Schrödinger presents a nice discussion of why physicists have their work cutout for them when dealing with anything other than infinitely large single perfect crystals.]

lbs(avpd.)]; its operating temperature is slightly above room temperature - no cryogenic temperatures needed here; it comes standard with a wide array of input/output capabilities including speech, vision, hearing, taste, feel and smell - try sniffing something with a Cray-1; and it can be powered almost indefinitely by cookies and milk. Its basic functional unit, the neuron, is composed of a cell body, an axon and multiple dendrites; the neurons of the brain are so large that they can easily be seen with an optical microscope using the proper staining technique - no quantum dots *schleping* around in this computer. The brain at every level is amorphous.

We are now ready to examine the various types of coherers, made from these less-than-perfect materials, and their behaviors.

CHAPTER 4 - WHAT IS KNOWN (pre-1970)

“Ask him the time and he would tell you how to make a watch. And throw in a history of Switzerland. The information was usually useful.”
- novel, The Red White and Blue, by John Gregory Dunne

§1. INTRODUCTION. - The existence of the coherer in one form or the other spans a period of at least 100 years (~1878 to the present). In this time, there have been many investigations into its behavior and just as many attempts at trying to explain the mechanism behind its actions. Any viable model of coherer behavior must be able to address all the known idiosyncrasies of this device, and it is for this reason that this and next section are devoted to a review of all the relevant experimental data that could be located. See APPENDIX C, Part I for a complete description of the literature search strategy.

§2. SITE OF COHERER ACTION. - The first thing most, if not all, investigators agree on was that coherer behavior was not a bulk phenomena, but instead almost entirely depends on the surface condition of the active material. We know this from experiments by J. C. Bose in which he electroplated the active material - in this case cobalt - onto a steel substrate and found that its behavior was, within his powers of observation, unchanged. Also R. H. Goddard noted that it had been shown experimentally [72] that silver filings do not function as a coherer unless they are first exposed to hydrogen sulfide gas, H_2S, but if exposed too long the sensitivity declines due to the thickness of the film - the H_2S apparently created a film of silver sulfide, Ag_2S, on the metal surface. That the oxygen present in air was the culprit in forming most of the films that allowed coherer action to take place was shown in a series of elegant experiments by R. H. Goddard. [73] Goddard constructed a glass apparatus in which he could generate metal filings in a vacuum, and then transfer them - still under vacuum - to a glass coherer cell whose electrodes could be made to press on the metal filings with various pressures. What he found was that for copper and iron, the resistance of the filings created in a vacuum was ohmic, i.e., the I-V curve was symmetrical and linear. When the copper filings created in a vacuum were exposed to pure dry oxygen, their resistance became nonohmic, i.e., asymmetrical and nonlinear, with the I-V curve bending over towards the current axis, which was what we would expect due to the rectifying action of the cuprous oxide, [74] Cu_2O, film. However, aluminum and magnesium filings gave nonohmic

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[72] A. Blondel; Sur les cohéreurs Marconi [On the Marconi coherers]; L'Eclairage Electrique [Electrical Illumination]; Vol. 16; 1898; pp. 316-317. [Or see Science Abstracts, Series A; Vol. 2A; 1899; Abstract No. 457.]

[73] R.H. Goddard; On the Conduction of Electricity at Contacts of Dissimilar Metals; Physical Review; Vol. 34; 1912; pp. 423-451.

[74] The suffix 'ous' refers to the lowest valence state of a metal, while the ending 'ic' refers to highest valence state.

resistances even when prepared in a vacuum. In addition, magnesium required application of considerable mechanical pressure to achieve conduction. This curious behavior probably indicates that either the vacuum was not very good and/or the process of creating the filings somehow contaminated the surface of these two metals. Goddard noted, in passing, that when aluminum or magnesium filings were created in air they gave off a garlic-like odor for a short time (about 30 seconds), when the filings were first produced in a vacuum and then exposed to room air the same garlic odor was present but lasted for almost a day. This odor would appear to substantiate the idea of some type of inadvertent contamination being present, and since it occured no matter whether the filings were created in air or vacuum, the contamination was most likely coming from the metal file used to shave the metal. A possible reason why the contamination did not affect the iron and copper experiments was that these two elements were much less chemically reactive than magnesium and aluminum. A better way of producing filings would be to rub together two pieces of the <u>same</u> metal, but even this process might not be totally free of untoward complications.

Further support for the surface effect point-of-view came from, for example, the work of Clement Dexter Child. Child, who is most famous for the law bearing his name and that of Irving Langmuir and having to do with electron current flow in thermionic planar diodes, investigated the properties of the E. Aschkinass tin foil detector in 1896.[75] The tin foil detector was made by taking a

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[75] C.D. Child; The Resistance of Tin-Foil as Changed by Electric Waves; Physical Review; Vol. 3; July 1895-June 1896; pp. 387-389. [The paper in which Child first formulated his law was,

C.D. Child; Discharge from Hot CaO; Physical Review; Vol. May 1911; Vol. 32; pp. 492-511. [The Child-Langmuir law or 3/2 law, as it was sometimes called, assumes a planar (one dimensional) model of the thermionic diode, even though the apparatus actually employed by Child to validate this law was <u>not</u> a planar diode. In fact, solving these equations for different geometries was difficult and, in some cases, impossible. Hence, this planar model was applied to all types of electrode geometries, because it was exactly and easily solved. A similar *sans souci* is found today in applying the planar Fowler-Nordheim model of tunneling/field emission to the square of foil, fastening in to a block of wood using shellac, paraffin, wax , etc. and slitting it, clean across, with a sharp knife as if to create a grating. If the battery current was made to traverse the slits in completing the circuit, the foil grating would act like a coherer in the presence of RF (Radio Frequency) radiation. He managed to convincingly demonstrate that the effect of RF radiation on the tin foil was not a bulk effect, as was supposed by Aschkinass, but rather depended on the quality of contact between the cut edges of the foil.

§3. RF FREQUENCY SENSITIVITY. - The frequency range over which the coherer is sensitive is truly awesome. Filings coherers act as good microphones and during their heyday at the start of the 1900s they were used to detect frequencies that easily reached the VHF (30-300 MHz) band. It is not generally appreciated that the early spark gap transmitters operated at high frequencies, in the VHF (30-300 MHz) and UHF (300-3000 MHz) bands. Marconi, himself, wrongly believed that transatlantic wireless could only be done with high frequencies because low frequency earthwaves tended to be attenuated rapidly by the Earth's surface conductivity; the existence of the Heaviside layer in the ionosphere, which refracts low frequency, e.g., AM radio, skywaves back to earth at considerable distances from their source, was officially only confirmed in the mid 1920s. Note, the Heaviside layer was originally called the Kennelly-Heaviside layer, but in fact Balford Stewart had postulated the existence of an

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point-plane electrode configuration used in STMs (Scanning Tunneling Microscopes) and other related contrivances.

In the interests of fairness and accuracy, the so-called 3/2 law should actually be known as the Lilienfeld-Child-Langmuir law, since, as was pointed out by Julius Edgar Lilienfeld, he saw it first,

J.E. Lilienfeld; A reply to Mr. Irving Langmuir's paper "The effect of space charge and residual gas on thermionic currents in high vacuum."; Physical Review; Vol. 3 (2nd Series); January-June 1914; pp. 364-365.]

ionosphere before either Kennelly or Heaviside. But that's another long story and we will not go into it here. Coherers can be cohered by frequencies from 0 Hz (DC) up to, at least, the microwave range; discussion of the behavior of coherers at the lower frequency limit will be postponed until we get to the phenomenon of 'critical voltage'. The upper RF frequency limit of the coherer depends on its switching (commutation) time, which a few modern researchers have tried to measure. In 1966, Salmer and Gabillard [76] determined an upper limit to the switching time of a Branly filings coherer. What they found was surprising, the coherer switching time had an upper limit of a nanosecond (10^{-9} s). The paper, while giving a very detailed and lucid description of the arrangement of the electronics, gives almost no detailed information about the construction of the coherer, other than to indicate that it is a Branly filings coherer employing aluminum powder of 50-80 μ (1 μ = 10^{-6} m) size.

The experimental method of Salmer and Gabillard was very straightforward. The coherer was in series with 100 Ω (the input resistance of a high speed 'scope); this series circuit was connected across a function generator which was set to produce a single shot sawtooth wave of adjustable amplitude; the sawtooth generator also provided a sync pulse to the 'scope monitoring the voltage across the 100 Ω resistance. This sync pulse was used to trigger the 'scope time base. With the coherer in its decohered (high resistance) state, a single sawtooth was generated which proceeded to ramp up in voltage. As long as the amplitude of the sawtooth wave was below the critical voltage of the coherer, almost no current flowed through the series circuit, and so the voltage

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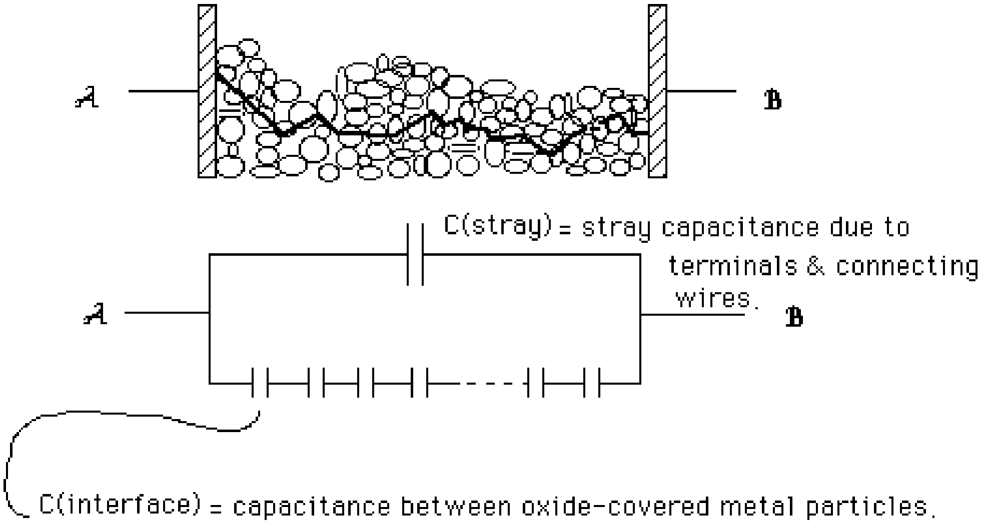
[76] G. Salmer, R. Gabillard; Sur la rapidité de fonctionnement du cohéreur de Branly [On the Rapid Functioning of the Branly Coherer]; Comptes Rendus Hebdomadaries des Seances de l'Academie des Sciences, Series B Science Physiques (Paris); Vol. 262; April 18, 1966; pp. 1043-1046.

across the current viewing (100 Ω) resistor was negligible. But as soon as the sawtooth amplitude reached the critical voltage, the coherer's resistance drops dramatically, and so a voltage now appeared across the current viewing resistor. At the critical voltage, the current through the series circuit rapidly rose as the coherer entered its low resistance state, then the current plateaued for a fraction of a nanosecond, and finally continued to rise at a slightly more leisurely rate. The rise in the current to its plateau took no more than a nanosecond. To reset the experiment the coherer must be tapped to return it to the decohered (high resistance) state, and the 'scope must have its time base rearmed.

There were a couple interesting things about this endeavor. First, as has already been stated, very little was know about this particular coherer, but from the value given for its initial (decohered) resistance, 1000 MΩ, we can surmise that the oxide layer was quite thick - this was corroborated by the fact that the critical voltage was on the order of 1-10 V. Second, the authors conceded that their then state-of-the-art measurement only yielded an upper limit to the switching time due to the finite response time of the 'scope (~0.3 ns), and the time constant of the generator plus series circuit; the real switching speed of the coherer may be much faster.

Although these researchers did not indicate the size of the coherer, it was definitely not a microminiature device. The question then arises as to how it can switch as fast as does given its macroscopic size? A possible answer is depicted in Fig. 3, where I have drawn an equivalent circuit of a filings coherer. Conduction through the filings occurs predominantly via a single, though tortuous, path; a different single path will be used each time the coherer coheres. The chain of particles forming the path between the end electrodes is actually a very large number of capacitors in series, due to the insulating film present at the surface of each particle. Because of the large number of these capacitors in series, their total capacitance remains reasonably small, as does the RC time constant.

FIGURE 3 - Equivalent Circuit of a Filings Coherer



The thick line indicates the current path through the powder (——).

C(stray) = stray capacitance due to terminals & connecting wires.

C(interface) = capacitance between oxide-covered metal particles.

C(tot. int.) = (1/N)Σ C(int.), where N is the number of particles in the current path. Thus, the total interfacial capacitance always remains low.

Lastly, the authors of this paper did not appear to have done a very thorough literature search, since their bibliography only contained five papers, four pre-1900 and one from 1905, and their abstract stated that although the coherer speed compared favorably with modern semiconductor devices its applicability would be limited because of the need to manually decohere it. It appears as if they were unaware of self-restoring coherers.

The highest frequency RF energy that a coherer has been shown to respond to was ~15 GHz (15 X 10^9 Hz). This was not the result of a wireless telegraphy system; instead it was a desktop experimental setup for measuring wavelength by means of a Rowland grating. [77] J. C. Bose was interested in coming up with a way of determining the wavelength of RF energy without Lecher wires, tuned cavities, etc. The reason why Bose wanted to stay away from secondary tuned circuits was that they have the nasty habit, when hit with a transient sinusoidal waveform, of responding even if they are not tuned to the frequency of the incident waveform. This lack of selectivity holds even for the continuous sinusoids, i.e., the secondary tuned circuit will respond to all harmonics of the fundamental frequency, but this was easier to discern, than the case of a transient sinusoidal waveform, due to its regularity.

Bose's experimental setup was as follows: a Rowland grating, fashioned of a wooden frame and strips of metal, was stationed on a rotating table, whose rotation in degrees could be read off of a scale along its edge; in front of a collimated microwave source, and on the other side of the grating, directly opposite the microwave source was a detector (a Bose spring coherer).

Given that Bose performed these experiments around 1896, the question arises as to the type of microwave source available to him? I suppose Bose might have called it a Bose oscillator and, in fact, Poincaré and Vreeland refer to it as such. [78] But Bose's oscillator appears to be a modified form of Righi's

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[77] J.C. Bose; On the Determination of the Wave-length of Electric Radiation by Diffraction Grating; Proceedings of the Royal Society (London); Vol. 60; 1896-97; pp. 167-178.

[78] Henri Poincaré, Frederick K. Vreeland; Maxwell's Theory and Wireless Telegraphy; McGraw Publishing Co.; 1904; pp. 88-89.

oscillator (see Fig. 4).[79] The Righi oscillator in one form or the other was the main source of microwaves even after the advent of the vacuum tube; Righi oscillators also worked at lower frequencies and were employed by Marconi in his first commercial wireless telegraph transmitters. The use of Righi oscillators as microwave sources was confined mainly to the laboratory, and it was in this setting that, for example, Nichols and Tear generated 1.8 mm (167 GHz) waves in an effort to bridge the gap between radio waves and far infrared waves in 1923.[80]

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[79] Ibid.; pp. 85-87, Fig. 4.

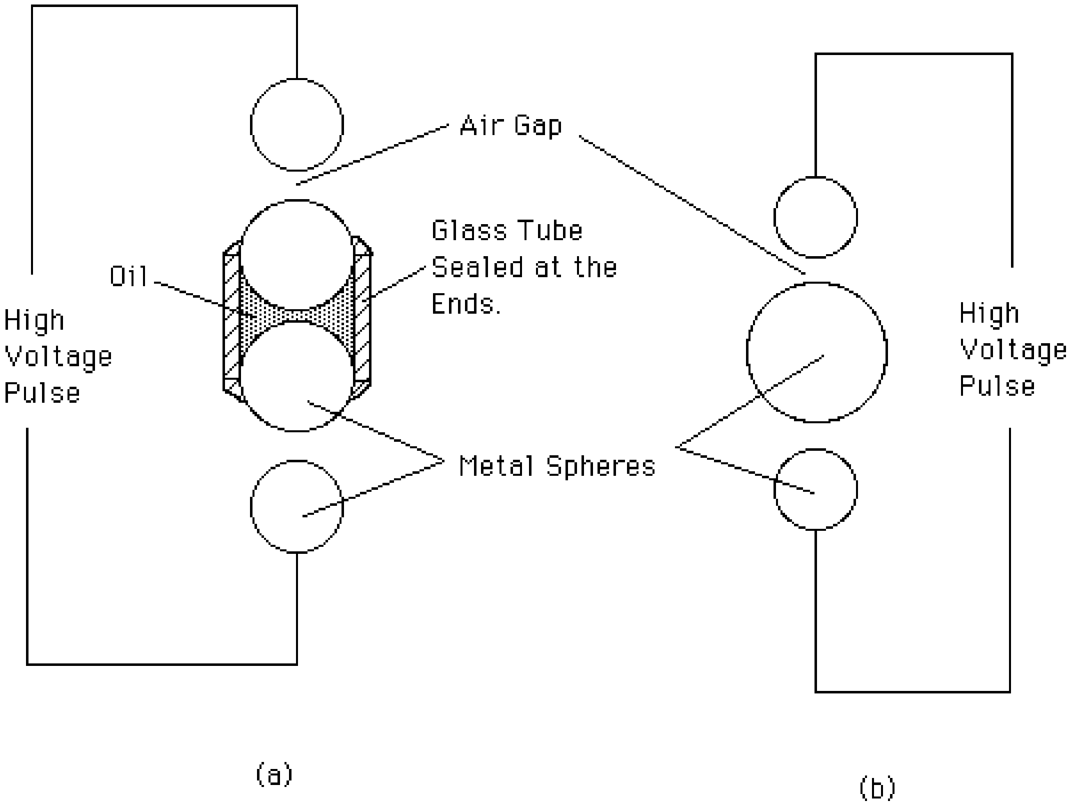
[80] E.F. Nichols, J.D. Tear; Short Electric Waves; Physical Review; Vol. 21; June 1923; pp. 587-610. [A prequel to their research can be found in the following article,

E.F. Nichols; The unobtained wave lengths between the longest thermal and the shortest electric waves yet measured.; in A.E. Kennelly, W.D. Weaver (Eds.); Transactions of the International Electric Congress, St. Louis, 1904, Vol. 1 of 3; J.B. Lyon Co.; 1905; pp. 438-442.

For a review of the subject of the generation of ultra short waves see,

W.H. Wenstrom; Historical Review of Ultra-Short-Wave Progress; Proceedings of the IRE; Vol. 20; No. 1; January 1932; pp. 95-112.]

FIGURE 4 – a) Righi Oscillator, b) Bose Oscillator



Having established that the coherer could detect high frequency RF energy, the question naturally arose as to whether or not it could detect electromagnetic energy of even higher frequencies, e.g., light, x-rays and/or gamma rays. A tentatively negative answer to this question, at least with regards to x-ray and gamma rays, was provided by C. Jensen. [81] In his experiments, Jensen exposed coherers (Kohl wireless telegraphy detectors) to x-rays from a Röntgen tube, which together with its electrical circuits was housed inside a

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[81] C. Jensen; Über einige Versuche mit Kohärern [On some Experiments with Coherers]; Physikalische Zeitschrift [Physical Journal]; Vol. 2; 1901; pp. 211-213. [Or see Science Abstracts, Series A; Vol. 4A; 1901; Abstract No. 855. I have not been able to locate a description of the Kohl coherer or, for that matter, any information on Kohl himself.]

metal box provided with a thin aluminum window through which only the x-rays could pass. The RF noise produced by the x-ray tube and its associated circuits was therefore trapped inside the box and so could not affect the externally located coherer. He also exposed them to Becquerel rays (alpha, beta and gamma rays) from a sample of naturally decaying radioactive mineral. The lack of any discernible response on the part of the coherer to any of these radiations does not, of course, prove conclusively that it could not detect these emanations. O. Leppin performed some inconclusive experiments that might have indicated a sensitivity of the coherers to light. [82] Today, as a result of the work on laser heterodyning, we know that coherers in the form of metal-oxide-metal [MOM] 'diodes' do respond to frequencies in the infrared and visible range.

§4. WHAT HURMUZESCU SAW: THE DURATION EFFECT. - While we are speaking about the time element in the operation of the coherers, I should like to mention the researches of one Dragomir Hurmuzescu. [83] As a result of his

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[82] O. Leppin; Wirkung vershiedenartiger Wellen auf den Branly'schen Cohärer [Action of different types of Waves on the Branly Coherer.]; Annalen der Physik und Chemie; Vol. 65; No. 4; 1898; pp. 885-889. [Or see Science Abstracts, Series A; Vol. 1A; 1898; Abstract No. 1364.]

[83] [D.] Hurmuzescu; Sur les cohéreurs [On Coherers]; Annales Scientifiques de l'Université de Jassy; Vol. 2; March 1903; pp. 141-165. [Or see Science Abstracts, Series A; Vol. 7A; 1904; Abstract No. 370. This journal of the University of Jassy (a.k.a. Iassy or Iasi, a small town in eastern Rumania) is, needless to say, a difficult journal to get a hold of. But according to,

Henri Poincaré, Frederick K. Vreeland; Maxwell's Theory and Wireless Telegraphy; McGraw Publishing Co.; 1904; p. 238,

Hurmuzescu's article was reprinted in a more widely available French journal. The reprint citation is:

[D.] Hurmuzescu; Sur les cohéreurs [On Coherers]; L'Eclairage Electrique [Electrical Illumination]; Vol. 35; No. 26; June 27, 1903; pp. 487-495.

Just as I was finishing translating Hurmuzescu's article, I learned that there was an English language version of Hurmuzescu's article. According to,

V.J. Phillips; Some Filings-Coherer Measurements; IEE Conference on the History of Electrical Engineering (Manchester); 1975; paper 13,

the citation to the English version is,

[D.] Hurmuzescu; The Electrical Engineer; July 24, 1903; p. 118.

After much head scratching I have discovered that this citation is wrong, it should read,

Anon.; Coherers; Electrical World and Engineer (New York); Vol. 42; No. 4; July 25, 1903; p. 149.

This last article turned out to be only a long abstract of the original paper.]

investigations, Hurmuzescu showed that in the case of filings coherers of the positive type, their minimum resistance as a result of exposure to RF energy was a function of the time of exposure, i.e., for times of exposure which he designated as ‘normal time’ the resistance of the coherer was a minimum. For times greater or less than this normal time the resistance was usually higher, the exception being certain coherers where the resistance for times greater than the ‘normal time’ stayed equal to the minimum resistance. Because of the unusual nature of these results, it will help to examine the details of Hurmuzescu’s experimental methodology.

The observation time of the coherers was divided into three periods. The First Period, right after the coherer was first assembled and its resistance was approaching a steady state value in the absence of RF energy. The Second Period, when the coherer was first exposed to RF energy and its changes in resistance were continuously monitored - sort of a burn-in period. The Third Period, at this point the characteristics of the coherer should be stable, and it was during this period that Hurmuzescu made his determinations of resistance versus time of application of the RF energy. The duration of the RF pulses was precisely controlled by the clever use of a pendulum switch, which gated the primary current to the Ruhmkorff coil [84] ; a metal tine attached to the pendulum bob form one side of the switch, the other side being a pool of mercury located at

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[84] The Ruhmkorff coil was, of course, not invented by the German instrument maker Heinrich Daniel Ruhmkorff, but rather by an American patent examiner named Charles Grafton Page. This bit of revisionist history was given in the following book,

Florian Cajori; A History of Physics…; The Macmillan Co.; 1935; pp. 250-252.

And it was backed up by the following reference,

C.G. Page; Magneto-Electric and Electro-Magnetic Apparatus and Experiments; The American Journal of Science and Arts; Vol. 35; January 1839; pp. 252-268.

the bottom (lowest point) of the pendulum's travel. [85] The resistance measurements were performed with either a Wiedemann-d'Arsonval differential galvanometer or a Wheatstone bridge. Hurmuzescu indicated that if one used the Wheatstone bridge technique, there was the possibility of a measurement artifact due to the 'extra currents' which flow when the bridge is unbalanced due to the coherer's change in resistance - no 'extra current' occur with the Wiedemann-d'Arsonval differential galvanometer. There was a simple way of testing for this artifact which involved inserting a large value resistor in series with the coherer to limit the magnitude of the 'extra current'. If the coherer behaves the same with and without this resistor in series with it, then the 'extra current' did not influence the measurement.

An interesting observation made by Hurmuzescu during The First Period of observation, i.e., right after the filings coherer had been assembled but before any RF was applied, was the time variation in its resistance. Different metals or mixture of metals exhibited vastly divergent approaches to their steady state value of resistance. Note, these spontaneous variations in resistance were most likely the result of the varying rates and types of oxidation of the filings upon exposure to air. On the other hand, if the metal filings were <u>first</u> oxidized by

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[85] This idea of using a pendulum switch was by no means new, Karl Ferdinand Braun had made use of this same idea around 1883 when he was trying to show that unipolar conduction (rectification) was <u>not</u> due to heating of the crystal point contact junction. His pendulum switch produced short duration voltage pulses across the crystal point contact diode, too short, he believed, to generate any significant heating from the resulting current, which he was able to show was still rectified. See,

[K.]F. Braun; Einige Bemerkungen über die unipolare Leitung fester Körper [Some Observations on unipolar Conduction in solid Bodies]; Annalen der Physik und Chemie; Vol. 19 (3rd Series, a.k.a. the New Series); 1883; pp. 340-352.

Even today the pendulum switch is still out and about. Witness its most recent resurrection in the testing of lightning arrestors and surge suppressors,

L. Dayton; Pendulum swings into action against lightning; New Scientist; Vol. 133; No. 1803; January 11, 1992; p. 23.

heating in air and then allowed to cool, the instabilities observed during The First Period were almost nonexistent.

§5. CONFUSION OVER THE CONCEPT OF A 'CRITICAL VOLTAGE'. - One of the really 'hot' controversies concerning coherers was the concept of the 'critical voltage'. It was initially thought that a coherer in the high resistance state could be made to cohere by simply increasing the DC bias. A number of scientists claimed to have measured this critical voltage and to have shown a correlation between the size of this voltage and the sensitivity of the coherer to RF energy; the correlation was a negative one, the smaller the critical voltage the higher the RF sensitivity. W. H. Eccles, in a series of exhaustive experiments, [86] produced data that he believed - as did others who read his paper, such as J. A. Fleming [87] - that there was no such thing as a critical voltage. What Eccles did was the following. He took commercially made filings coherers of known RF sensitivity and proceeded to carefully measure the DC bias necessary to cause them to coherer. Part of the care exercised by Eccles in measuring the critical

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[86] W.H. Eccles; Some Experiments on Filings Coherers; The Electrician (London); Vol. 47; 1901; pp. 682-685.

Idem; Some Experiments on Filings Coherers; The Electrician (London); Vol. 47, 1901; pp. 715-717.

William Henry Eccles is most famous as the co-inventor, with F.W. Jordan, of the bistable multivibrator otherwise known as the flip flop; a device which no self-respecting computer would be without:

W.H. Eccles, F.W. Jordan; Trigger Relay; The Electrician (London); Vol. 83; September 19, 1919; p. 298. [Or see Science Abstracts, Series B; Vol. 22B; 1919; Abstract No. 932.]

Note, the astable version of the multivibrator, which is used even today to produce square waves, was detailed in the article directly after the one on the flip flop:

W.H. Eccles, F.W. Jordan; Trigger Relay; The Electrician (London); Vol. 83; September 19, 1919; p. 299.

Another invention of Eccles and Jordan which is still used today is their triode-sustained tuning fork, whose transistorized version finds use as a light chopper and as a master oscillator for the fuze of the Mk12 reentry vehicle which is part of the Minuteman missile system. For a description of their original circuit see,

W.H. Eccles, F.W. Jordan; Sustaining the Vibration of a Tuning-fork; The Electrician (London); Vol. 82; June 20, 1919; pp. 704-705.

[87] [Sir] John Ambrose Fleming; The Principles of Electric Wave Telegraphy and Telephony; Longmans, Green and Co.; 1919; Chap. VI; pp. 383-384.

voltage was to avoid the creation of sparking due to the sliding contact of the potentiometer used to adjust the DC bias. To achieve the perfect sliding contact, Eccles constructed his potentiometer from a graduated cylinder filled with a copper sulfate solution, two fixed copper electrodes were located one at the top and one at the bottom of the cylinder, and the movable contact consisted of a copper electrode insulated over its whole length except at its very tip. Using this 'quiet' potentiometer, Eccles proceeded to show two things: first, that the critical potential was quite variable, i.e., 20-60% variation in the same coherer; and second, that the correlation between the critical voltage and the RF sensitivity was for the most part quite loose.

Part of the reason for the variability in the critical voltage of a particular unit turned out to be due to the microphonic susceptibility of these filings coherers. They were being cohered by sound or vibrations transmitted through the structure of the building. In an attempt at obtaining more reproducible results, Eccles finally resorted to measuring the I-V characteristics of the filings coherers while they were tapped at a rate of 50 times/second. This ploy of increasing the unwanted trepidations did indeed yield more reproducible results. In particular, the I-V curves resembled the I-V curve of a forward biased PN junction. From these observations, Eccles concluded that there was no such thing as a critical voltage because no matter how small the voltage impressed across the coherer, the resulting current was always measurable. The problem with this approach was that Eccles was actually measuring the I-V curve of mechanically cohered coherers, i.e., the mechanical tapping at 50 beats/second was causing alternating coherence and decoherence of the coherers with the result being that the average current was predominantly the current flowing through the coherer in its mechanically cohered state. Further evidence refuting Eccles claims of the nonexistence of a critical voltage comes from an earlier paper by Guthe and Trowbridge. [88] In this paper, the authors measured the I-V curve of electrically cohered coherers, and obtained curves that were very similar to those obtained by Eccles. So the point is that it is very difficult, if not impossible, to measure the I-V curve of a decohered coherer, but it is trivial to obtain the I-V curve once the coherer is in the cohered state.

The reason why decohered coherers are so difficult to electrically characterize is directly traceable to the thinness of the nonconducting film needed to assure sensitivity in the detection of RF energy, this thin nonconducting layer makes the coherer an extremely sensitive microphone. Support for this assertion can be found in a pair of papers by E. C. Green. [89] Green's papers, which appeared in 1917, were concerned with utilizing the coherer as a detector of lightning strikes and high frequency transients in high tension power lines. To this end, Green produced a filings coherer consisting of

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[88] K.E. Guthe, A. Trowbridge; On the Theory of the Coherer; Physical Review; Vol. 11; 1900; pp. 22-39.

[89] E.C. Green; The Development of the Coherer and some Theories of Coherer Action; General Electric Review; Vol. 20; May 1917; pp. 369-374.

Idem; Discharge Alarms for Lightning Arresters; General Electric Review; Vol. 20; July 1917; pp. 582-587.

Because of my interest in Green's work, I checked the Author Index of the Science Abstracts, Series B, for any further articles by this author for ten years (1917, Vol. 20B to 1927, Vol. 30B) after this pair of articles appeared. However, no more articles by E.C. Green were found. In an effort to tap all possible sources of information regarding Green, I also tried contacting the General Electric library at the corporate R&D facility in Schenectady, NY. According to the librarian at the Whitney Library, (518)387-7539, there are no entries relating to E. C. Green in their card file. Note, the Whitney Library is now the main G.E. library since the real Main Library was closed in 1986 probably as a direct result of Jack Welch's (CEO of G.E.) "…lean and mean…" policy. The Whitney librarian suggested that I try the Hall of History museum/library, which is also in Schenectady, but is not associated with G.E. although most of its materials and displays feature G.E. technology. Since the Hall of History, Bldg. 8, Rm. 310, 1 River Rd., Schenectady, NY 12345, (518)385-1104, is a private concern, their research services must be selfsupporting and so cost $35.00 per hour of search time. One hour's worth of search time revealed no additional information about E.C. Green's life or work. There is no photograph of him, no biographical file, and his name does not appear in the standard histories of G.E. engineering: Hammond Historical Files, Workshop for Engineers (Story of G.E.) or the index of the Schenectady Works News.

40-60 mesh[90] oxidized nickel. The oxidized nickel filings were sealed in an A-shaped glass vessel with "…sufficient amount of gas to stabilize the oxidation of the granules." Because as Green stated, he wanted to make his coherers immune to any wireless (RF) effects, he employed a very thick oxide layer together with other precautions such as keeping the lead lengths short and employing extensive electrostatic shielding. Due to the thickness of the oxide layer, these coherers exhibited a very reproducible critical voltage. Consider, for example, coherer Serial No. 1065 which yielded the following critical voltages after repeated measurements,

TABLE 1

	310
	300
	280
	300
	335
	325
	325
	320
	320
	335
Average:	315.0
Sample Standard Deviation:	17.48
Coefficient of Variation [(17.48/315)100%]:	5.5%

The small size of the coefficient of variation, 5.5%, underscores how tight the distribution of critical voltages was for this particular coherer. In addition, the resistance of this coherer before coherence was ~10^9 Ω and after coherence it dropped to 3.08 Ω, this dramatic change in resistance owed its existence to the rather robust oxide film employed by E. C. Green. With regards to the use of the

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[90] 40-60 mesh[/inch] is a measure of the size of the nickel filings.

coherer as a detector of high frequency transients on the power lines, Green states the following law, which I have not seen before, "…due to the fact that the critical voltage of a coherer is a function of frequency, an increase in frequency causing a great decrease in the voltage necessary to produce coherence." E. C. Green sanguinely states this rather startling law <u>without</u> providing any experimental proof.

An observation made around 1900 by a telephone engineer appears to contradict the aforementioned law of Green's. J. De Pauw reported that he had witnessed some very peculiar behavior with respect to accidentally crossed ["…mélangés…"] wires in telephone circuits. [91] He noticed that on crossed lines, which were used <u>both</u> for telephony and telegraphic service, that while the telephone signal could still be propagated without undo interference or attenuation, telegraph signals, however, could not be transmitted until the lines were uncrossed, i.e., if line A and line B were crossed, a telegraph signal sent down A, instead propagating all the way to other end, would instead jump over to B at the point where A and B crossed. De Pauw credited this behavior to the presence of a thick layer of copper oxide at the surface of the bare copper or bronze wires used for the telephone/telegraph lines. When two lines cross, a mechanical junction (coherer) was formed, and, according to De Pauw's interpretation of his experiences with them, these layers act as a dielectric to the alternating or undulating telephone signals, but act like a conductor to the

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[91] [J.] De Pauw; Deux constatations intéressantes en téléphonie. [Two interesting findings in telephony.]; Société Belge d'Électriciens, Bulletin Mensuel [Society of Belgian Electricians, Monthly Bulletin]; Vol. 19; January 1902; pp. 9-11. [This journal, as one might guess, was difficult to find. I was able to get a copy of this article only through the auspices of the Library of Congress. **Warning**, do not confuse J. De Pauw with the Dutchman, L.J. van der Pauw, who is famous for his work on the measurement of specific resistivity, a.k.a. sheet resistivity, see for example,

L.J. van der Pauw; A Method of Measuring Specific Resistivity and Hall Effect of Discs of Arbitrary Shape; Philips Research Reports; Vol. 13; No. 1; February 1958; pp. 1-9.]

essentially DC (0 Hz) telegraph signals - the exact opposite behavior predicted by E. C. Green.

§6. IS THERE A BEST MATERIAL OUT OF WHICH TO CONSTRUCT COHERERS? - One of the more interesting questions with regards to the concept of critical voltage was how this voltage was affected by the material used in the construction of the coherer. Wolcott [92] reviewed the critical voltages of a number of metals, and as a result of his survey was able to explain why nickel was the metal of choice in many commercial coherers, such as Marconi's filings coherer. What he found was that nickel had the lowest critical voltage, and so was the most sensitive for wireless telegraphy. On the other hand, aluminum, while not having as low a critical voltage as nickel, gave a much more consistent response. Wolcott then suggested that if sensitivity was not of paramount importance, then aluminum should be employed. That aluminum should have such a regular response is not surprising given the tenacity and hardness of its oxide film (alumina, Al_20_3). [93] The reason why aluminum was not utilized earlier by, for instance, David E. Hughes was probably due to its cost; Lord Kelvin in 1856 referred to aluminum as one of the "…rarer metals…", and was forced to borrow the aluminum bar he used in his thermoelectric experiments from the

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[92] E.R. Wolcott; Sensitiveness of the Coherer; Bulletin of the University of Wisconsin; Vol. 3; No. 1; 1901; pp. 1-20. [Or see Science Abstracts, Series A; Vol. 5A; 1902; Abstract No. 2091. Wolcott's article was actually his Bachelors thesis, and for reasons which I do not understand his name appears nowhere it.]

[93] There is a large body of experimental evidence pointing to alumina films on aluminum being amorphous. The amorphous nature of alumina films is maintained even at relatively high temperature in contradistinction to what happens with the oxide layers of other metals. For more information see,

Oswald Kubaschewski, B.E. Hopkins; Oxidation of Metals and Alloys; Butterworths; 1967; p. 53 & pp. 256-257.

Baron Liebig because he could not afford, at the time, to buy any for himself.[94] During the middle of the nineteenth century aluminum was more precious than gold. Before Charles Martin Hall in America and Paul Louis Toussaint Héroult in France independently[95] discovered the electrolytic process (1886) for reducing aluminum from its oxide, Al_2O_3, the only way of producing aluminum was by a very complex and costly chemical reduction. In fact, aluminum was so expensive in the pre-Hall/Héroult process days that royalty often sought to impress one another by setting their dinner tables with aluminum flatware (knives, spoons & forks) instead of their silver or gold utensils.[96] Besides being light weight - unlike their silver or gold counterparts - and having a bright finish, aluminum flatware did not tarnish, as did silver, or wear out due to mechanical friction, as was the case with unalloyed gold. Once aluminum became plentiful, almost too plentiful from Hall's point-of-view since initially he was producing more than he could sell, people rapidly found applications for this new metal.[97] And by

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[94] Sir William Thomson, Baron Kelvin; Mathematical and Physical Papers, Vol. II; Cambridge University Press; 1884; Article No. 91, On the Electro-Dynamic Qualities of Metals, p. 254 & Article No. 89, On the Thermo-Electric Position of Aluminum, p. 181.

[95] Not only did Hall and Héroult independently and simultaneously discover the same process for making aluminum electrolytically, but they both were born in December of 1863 and died in December of 1914, see,

G.B. Kauffman, M.L. Adams; Aluminum - an active metal; Education in Chemistry; Vol. 27; No. 2; March 1990; pp. 36-39.

[96] According to

Alfred Morgan; Adventures in Electrochemistry; Charles Scribner's Sons; 1977; p. 72, Emperor Napoleon III provided his most important dinner guests or those he wished to impress most with aluminum utensils, while the lesser lights had to make do with the rather clunky gold implements. Note, Morgan's book was originally published in 1959 with the rather unpretentious title, Things a Boy Can Do with Electrochemistry.

[97] This according to

H.S. Jones; Aluminium-Surfaced [sic] Mirrors in Astronomy; Nature; Vol. 134; Oct. 6, 1934; p. 522,

Thomas Alva Edison was the first to patent, in 1890, a process for evaporating aluminum onto, for example, glass surfaces; eventually aluminum displaced silver as the reflective coating of choice on all types of mirrors employed in scientific work. Note, from a reflectivity point-of-view silver is still superior to aluminum, but silver films tarnish rapidly under normal atmospheric conditions. Today, both aluminum and silver reflective films can be overcoated with a very thin (~ $\lambda/4$) SiO_2 protective coating, this transparent coating allows the mirror to be cleaned and, in addition, reduces the tarnishing rate for silver.

1898, Édouard Branly and Oliver Lodge were arguing, respectively, for and against the use of aluminum in coherers; Branly's position turned out to be the correct one. For example, Minchin [98] claims that the most sensitive coherer he ever built employed a piece of carbon - he does not mention the exact type of carbon, i.e., coal, coke, graphite, etc. - in contact with an aluminum wire. Originally, Minchin employed a telephone receiver in the coherer circuit, and in this configuration the coherer was self-restoring. Later on, he used a relay in place of the telephone receiver, and found that the same coherer was now nonself-restoring, requiring a mechanical shock to decohere it! This fusing of the carbon-aluminum coherer is most puzzling since carbon does not weld. In fact, it does not even melt, it sublimes. And aluminum is notoriously hard to weld, even to itself unless it is in an inert gas atmosphere. A possible explanation for the fusing of aluminum and carbon could be the formation of aluminum carbide (Al_4C_3) at the interface.

While we are on the subject of which metals make the best coherers, I want to mention some research done by a Strachan. [99] Strachan's series of articles examined and enumerated all known types of crystal detectors together with their properties. In the course of his investigations, he mentioned that one

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[98] G.M. Minchin; A Receiver for Electric Oscillations; The Electrical Review (London); Vol. 51; No. 1302; November 7, 1902; p. 770. [Or see Science Abstracts, Series A; Vol. 6A; 1903; Abstract No. 1058. Note, a journal called *The Electrical Review(New York)* was also published, do not confuse the two - as I did.]

[99] J. Strachan; The Crystal Detector in Theory and Practice, Parts I-VII; The Wireless World and Radio Review; Vol. 14; May-July 1924; pp. 216-219, 245-249, 278-281, 338-341, 396-398, 424-426, 462-464.

could obtain perfectly readable AM (Amplitude Modulated) signals using a crystal detector without the crystal! If one removed the crystal from its copper or brass cup and proceeded to probe the inside of the cup with the catwhisker, lo and behold one detected a radio signal. Strachan realized, of course, that his crystalless detector was in fact functioning as a coherer, but without a DC bias supply. Further inquiry disclosed that the best coherer was one fashioned of a particular specimen of brass, which according to Strachan was only slightly inferior to the most sensitive galena detectors; coherers made of brass exhibited a wide range of sensitivity depending on certain unknown variables in the brass or on its surface. Next to brass, detectors made of presumably oxidized cerium worked better than all the metals and alloys he had tried. From all my readings, Strachan appears to be the only person to have recommended cerium as the element which forms the best coherer. It should be pointed out that cerium does, in fact, oxidize in air at room temperature (20ºC), [100] but this does not explain, by itself, why Strachan found that it made a very sensitive detector. [101]

Having given over a considerable amount of space to discussing which metal makes a better coherer, I shall now devote a paragraph to the opposing camp. A paragraph is all I will need since I was only able to find a single individual who believed that the sensitivity of a coherer was independent of the metal used in its construction. In 1910, Carl Kinsley wrote a paper devoted to

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[100] D. Cubicciotti; The Reaction of Cerium with Oxygen; Journal of the American Chemical Society; Vol. 74; 1952; pp. 1200-1201.

[101] There has been some recent interest in using cerium oxide in semiconductor devices, specifically MOS (Metal-Oxide-Semiconductor) structures. To this end, there has been a modest amount of research done with respect to investigating the dielectric properties of this oxide,

S. Mochizuki; Infrared Optical Properties of Cerium Oxide; Physica Status Solidi B, Basic Research; Vol. B114; 1982; pp. 189-199.

Z.T. Al-Dhhan, C.A. Hogarth; Optical Absorption in Thin Films of Cerium Dioxide and Cerium Dioxide Containing Silicon Monoxide; Physica Status Solidi B, Basic Research; Vol. B137; 1986; pp. k157-k160.

determining the sensitivity of coherers, specifically filings coherers.[102] In his paper, Kinsley proposed two tests that could be employed to rank coherers as far as their sensitivity is concerned. 1) The Field Test, for a fixed transmitter power and transmitter to receiver distance, the antenna attached to the coherer at the receiver is gradually shortened until the coherer ceases to function; the shorter the antenna which still allows the coherer to function, the more sensitive the coherer. 2) The Lab Test, in essence this test simply measures the DC critical voltage of the coherer, a DC voltage is applied across a decohered coherer and slowly increased until the coherer coheres; the lower the critical voltage the more sensitive the coherer. Kinsley claimed that these tests correlated with one another, and provided experimental evidence supporting his contention. He then goes on to state that the active material (metal) of the filings coherers he tested does not affect the sensitivity. Further he says, "Coherers of any degree of sensitiveness desired may be made of any metal." All of this may appear to be quite radical, but it actually was not. What he goes on to say is that, "It is only necessary to treat each metal in accordance with its peculiar nature." In other words, by proper processing any metal can be made to coherer, and with the sensitivity desired. This is pretty much the message Édouard Branly espoused when he stated that one could make a filings coherers out of gold or platinum, but that one had to exercise care in how the materials were processed and, in particular, the conditions under which they were used - this last point is the main difference between Branly's and Kinsley's view of coherers. Kinsley's idea that the sensitivity of a filings coherer was independent of the base metal used to produce the filings does <u>not</u> necessarily mean that the oxide layer acts merely as a spacer, i.e., as a means for controlling the distance between the electrodes

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[102] C. Kinsley; Coherers Suitable for Wireless Telegraphy; Physical Review; Vol. 12; No. 3; January-June 1901; pp. 177-183.

without actually taking an active part in the conduction process, since the processing of the base metal can create substantially different surface characteristics even on the same metal.

The modern reincarnation of the coherer, i.e., the MOM ‘diode’ used in laser heterodyning, is constructed from a diverse - one might say arbitrary - pairings of metals and metalloids, e.g., tungsten-gold, tungsten-nickel, tungsten-graphite (actually pencil lead), gold-gold, etc. For all the effort expended on trying different pairings of metals and metalloids, there is still no consensus on which combinations work the best, although, individual researchers have their favorites: Samuel I. Green indicated that <u>one</u> of his gold-gold ‘diodes’ had a sensitivity (output voltage/input RF power) of 1200 V/W - the highest he saw with any combination (see APPENDIX A).

§7. MECHANICAL JUNCTIONS AND THE MOST BIZARRE CANDIDATE FOR A COHERER. - As was discussed in an earlier section, there are many different types of coherers: solid-solid, solid-liquid and liquid-liquid, positive and negative, and nonself-restoring and self-restoring, etc. However, the one thing <u>all</u> coherers have in common is that they all possess, at least, one mechanical junction. Mechanical junctions are junctions which are so loose that they can easily detect mechanical disturbances in solid-solid coherers, e.g., David E. Hughes employed the carbon microphone he invented as an extremely successful coherer in his experiments on wireless telegraphy. So the question then becomes, what is the nature of this type of junction? The funny thing is that this type of junction is ubiquitous. Any time you lay something down on a table, for instance, you are creating a microphonic junction. The study of forces between objects in loose mechanical contact is usually the province of mechanical engineers and is called tribology. When you walk across a carpet on a very dry day and pick up a static charge which is uncomfortably dissipated upon touching a metal object, this is called triboelectricity. When you set your pen down on a table, the amount of force it takes to slide it across the table and keep it moving depends on the coefficient of friction (either static or dynamic), another tribo effect. Mechanical junctions are a surface, not a bulk effect.

Perhaps the strangest mechanical junction to be accused of coherer-like behavior was the early carbon filament incandescent lamp; the junctions here were presumably the interfaces between the crystallites making up the carbon filament. According to the editor of the journal, *The Electrician (London)*, carbon filament glow (incandescent) lamps attached to the supply circuits of the Calcutta Electric Supply Co. experienced a sudden and very noticeable increase in brightness immediately following lightning flashes which accompanied severe thunderstorms with the above-normal brightness fading away gradually after the demise of the responsible lightning bolt. The editor of this journal remarked as to how reproducible this effect was, and that, in his mind, the simplest explanation was that the lamps were acting as positive coherers, i.e., their nominal ‘hot’ resistance decreased in response to the RF energy radiated by the lightning bolt and picked up by the overhead feed wires. The note about this effect and its possible explanation produced three responses (letters to the editor), from different parts of the world, all corroborating the effect, but not necessarily agreeing with the editor’s “…ingeniously suggested…” explanation, *vis-à-vis* coherer behavior. The authors of the the three letters included: one person who had worked in mining operation in the Transvaal and Johannesburg, South Africa; someone who forgot to append their name to their letter and lived/worked in Madison, Wisconsin, USA; and, finally, the last letter was from a person in Schenectady, New York, USA. [103]

After becoming of aware of this phenomenon, I chanced upon a similar sounding occurrence in an article published in the *The Electrician* a few years earlier. [104] According to Oliver Lodge, he noticed that when he was operating a strong RF source (spark coil) at his lecture table, the fuses to the overhead lights blew out. Lodge indicated that his lecture table was illuminated by "…sundry Swan lamps…", [105] which apparently short-circuited, thus blowing out the fuses, due to the intense pulse of RF produced by some of the spark coils. The lamps had metal shades and were tilted towards the lecture table - and away from glaring into the eyes of the audience - by copper wires attached to the shades and stretched across the ceiling. It was these copper wires, acting as antenna, which directed the RF towards the lamps; once the copper wires were replaced by silk threads the problem disappeared. Note, Lodge does <u>not</u> explicitly state that the filaments of the glow lamps became noticeably brighter, but he does imply this by saying that the lamps short-circuited.

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[103] The original note by the editor can be found in,

Editor; A curious Phenomenon…; The Electrician (London); Vol. 45; August 31, 1900; p. 691. The three follow up letters can be found in,

S.P. Blackmore; To the Editor of The Electrician; The Electrician (London); Vol. 45; September 21, 1900; p. 829.

Anon.; Carbon Filaments and Lightning Flashes; The Electrician (London); Vol. 45; September 28, 1900; p. 841.

S.P. Blackmore; Carbon Filaments and Lightning Flashes; The Electrician (London); Vol. 45; September 28, 1900; p. 868.

[104] O. Lodge; The History of the Coherer Principle; The Electrician (London); Vol. 40; November 12, 1897; pp. 87-91.

Oliver J. Lodge; <u>Signalling Through Space Without Wires,</u> 3rd Ed.; "The Electrician" Printing and Publishing Co.; 1900; pp. 73-87. [Reprinted in 1974 by the Arno Press.]

[105] What Thomas Alva Edison was to electric light in America, so was Sir Joseph Wilson Swan in England. The Swan lamps mentioned by Lodge were carbon filament glow (incandescent) lamps. The Swan process of making carbon filaments involved dissolving gun cotton (nitrocellulose) in acetic acid and then the solution was squirted into alcohol. The thread, which resulted from this process, was then denitrated before being carbonized by heating in a furnace containing an inert atmosphere.

There was some evidence that, in order for carbon glow lamps to response to RF energy, they had to be illuminated, i.e., nominal current had to be forced through them. This evidence comes by way of the experiences of one Dr. William J. Morton, M.D. Dr. Morton's practice included electrotherapy, which apparently consisted of placing electrodes on his patients and then subjecting them to different types of high voltages but low currents. The sources of these high voltages were spark coils, static influence machines or the Edison 110 VDC system, which normally provided power for electric illumination. While the spark coil and/or static influence machine voltages could be applied to the patient directly, the voltage from the Edison 110 VDC system had to be current limited so as not to cause any irreversible heart oscillations or burns to the epidermis. Morton employed the Vetter method of controlling the current, i.e., a 16 candle power (50 watt) carbon glow lamp was put in series with a pulverized carbon rheostat in one leg of the two wire DC system. By adjusting the resistance of the rheostat, the current flowing through the patient could be doled out in quantities smaller than a milliampere to as much as 100 mA or more, no doubt for the most robust or recalcitrant clients. Normally, only a milliampere or so was applied to a patient. The rheostat consisted of powdered carbon between two movable electrodes, which when squeezed together changed the resistance offered by the carbon to the passage of current. Morton discovered that the sparking of his electrostatic machine, which was located some 15 feet away from the Vetter controlled DC electrotherapeutic unit and electrically isolated from it, caused sudden transient increases in the current flowing through the DC unit. To be exact, it was Dr. Morton's hapless patients - as he relates it - who first indicated that something was amiss by their physiological reactions to the pulses of increased current. Morton was able to confirm the 'reality' of their complaints by examining the current meter in the circuit which indeed registered the transient increases in current. By substituting a water resistor for the pulverized carbon rheostat and noting that the transient current increases in the DC electrotherapeutic unit no longer accompanied the sparking from the electrostatic unit, all other things being the same, Morton surmised that the carbon rheostat was acting like a coherer. The important point here was that the 16 candle power carbon glow lamp was still in the circuit, which showed that the lamp did not act like a coherer itself at these low currents. [106]

It should be noted that at this time, circa 1900, the carbon filament lamp had only been in service for about 20 years. Thomas Alva Edison obtained his first fully functional prototype carbon filament lamp between December 1879 and January 1880 using a carbonized, untreated cotton thread; the actual production units used a filament composed of carbonized bamboo, specifically a Japanese bamboo called "Madake", which did not shrink much during the carbonization

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[106] Oliver J. Lodge; Signaling Through Space Without Wires, 3rd Ed.; "The Electrician" Printing and Publishing Co.; 1900; pp. 111-114. [Reprinted in 1974 by the Arno Press. At the end of a book Herman Goodman, there is the following tantalizing entry in his Chronology of Electricity and Electrotherapeutics: "1881-W.J. Morton inaugurates spark gap currents (Morton Wave)." Exactly what a 'Morton Wave' is or was and why he should be famous for having discovered it, I have not been able to determine, yet. See,

Herman Goodman; Story of Electricity and a Chronology of Electricity and Electrotherapeutics; Medical Life Press; 1928; p. 61.]

process and proved to be much more resistant to mechanical shocks.[107] The process of carbonization simply involved heating the cotton or bamboo in an inert gas furnace with provisions made for maintaining a continuous stream of the inert gas so as to carry away the volatile organic gas and vapors until all the organic matter was reduced to carbon. As was mentioned earlier in the section entitled MATERIALS, pyrolytic carbons can be one of two classes: graphitizing or nongraphitizing carbons. None of the references, I've cited so far, mentions in which of the classes cotton and bamboo falls into. The 'hot' resistance of the commercial carbon filament lamps was on the order of a 100 Ω. This rather high resistance was, in fact, one of the major reasons for going to a carbon filament, as opposed to say a platinum filament as was originally contemplated by Edison. The reason why a high resistance filament was desired had to do with the DC power distribution scheme and the fact that lamps would be hung on the power line in parallel.

Only a few years after 1900, articles started appearing in technical journals pointing to the fact that light bulb carbon possessed a negative temperature coefficient of resistance. These assertions became even more puzzling when compared with pure artificial graphite (a.k.a. Acheson graphite) which became generally available around 1900. Comparison of these two similar seeming materials showed them to possess totally different electrical characteristics: light bulb carbon had a high resistance and a negative temperature coefficient of resistance, while Acheson graphite's resistance was very low and its temperature coefficient of resistance was slightly positive. In

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[107] John W. Howell, Henry Schroeder; History of the Incandescent Lamp; The Maqua Co.; 1927; pp. 75-77.

Robert Friedel, Paul Israel, Bernard S. Finn; Edison's Electric Light, Biography of an Invention; Rutgers University Press; 1987.

other words, light bulb carbon had qualities usually associated with semiconductors, while the corresponding characteristics of Acheson graphite made it appear to be metallic. By 1910, it was generally known that light bulb carbon and graphite were very different materials, electrically speaking.[108] More quantitative data regarding the difference between light bulb carbon and graphite was obtained in the 1930s by a Japanese researcher, Zenji Nishiyama.[109]

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[108] E.F. Northrup; Some Effects of Temperature Upon the Resistance of Graphite and Carbon.; Metallurgical and Chemical Engineering; Vol. 11; January-December 1913; p. 275.

[109] Z. Nishiyama; Electrical Resistance of Carbon; Tohoku University Science Reports, Report No. 286 from the Research Institute for Iron, Steel and other Metals; Vol. 21; March 1932; pp. 171-192. [Note, this report is in English. Unfortunately, the journal containing this article is extremely difficult to locate in North America. Temple University's Interlibrary Loan Department tried unsuccessfully to obtain this article for more than 6 months. Although its English language version appears to be unavailable, the same article can be found in a widely disseminated German journal,

Z. Nishiyama; Über den elektrischen Widerstand des Kohlenstoffs. [On the electrical Resistance of Carbon.]; Zeitschrift für Physik; Vol. 71; August-September 1931; pp. 600-615.]

Nishiyama studied the electrical conductivity and crystal structure of man-made amorphous carbon filaments. [110] His hope was to understand the reason why certain types of carbon acted like metals (the graphites) and other acted like semiconductors (the amorphous carbons). These filaments were made by taking a carbonized rayon thread, they were mounted inside a glass enclosure, the air was evacuated from the enclosure and then enclosure was backfilled with carbon tetrachloride (CCl_4) vapors, and finally enough current was passed through the carbonized rayon thread to raise its temperature to approximately 1500ºC. Note, CCl_4, unlike the gasoline used in the commercial process, was <u>not</u> flammable. The original carbonized rayon thread began to increase its cross sectional area by the process of accretion as the heat from it decomposed the CCl_4 and the resulting carbon particles deposited themselves onto the thread. Eventually the original carbonized rayon thread of 0.002 mm diameter reached the desired diameter of 0.12 mm. At the end of this process the resulting carbon filament had a metallic sheen and was quite solid and uniform in appearance. These

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[110] A similar process was used commercially to make the carbon filaments for glow (incandescent) lamps. Initially, carbon filaments were made by the method pioneered by Thomas A. Edison, i.e., carbonizing slivers of a particular type of bamboo. Later on it was discovered by William E. Sawyer and Albon Man that the efficiency (light power output/electrical power input), electrical resistance and overall reproducibility of carbon filaments could be improved by the process of ‘treating’. Treating consisted of passing an electric current current through a regular carbon filament in the presence of gasoline vapors - the air having been previously pumped out. This process was so successful, that after the patent of Sawyer and Albon expired, Edison’s company also employed it. See,

John W. Howell, Henry Schroeder; <u>History of the Incandescent Lamp</u>; The Maqua Co.; 1927; pp. 79-81.

It should be noted that the process of treating must have been quite exhilarating - if that’s the right word for it - for the assembly line worker performing this manufacturing step. On p. 79 of Howell & Schroeder’s book, there is an actual photograph of a work station used for performing this process. On the right hand side of the workbench is a large glass bottle of gasoline (a couple of liters), with a hose leading from it, floating in an even larger glass jar of water. On the left hand side of the bench are five chambers in which the filaments are heated in the presence of the gasoline vapors after first being evacuated. And for the *pièce de résistance*, in front of the gasoline bottle, there is an enormous knife switch - looking like something off the movie set of Frankenstein - which was presumably used to energize the filaments! As I said, an exhilarating experience. The authors sanguinely pointed out that the gasoline supply was <u>eventually</u> moved outside the building to an underground tank; the gasoline vapors being then brought to the work station via pipes.

essentially amorphous carbon filaments were then quantified with respect to their electrical resistance and crystallite size before and after certain heat treatments. The resistances of the carbon filaments were always determined in a vacuum to preclude any possible artifacts due to oxidation and to avoid, as much as possible, the effects of occluded gases in them. The crystallite sizes were ascertained using the Debye-Scherrer-Hull x-ray method (see APPENDIX D).

There were five degrees of heat treatment: 1) none, 2) 2500ºC for 1/2 hr., 3) 2500ºC for 1 hr., 4) 3000ºC for 1/2 hr. and 5) 3000ºC for 1 hr. All the heat treatments were performed in an inert atmosphere. Nishiyama's results were as follows. The carbon filaments without heat treatment had a high resistivity and a sizable region of negative temperature coefficient of resistance - room temperature included. The temperature coefficient eventually went to zero and then became positive at >1000ºC. With increased heat treatment, the overall resistivity of the filaments dropped, the zero of the temperature coefficient moved to lower temperatures and concomitantly the area of positive temperature coefficient began to dominate. The size of crystallites were very small for the case of no heat treatment, but increased significantly with increasing temperature of the treatment; the lattice constant, on the other hand, did <u>not</u> appear to change, i.e., the crystallite structure did not change only their size changed, which meant no phase transition. These results confirmed in Nishiyama's mind that amorphous carbons behaved like semiconductors, while graphitic carbons, i.e., those with large crystallites, could almost have passed for metals, i.e., low resistivity and a positive temperature coefficient.

Nishiyama's theoretical considerations led him to enumerate three probable causes of the observed resistivity versus temperature response of the carbon filaments:

1. The effect of contaminants.
2. The influence of the space between crystallites.
3. The variability of the number of free electrons in the surface layers of the crystallites.

He rejected the first cause by citing Matthiessen's rule. Specifically, Matthiessen's rule stated that for small amounts of impurities the slope of the resistivity versus temperature curve will be independent of the amount of the impurities. The amount of contamination in the rayon thread, which was used as the core of the carbon filament, was assumed to be indicated by its ash content of 0.2-0.4 % [by weight?]; the layers deposited by the decomposition of CCl_4 were assumed to be 100 % pure. These numbers were presumably obtained by heating a known weight of the rayon thread in either an air or pure oxygen environment until all the carbon was volatilized as either CO or CO_2; the remaining ash was then weighed after cooling. Since the resistivity versus temperature curves for the five cases of heat treatment were <u>not</u> parallel to one another, this behavior cannot be blamed on impurities according to Nishiyama.

The spaces between the crystallites could allow currents to pass provided that they [the spaces] were small; the existence of small fissures and gaps between the crystallites was deduced from the decreased density of amorphous carbon versus graphite. This type of conduction, originally postulated by J.

Frenkel in 1930, [111] was thought to be due to the wave like nature of the electron, i.e., quantum mechanical tunneling. Because the probability density function for the electron in the space between the crystallites drops off exponentially, these spaces increase the resistivity of the sample. Unfortunately, since an increase in temperature increases these spaces and hence the resistivity of the amorphous carbon, which contradicts the empirical data, this mechanism cannot by itself account for the observed conduction behavior.

The third mechanism depended on the difference in the crystallite lattice spacing in the interior of the crystallite versus that at its surface. Specifically, Nishiyama proposed that the lattice spacing was greater at the surface of the crystallite than in its interior and that because of this, the number of free electrons at the crystallite surface increased with temperature faster than in the interior.

In 1952, a physicist named S. Mrozowski revisited the question of the electrical properties of various types of carbons produced by heat treatment. [112] He claimed that his carbon samples were better than Nishiyama's, and hence that his data more accurately reflected the true state of affairs. In addition, he took exception to Rosalind Franklin's terminology of 'nongraphitizing carbons' used to describe those organic compounds or mixtures which to do not yield graphite upon pyrolysis in an inert atmosphere. Mrozowski's basis for his objection to this nomenclature was his contention that 'nongraphitizing carbons' do eventually yield graphite upon significantly robust pyrolysis. This claim of Mrozowski's does not coincide with the recent facts, e.g., in 1963, J. C. Lewis *et al.* showed by x-ray crystallographic methods that their vitreous carbon remained in the vitreous (amorphous or glassy) state even after 3 hours at 2750ºK which is a normal

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[111] J. Frenkel; On the Electrical resistance of Contacts between Solid Conductors; Physical Review; Vol. 36; December 1, 1930; pp. 1604-1618.

[112] S. Mrozowski; Semiconductivity and Diamagnetism of Polycrystalline Graphite and Condensed Ring Systems; Physical Review; Vol. 85 (2nd Series); No. 4; February 15, 1952; pp. 609-620.

Idem; Errata: Semiconductivity and Diamagnetism of Polycrystalline Graphite and Condensed Ring Systems; Physical Review; Vol. 86 (2nd Series); April-June 1952; p. 1056.

graphitizing temperature.[113] Mrozowski did agree that amorphous carbons behaved like semiconductors and based on experimental results he assigned the conductivity to the presence of excess electrons due to the donor sites in the carbon ring structures found in the tiny graphitic crystallites making up the amorphous carbon. He also gave a rather detailed justification for this experimental result in terms of the carbon ring structure of graphite. In what must be a good example of the tenuousness of theoretical constructs, Mrozowski, a few months later, revealed that the data had a sign error in it, meaning that the conductivity was actually due to excess holes resulting from the presumed presence of acceptors or traps. So go the plans of mice and men!

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[113] J.C. Lewis, B. Redfern, F.C. Cowlard; Vitreous Carbon as a Crucible Material for Semiconductors; Solid-State Electronics; Vol. 6; 1963; pp. 251-254.

§8. MECHANICAL JUNCTIONS: RIGID VERSUS LOOSE. - Since all coherers have mechanically loose junctions, the question naturally arises as to whether or not the incoming RF energy reacts differently to rigid versus loose junctions. A relatively recent paper, circa 1928, sheds some light on this question. Todesco and Rossi [114] built a fixture composed of a fixed 4 mm dia. steel sphere and a movable, by micrometer screw, steel plate. This apparatus was hung on elastic cords to damp out vibrations and then the whole thing was ensconced in a heavy steel box mounted on the floor. Fig. 5 is a top view of the mechanisms used to bring the two surfaces into contact. Besides the micrometer screw, a set of heating coils wrapped around the pair of iron bars could also be used to change the spacing between the steel sphere and plate via the coefficient of thermal expansion of the bars.

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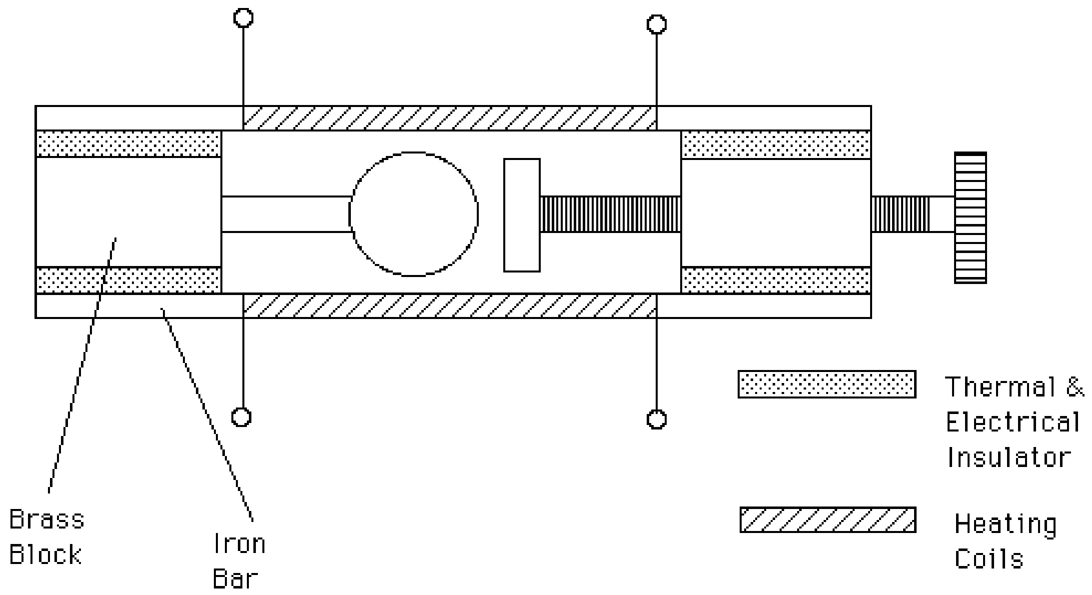
[114] G. Todesco, B. Rossi; Contributo allo studio dei contatti imperfecti metallici [Imperfect Metallic Contacts]; Accademia Nazionale dei Lincei. Atti. Classe di Science Fisiche, Mathematiche, e Naturali. Rendiconti [National Academy of Rome, Class of Physical Sciences, Mathematics and Natural. Proceedings]; Vol 7; April 1, 1928; pp. 568-573. [Or see Science Abstracts, Series A; Vol. 31A; 1928; Abstract No. 2814. I wish to thank Massimo Musumeci, Department of French and Italian, Temple University for the masterful job he did translating this paper for me. Examination of Science Abstracts, Series A, from Vol. 31A (1928) to 41A (1938) revealed no other papers by either of these authors on coherers or imperfect metal contacts, this seems to have been their first and last paper on the subject; it was also their last collaboration. Today, Dr. Bruno Rossi can be found at the Massachusetts Institute of Technology, Center for Space Research, Cambridge, MA 02139, Rm. 37-667, (617)253-4283. My advisor, Dr. Thomas E. Sullivan, wrote to Rossi to see if he had any photographs or drawings of the various pieces of equipment he and Todesco employed in their studies on imperfect contacts. Regrettably, Rossi did not have any archival material relating to this work.]

FIGURE 5 - Rossi & Todesco's Apparatus



The idea of using thermal expansion to actuate and control the movement of electrodes over very small distances had been around for awhile, and did not originate with Rossi and Todesco.[115] However, regardless of who first

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[115] Six years before Rossi and Todesco published their paper, an American physicist named James W. Broxon employed a thermally driven interferometric device to refute the 'electron atmosphere' theory of Robert Williams Wood, see APPENDIX B & E for a discussion of this theory,

J.W. Broxon; Electrical Conduction Across Minute Air-Gaps; Physical Review; Vol. 20 (2nd Series); No. 5; July-December 1922; pp. 476-485 (in particular, see p. 478).

A thermal expansion actuator eventually found itself incorporated into a commercial piece of standard laboratory equipment, the ultramicrotome. With the advent of the EM (Electron Microscope) just before WWII, there arose the need to be able to section biological material to thicknesses of ~300 Å. Such incredibly thin sections could not be had using a blade advanced by conventional mechanical means due to gear backlash and even the variability of the lubricating oil film thickness. Hence, Sanford B. Newman, Emil Borysko and Max Swerdlow in 1949 proposed the first ultramicrotome utilizing a thermal expansion actuator: a brass sample holder cooled ~25ºC below room temperature, using Joule-Thomson expansion of CO_2, and then allowed to slowly warm up. A year later, M. Eden *et al.* proposed a scheme whereby the sample holder was heated ~10ºC above room temperature, using heating wire wrapped around the sample holder *à la* Todesco and Rossi, then allowed to slowly cool down. See,

S.B. Newman, E. Borysko, M. Swerdlow; Ultra-Microtomy by a New Method; Journal of Research of the National Bureau of Standards; Vol. 43; No. 3; September 1949; pp. 183-199.

M. Eden, A.W. Pratt, H. Kahler; A Microtome Specimen Holder Advanced by Thermal Expansion; Review of Scientific Instruments; Vol. 21; No. 9; September 1950; pp. 802-804.

discovered this idea, it had enough merit that it was and is used by many researchers. In fact, this same idea of using thermal expansion to control the spacing between two surfaces for the purposes of studying tunneling was rediscovered by Russell D. Young at the NBS (now NIST) in 1966 [116] and later rerediscovered and brought to a high degree of perfection by a group of researchers at IBM's Yorktown Research Center in 1976. [117] With this apparatus, Todesco and Rossi were able to show that when the steel ball and plate were brought into light contact, the I-V curve was symmetrical with respect to the polarity of the applied DC voltage and nonlinear with the current increasing faster than the voltage as is the case for the I-V curve for a forward biased diode. In order for there to have been conduction currents of the magnitude they measured, the surfaces would have had to be in contact. This contact was probably due to a metallic bridge or filament forming between the spherical and the plane electrodes.

Besides needing a better actuator for advancing the sample, a better blade was also needed. Metal blades could not be used because the polycrystalline nature of most metals caused the resulting blade edge to possess a sawtooth profile. In 1950, H. Latta and J. Hartmann introduced the fractured glass microtome blade. This glass blade had the necessary smooth cutting edge due to the amorphous (vitreous) nature of glass. For general information on this topic see,

Roger Buvat; Plant Cells, An Introduction to Plant Protoplasm; World University Library; 1969; pp. 64-72.

Ernst Ruska; The Development of the Electron Microscope and of Electron Microscopy; in W. Odelberg (Ed.); Les Prix Nobel, 1986; Almqvist & Wiksell International; 1987; pp. 58-83.

[116] R.D. Young; Field Emission Ultramicrometer; Review of Scientific Instruments; Vol. 37; No. 3; March 1966; pp. 275-278. [I wish to thank Dr. Thomas E. Sullivan for bringing this paper to my attention.]

[117] W.A. Thompson, S.F. Hanrahan; Thermal Drive Apparatus for Direct Vacuum Tunneling Experiments; Review of Scientific Instruments; Vol. 47; No. 10; October 1976; pp. 1303-1304. [I wish to thank Drs. Thomas E. Sullivan and Paul Cutler for bringing this paper to my attention. Extensive data on the true, i.e., differential, coefficient of thermal expansion for various metals can be found in the following references,

F.C. Nix, D. MacNair; The Thermal Expansion of Pure Metals: Copper, Gold, Aluminum, Nickel, and Iron; Physical Review; Vol. 60; October 1941; pp. 597-605.

Idem; The Thermal Expansion of Pure Metals. II: Molybdenum, Palladium, Silver, Tantalum, Tungsten, Platinum, and Lead; Physical Review; Vol. 61; January 1942; pp. 74-78.]

In an effort to check some observations made by an earlier researcher, H. Pélabon, they attempted to see if the imperfect contacts would rectify RF current. The answer was, no, which was not surprising given the symmetrical nature of the DC I-V curve. But here comes the strange part. While no rectification took place when the two electrodes were held rigidly in position, if they arranged things so that one of electrodes could move, even slightly, rectification took place! Note, one way to achieve the rectifying configuration was to allow one electrode to rest on top of the other, e.g., by employing two steel ball bearings, one on top of the other, as the electrodes. Because making I-V measurements on such nonrigid electrode configurations was so difficult due to microphonics, these authors could provide no such curves. However, they did state that the DC resistance of the rigid configuration was usually higher than that of the nonrigid arrangement.

As was indicated in the footnote, this paper by Todesco and Rossi was the only paper written by either author on the subject of imperfect metallic contacts. After this paper they went their separate ways: Todesco to relative obscurity and Rossi to fame. Bruno B. Rossi went on to investigate the nature of cosmic rays, which had become a hot research topic in the 1920s and 1930s. He contributed much to the understanding of the nature of cosmic rays, and for this reason his name is usually mentioned in books on the history of particle physics. His coincidence circuit composed of vacuum tubes and connected to two or more Geiger-Müller (GM) tubes, allowed one to detect the direction of motion of a single cosmic ray particle by arranging two GM tubes in a line, or the occurrence of a shower, caused by a single incoming cosmic ray particle, by arranging the

GM tubes in a noncolinear fashion, e.g., at the vertices of a triangle. [118] Rossi's coincidence circuit is still the mainstay of particle physicists.

It is at this point that I must set the record straight, Todesco and Rossi were not the first researchers to discover that rigidly positioned mechanical junctions lose their ability to rectify. The credit for this discovery should actually go to H. Pélabon. Note, this is not simply hairsplitting on the basis of priority alone. Pélabon produced a large body of work about this phenomenon over a period of time (1925-1929), and performed some ingenious experiments whose correct interpretation might lead to the answer of the question of how and why this process takes place. Todesco and Rossi do reference one of Pélabon's papers, [119] but did not mention that he discovered the curious electrical behavior that results from changing the rigidity of a mechanical junction. In fact, the way in which they presented their findings almost made it look like they thought they were the first ones to discovered it.

Pélabon began his investigations [120] into the properties mechanical junction based on a very curious fact. According to J. Cayrel, [121] catwhisker

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[118] B. Rossi; Counters; Nature; Vol. 125; 1930; p. 636. [Note, Rossi was not the first person to employ vacuum tubes as coincidence detector, and says so at the very start of his Nature article. According to Rossi, W. Bothe first used a vacuum tube with two grids (a tetrode) as a coincidence detector for two GM tubes; the reference for this work is,

W. Bothe; Zur Vereinfachung von Koinzidenzzählungen [To Simplify Matters of Coincidence Counting]; Zeitschrift für Physik; Vol. 59; Dec. 1929 - Jan. 1930; pp. 1-5.

Rossi's original contribution was to use an arrangement of triodes as the coincidence circuit, this scheme had the obvious advantage that coincidences in any number of GM tubes could be detected.]

[119] H. Pélabon; Sur la détection par les contacts métalliques [On Detection by Metallic Contacts]; l'Onde Electrique [Electric Wave]; Vol. V; 1926; pp. 464-475.

[120] H. Pélabon; Sur la détection [On Detection]; Comptes Rendus Hebdomadaries des Seances de l'Academie des Sciences (Paris); Vol. 181; November 1925; pp. 776-778.

[121] J. Cayrel; Sur la détection des galèna [On Detection by Galena]; Comptes Rendus Hebdomadaries des Seances de l'Academie des Sciences (Paris); Vol. 180; June 1925; pp. 1728-1731.

diodes using a single crystal of galena, exhibited their highest sensitivity when the Miller (111) plane - a crystallographic designation which can be found in most books on solid state physics - was the face in contact with the metal catwhisker. Cayrel reasoned that this was so because the planes of atoms in the (111) direction are made of alternating layers of lead and sulfur atoms, i.e., the planes normal to the (111) direction are composed of atoms of one species, either lead or sulfur; galena (PbS) has the same crystal structure as salt (NaCl). [122] Note, both Pélabon and Cayrel credit Ms. Paule Collet with having suggested that a pellicle of sulfur or related elements (such as tellurium or selenium) was responsible for the sensitivity of certain galena samples. [123] Exactly how Cayrel exposed the Miller (111) plane of galena was not delved into, but presumably he was able to cleave the single crystals of galena that he used in his experiments. [124]

Pélabon took Cayrel's observation and went one better, he took a freshly cleaved piece of lead, vapor deposited a thin layer of sulfur on the lead, and then probed the coated lead surface with a catwhisker. In essence, Pélabon built an artificial catwhisker diode, and what he found was that it worked quite well as a detector of AM (Amplitude Modulated) radio waves. Further investigation revealed that the sulfur could be replaced by many other materials, e.g.,

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[122] Charles Kittel; Introduction to Solid State Physics, 4th Ed.; John Wiley & Sons; 1971; p. 26.

[123] P. Collet; Les propriétés détectrices de la galèna [The Detection Properties of Galena]; Annales de Physique; Vol. 15; Series 9; 1921; pp. 265-361.

[124] Leonard Benjamin Williams Jolley; Alternating Current Rectification; John Wiley & Sons; 1924; pp. 332-333. [Jolley points out that natural galena forms a cubic structure, which means that the Miller (111) plane is not directly accessible except by cleaving; if galena crystallized in an octahedral form the (111) plane would be directly accessible. According to

Paul Ramdohr; The Ore Minerals and their Intergrowths; Pergamon Press; 1969; pp. 634-635.

cleavage of galena along the Miller (111) plane is possible.]

dielectrics and semiconductors, which could be prepared in the form of a fine powder such as coal, amorphous boron, selenium, red phosphorous, arsenic, antimony, iodine, etc. and the base metal, likewise, could be nickel, iron, bismuth, copper, tin, gold, etc. Eventually Pélabon, while trying to reduce the detector to its essence, abandoned the catwhisker configuration completely in favor of a ball-plane, ball-ball or cylinder-cylinder contact. In the case of these configurations, the material separating the two metal electrodes could be air, in which case the electrodes would be brought into close proximity with one another via a gear reduction drive mechanism; usually, the one electrode was lowered onto the other with the upper electrode having some degree mechanical freedom. The two electrodes could also be maintained in close proximity by resting one electrode on top of the other after having had some cork dust, silica or lycopode powder ("…a fine yellowish flammable powder composed of lycopodium spores…" where lycopodium is "…a large genus of erect or creeping club mosses…" [125]) sprinkled on the top surface of the lower electrode before the upper electrode was lowered onto it. These powders were thought to act as insulating microscopic springs, keeping the two balls apart while at the same time allowing relative motion to take place between them.

Having reduced the catwhisker diode down to what he perceived to be its essence, Pélabon observed that there were three distinct types of behavior depending on how close the two electrodes were to one another. [126] At separation distances somewhat greater 10^{-6} cm, a characteristic rumbling sound

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[125] Anon.; Webster's Seventh New Collegiate Dictionary; G. & C. Merriam Co.; 1970; p. 505.

[126] H. Pélabon; Sur la détection par les contacts métalliques [On Detection by Metallic Contacts]; l'Onde Electrique [Electric Waves]; Vol. 5; 1926; pp. 464-475.

Idem; Sur la détection et la stabilité de certains détecteurs [On Rectification and the Stability of Certain Detectors]; Comptes Rendus Hebdomadaries des Seances de l'Academie des Sciences (Paris); Vol. 182; January 1926; pp. 124-125.

was heard without any attendant demodulation of the incident AM signal, this rumbling or sometimes frying sound was similar to that heard in the case of a uncohered coherer while listening for a CW (Continuous Wave) signal, i.e., wireless telegraphy. [127] A possible explanation for this sound occurred to Samuel I. Green, who observed a similar effect, i.e., noisy signals, while investigating the behavior of MOM ‘diodes’ (see APPENDIX A). Green postulated that the sound was the result of currents induced in the external circuit due to the environmental vibrations causing relative motion between the two metal balls, which have different work functions. In other words, when the two balls are connected electrically, via an external circuit, a contact potential results (contact potential = difference in work functions), the balls form a capacitor whose capacitance is modulated by environmental vibrations causing relative motion between them, and this modulation results in changing amounts of charge on the balls which is manifested as changing currents in the external circuit. As I explain in APPENDIX A, it is my opinion that this was actually 1/f noise, which is quite common in granular materials, i.e., mechanical junctions. When the separation distance was further reduced to around 10^{-6} cm, the rumbling and/or frying sound was replaced by the audio signal from the demodulated AM radio signal. Further reduction in the electrode separation distance ultimately resulted in silence due to the formation of a low resistance ohmic contact between the two electrodes. The metal balls employed by Pélabon weighed upwards of a pound or more, and hence if they were allowed to rest on top of another ball or a plate, their weight would surely result in the breaching of any oxide or other surface dielectric layer. This was the reason for sprinkling the silica dust or other powders between the two balls.

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[127] A. Douglas; The Crystal Detector; IEEE Spectrum; Vol. 18; No. 4; April 1981; pp. 64-67.

Pélabon was, of course, fascinated by the ability of these metal-on-metal structures to demodulate radio telephony signals, fascinated by the simplicity of the detector and the absolute requirement that one of the electrodes be free, i.e., not rigidly positioned. As was stated previously, his favorite detector configuration was the one with two ball bearings arranged on top of one another with a pinch of silica or lycopodium powder between them. Pélabon mentioned that J. Cayrel, presumably after having read about Pélabon's detector, tried and succeeded in building such a detector using two gold rings or cylinders; according to Pélabon, Cayrel published an account of his experiment in *l'Onde Électrique*, but there is no indication of when - I am still searching for it.

Another arrangement popular with Pélabon was to have two identical ball bearings, each hanging by a wire, with the distance between the wires adjustable at their pivot points. Thus by reducing the separation between the two support wires to less than the distance between the centers of the balls, the balls would be pressed against one another. In this configuration, Pélabon observed that demodulation would persist only as long as there was some imperceptible relative motion between the two balls. That this slight amount of motion was absolutely necessary was demonstrated by using two massive ball bearings, whose inertia was great enough to eventually damp out any external vibrations. After these two large ball bearings were brought into contact demodulation continued only until their inertia damped out most of the initial motion. Once the demodulation ceased, it could be brought back by simply lightly stroking one of the supporting wires with a fine camel's hair brush. Pélabon's explanation for this behavior relied on the following analogy with coherers: the two ball bearings demodulate as long as the oxide layer between them is intact (the sensitive or decohered state), inevitably this oxide layer will be either broken through or bridged by a metal whisker and, thus, was shorted out (the insensitive or cohered state); the relative motion between the two balls was necessary in order that any metal bridges were disrupted and any other breach of the layer healed by moving to a different part of the surface, i.e., the relative motion was like the mechanical shocks used to decohere the filings coherer. In a later paper, Pélabon [128] used the arrangement of one ball bearing on top of the other, the lower ball resting on a rigid insulator such as a glass plate, and introduced a layer of cloth between the lower ball bearing and the rigid insulator. With the cloth layer in place he found that the detector no longer demodulated the AM signal. My explanation is that the piece of cloth acts as a mechanical isolator/damper preventing external vibrations from causing relative motion between the two ball bearings that are astride one another.

§9. COHERERS MEET MOM 'DIODES': ECCLES' PRESCIENT MEASUREMENTS. - In an earlier section, it was stated that in some nonself-restoring coherers some sort of welding, fusion or sintering occurred between the microphonic surfaces. This behavior, which was by no means universal among coherers, brought to the fore the question of whether coherer action was thermal in origin?

As has been stated earlier, coherence in some filings coherers can be shown to be accompanied by the fusion or welding of filamentary chains of particles, implying a thermal process. The problem with this discovery was that it

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[128] H. Pélabon; Sur la rectification par les mauvais contacts purement métalliques [On rectification by imperfect purely metallic contacts]; Comptes Rendus Hebdomadaries des Seances de l'Academie des Sciences (Paris); Vol. 188; January 28, 1929; pp. 382-384.

is usually an artifact. W. H. Eccles pointed out that the scientists who demonstrated welding/fusion did so by subjecting the coherer to enormous amounts of RF energy, much higher than the coherer would normally ‘see’ when it was in use with the transmitting station hundreds of miles away. This lack of understanding of how the coherer was actually used persists even into recent times. For example, Gabillard and Raczy [129] in 1961 were investigating the formation of filamentary chains of metal particles in the filings coherer of Branly. These researchers did some very qualitative experiments, which they claimed supported their hypothesis that inhomogeneous electric fields arising from the asperities present on the filings created mechanical forces, which caused the filings to form long unidirectional chains. The problem with their methodology was that there was no control over the strength of the electric field induced across their coherer by the Ruhmkorff coil they employed as the source of RF energy. The distance between the Ruhmkorff coil and the coherer was unspecified, the secondary voltage across the secondary of the coil was not given, the length of the wires used to connect the coherer to the low voltage DC source and current meter were not provided, and the size and composition of the coherer are not mentioned. In general, the authors of this study seemed to prefer the quantifier “quelque [some]” over a more traditional unit of measure. This was anything but a carefully controlled experiment. What was even more

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[129] R. Gabillard, L. Raczy; Sur une explication possible de l’effet Branly [On a Possible Explanation of the Branly Effect]; Comptes Rendus Hebdomadaries des Seances de l’Academie des Sciences (Paris); Vol. 252; 1961; pp. 2845-2847. [That almost any detector employing a mechanical junction will exhibit sparking under a RF overload was brought to my attention while reading a biography of Robert Williams Wood. Wood mentioned that while living in Paris in 1913, he purchased a headphone radio set with a galena catwhisker diode for its detector. When tuning into the radio station in the Eiffel Tower, which towered above his apartment on the Avenue Charles Floquet, he noticed that, “Signals came in from the Eiffel Tower with such strength that you could often see a spark between the cat whisker and the galena crystal on my receiving set.” See,

William Seabrook; Doctor Wood, Modern Wizard of the Laboratory; Harcourt, Brace and Company; 1941; pp. 178-179.]

surprising was that 51 years earlier, Eccles had taken the time to perform a more quantitative examination of the same coherence phenomenon.

Eccles [130] went back to reinvestigate the behavior of coherers under conditions which more closely approximated the way they were actually employed in wireless telegraphy. Two types of self-restoring coherers were investigated, the first consisted of a lightly oxidized iron wire dipped in a pool of clean mercury, and the second was composed of a flat iron plate whose polished and lightly oxidized surface had a fine iron wire pressed against it with a constant force. According to Eccles, the procedure he utilized to oxide the iron wire (iron-mercury coherer) was as follows. He heated the iron wire inside a steam filled vessel until he achieved the desired thickness, as indicated by the interference color of the film. He indicated that a film whose inference color was blue was best and had a useful life, in air, of a month or two.

Eccles oxidized the iron plate (iron-iron coherer) by simply heating it in air until the interference color of the film indicated the desired thickness. He mentioned that these colors corresponded to those obtained when tempering steel. At the time I first read this, it seemed eminently reasonable that the tempering colors corresponded to an interference effect and hence provided a measure of the thickness of the oxide film, my ignorance of the tempering process being totally blissful. About a year later, during the course of reading a paper by Robert Williams Wood, I was rudely jolted into the real world by Wood's assertion that the tempering colors were <u>not</u> an interference effect at all. Wood

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[130] W.H. Eccles; On Coherers; Proceedings of the Physical Society (London); Vol. 22; 1910; pp. 289-312.

referred to the work of one A. Mallock, who showed that the tempering color did not change - though its intensity decreased - as the oxide film was reduced in thickness by gentle polishing. Continued polishing eventually removed all the color leaving a shiny clean metal surface. [131] Mallock's result was in concordance with optical theory with said that <u>no</u> interference effects could arise in the case of a thin transparent film (the oxide layer) on a mirror (the base metal). [132] The only way the film could appear colored was if the color were intrinsic to the film, itself. C. V. Raman, of Raman spectroscopy fame, agreed with Mallock's contention that tempering colors were <u>not</u> an interference effect. [133] The research engendered as a direct result of Mallock's initial experiment produced a large body of knowledge about tempering colors. Needless to say,

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[131] A. Mallock; Note on Certain Coloured Interference Bands and the Colours of Tempered Steel; Proceedings of the Royal Society (London); Vol. 94 (Series A); 1918; pp. 561-566 (in particular see p. 566).

Wood referred to these colors as a resonance effect, which would have depended on the frequency of the light, to distinguish them from interference effects, which depended on the structure having some relation to the wavelength of the light.

[132] The interference phenomenon called Newton's rings, which can give rise to light and dark bands under monochromatic light and colored bands with white light, requires two things: 1) constructive/destructive interference, <u>and</u> 2) that the interfering beams be of approximately equal intensity. Both conditions are met in the case of two glass surfaces with an air gap between them. In the case of a thin transparent film on a mirror, it was expected that the second condition would <u>not</u> hold. Robert Williams Wood showed, however, that in the case of a thin uniform layer collodion [nitocellulose dissolved in a mixture of ether and alcohol] on a mirror, colored bands <u>did</u> appear. See,

Robert W. Wood; <u>Physical Optics</u>; Macmillan; 1914; p. 172. [pp. 206-207 in the 1934 (3rd Ed.)]

In 1917, Lord Rayleigh decided to investigate Wood's experiment to see if he could verify and understand the mechanism behind its counterintuitive behavior. Rayleigh was able to verify <u>some</u> of Wood's results and agreed with Wood's explanation that the colors arose due to a "…frilling…" of the collodion film. However, the exact nature of this frilling and its influence on the light could not be determined. In the course of his paper, Rayleigh mentioned that Wood was <u>not</u> the first person to have seen this phenomenon and been puzzled by it. That honor apparently went to Henry A. Rowland, who - as Rayleigh relates it - wrote a letter to Rayleigh on March of 1893 in which he described a collodion on a mirror experiment identical in form and result to Wood's later work. See,

Lord Rayleigh; On the Colours diffusely reflected from some Collodion Films spread on Metal Surfaces; Philosophical Magazine [and Journal of Science]; Vol. 34 (6th Series); November 1917; pp. 423-428.

[133] C.V. Raman; The Colours of Tempered Steel; Nature; Vol. 109; January 26, 1922; pp. 105-106.

there were researchers who still supported the interference theory of temper colors, and their results and criticisms of Mallock's technique were as persuasive as the experiments and arguments mustered by the opponents of the interference theory.[134] Thus, the question of whether or not tempering colors were or were not an interference phenomenon spanned at least a quarter century, and might, for all I know, still be in progress today. Unfortunately, I was not able to delve any deeper into this fascinating subject due to time and space constraints. To complete our abrupt transition into the real world, it should also be noted that tempering colors are not even simply related to the surface temperature of the steel and do not even necessarily unequivocally quantify the degree of tempering.[135]

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[134] U.R. Evans; The Colours Due to Thin Films on Metals; Proceedings of the Royal Society (London); Vol. 107 (Series A); 1925; pp. 228-237.

F.H. Constable; The Cause of the Colours shown during the Oxidation of Metallic Copper; Proceedings of the Royal Society (London); Vol. 115 (Series A); 1927; pp. 570-588.

[135] The phenomenon whereby metals change color upon oxidation by heating has an extremely long history going back to at least the 1500s,

R.C. Gale; Note on "Temper" Colours; Journal of the Society of Chemical Industry, Transactions; Vol. 43; No. 50; December 12, 1924; pp. 349T-352T.

Nevertheless, the actual significance - with respect to tempering - of these colors was <u>not</u> generally known until the turn of this century. According to Gale, "Stead in 1900 showed that the colour of the film is dependent on the nature of the substance, the temperature of heating, and the time of heating…". An example of how different tempering conditions can produce the <u>same</u> tempering color was provided by the editor(s) of the journal *Nature* in their addendum to an article by C.V. Raman concerning tempering colors. According to the editor, the color called "…watchspringblue…" could be obtained by heating steel for a short time @ 300ºC or for 30 minutes @ 275ºK. This type of behavior was hypothesised to be due to the oxide existing in an "…open formation…" through which oxygen can freely move so as to reach the underlying metal according to Sir George Thomas Beilby. See,

C.V. Raman; The Colours of Tempered Steel; Nature; Vol. 109; January 26, 1922; pp. 105-106.

Anon.; Mr. Mallock has shown…; Nature; Vol. 109; January 26, 1922; p. 106.

Further information on the process of tempering can be found in the following references,

Denison K. Bullens; <u>Steel and its Heat Treatment</u>; John Wiley and Sons, Inc.; 1918; pp. 192-193.

Harry Brearley; <u>The Heat Treatment of Tool Steel</u>; Longmans, Green and Co.; 1918; pp. 108-111.

We would expect the iron-mercury coherer to be self-restoring since you can't weld anything to mercury, but the self-restoring behavior of the iron-iron coherer was more likely than not the result of the care taken by Eccles in controlling the DC bias and limiting the applied RF energy to real world wireless telegraphy levels. Three sets of measurements were made on each type of coherer: 1) the DC characteristics, i.e., the DC I-V curve; 2) the DC bias sensitivity curve, i.e., the output energy at the telephone receiver in series with the coherer for different polarities and values of the DC bias voltage with a fixed input of RF energy level; and 3) energy transfer ratio, i.e., the ratio of the RF input energy to the audio output energy at the telephone receiver. Note, the frequency of the RF energy was ~0.366 MHz.

The DC I-V curves for these coherers reveals that in their sensitive or decohered state, their resistance is normally much lower than that of for example a filings coherer: 50-2000 Ω for the iron-mercury versus about ~100,000 Ω for the filings coherer. This low DC resistance in the decohered state seems to be a general characteristic of metal-mercury coherers: the DC resistance of the Walter tantalum-mercury coherer is also usually in the range of 1200-1800 Ω.[136] The other striking difference between filings and metal-mercury coherers is the relative lack of sensitivity of the latter to vibration. **And lastly, the DC I-V curves were continuous all the way down to the origin, i.e., the decohered (or sensitive) detector did not appear to exhibit threshold behavior. There was no 'critical voltage' as was the case with filings coherers.** The DC bias sensitivity curves indicated that both the iron-mercury and the iron-iron coherers, when exposed to a fixed amount of RF energy, had an optimum bias. DC

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[136] L.H. Walter; Ibid.; p. 4.

voltages above or below this optimum value caused a reduction in the audio signal at the telephone receiver. This optimum DC bias was around 0.2-0.3 V. This was corroborated by the 0.2-0.4 V optimum bias found by Walter for his tantalum-mercury coherer.

Before going on, it should be mentioned Eccles coupled the RF energy inductively from the coil of a primary circuit to the coil of a secondary circuit which contained the coherer. Because of the large change in resistance experienced by the coherer in going from the decohered to the cohered state, Eccles had to make sure that the inductive coupling between the two circuits was very loose and that the tuning was slightly off center, otherwise the energy transferred would not be constant due the changing impedance of the receiving (secondary) circuit. The energy transfer ratio curves, as determined by Eccles, were linear, did not intersect the origin, and indicated that these particular coherers were, unlike the carbon microphone, not active devices, i.e., the ratio $E_{out}/E_{in} < 1.0$. A word of caution is in order with regards to this latter point, the audio energy produced at the telephone receiver was not determined in an absolute sense, [137] and so the energy transfer ratio was really not that well known.

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[137] Eccles' method of quantifying the audio output of the electromagnetic telephone receiver he used was as follows. He would listen to the tone produced by the action of the coherer on the RF signal, and then switch the telephone receiver to a different circuit which contained an interrupter producing the same tone by interrupting a known DC current. By adjusting the value of the known current until the amplitude of the sound it produced was equal, as judged by his hearing, to that created by the action of the coherer on the RF signal, Eccles was then able to quantify the audio output and so plot his energy transfer curve.

The linear energy transfer curve (output sound energy, which is related to the rectified current across the telephone receiver electromagnet coils, versus input RF energy @ 0.336 MHz) obtained by Eccles in 1910 using iron-mercury and iron-iron coherers, matches, with one exception, the linear responsivity curves (detected, i.e., rectified, output voltage versus RF input energy @ 75 GHz) obtained by Samuel Isaac Green *et al.* in 1969 using a phosphor bronze-tungsten MOM (Metal-Oxide-Metal) 'diode' (also see APPENDIX A). [138] The exception has to do with the fact that S. I. Green *et al.* observed polarity reversal of the rectified voltage at high RF input power levels; Eccles would not have been able to detect the same phenomenon, because the electromagnetic telephone receiver that he used to measure the coherer output, could not distinguish between rectified currents flowing in different directions. Note, Eccles was well aware that his linear energy transfer curve implied that the coherer was what Samuel Green later called a square law device, because he [Eccles] referred to this coherer as an integrating detector.

Eccles also measured the influence of the DC bias on the output of the coherer as judged by the loudness of the sound issuing from the telephone receiver: the DC Bias sensitivity curve. To this end, Eccles plotted for a given RF input power, the sound energy (y-axis) versus the bias voltage (x-axis). This procedure yielded a series of curves - one curve for each different RF input power. What he found was that the resulting curves had a maximum at an intermediate bias voltage; the size of the maximum increased as the RF input

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[138] S.I. Green, P.D. Coleman, J.R. Baird; The MOM Electric Tunneling Detector; in Jerome Fox (Ed.); <u>Proceedings of the Symposium on Submillimeter Waves</u>; Polytechnic Press (distributed by Wiley-Interscience); 1970; pp. 369-389. [I wish to thank Dr. Samuel Green for making me aware of the work done Kwok *et al.* of MOM 'diodes' which verified and extended his own work,

S.P. Kwok, G.I. Haddad, G. Lobov; Metal-Oxide-Metal (M-O-M) Detector; Journal of Applied Physics; Vol 42; No. 2; February 1971; pp. 554-563.]

power increased. These curves, for the iron-mercury coherer, tended to be very asymmetrical, i.e., the magnitude of the forward bias which yields the maximum sensitivity at a certain RF input power was different from the magnitude of the corresponding reverse bias, see Fig. 6. Eccles believed that this asymmetry was due to the material asymmetry of the coherer. When he made the same measurements utilizing a iron-iron coherer, he did in fact find that the curves were within experimental uncertainty symmetrical, see Fig. 7.

FIGURE 6 - Eccles' Rectified Audio Pwr. vs. DC Bias Voltage Plot;
MOM Detector: Fe-oxide-Hg, point-pool.

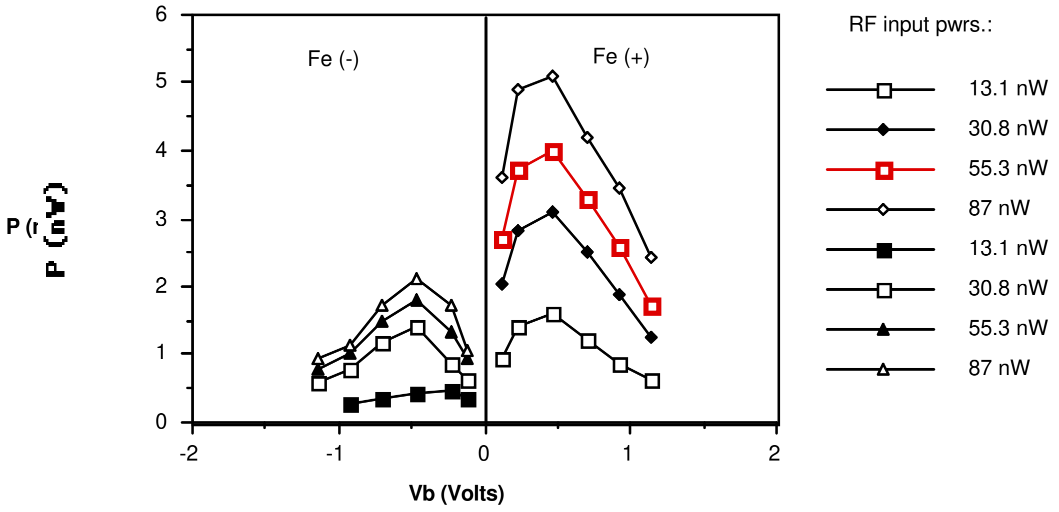
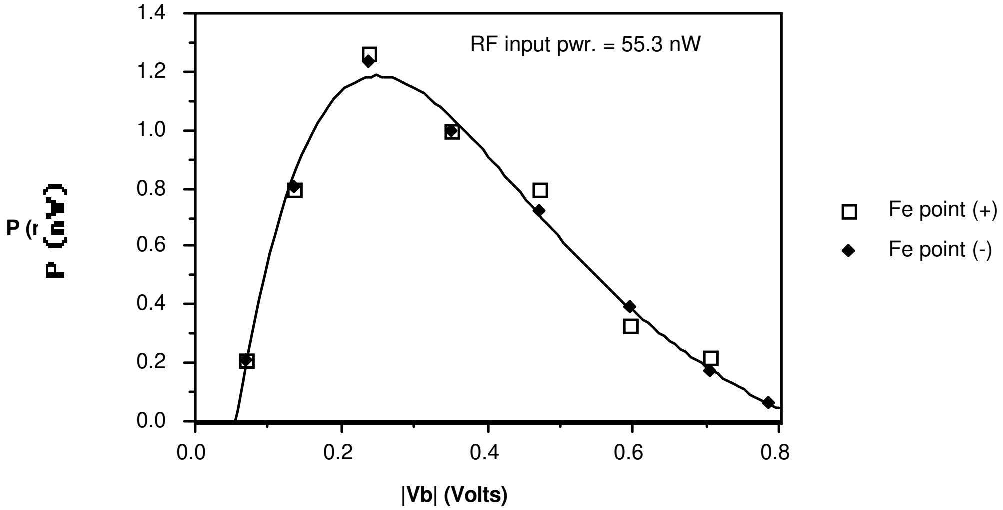


FIGURE 7 - Eccles' Rectified Audio Pwr. vs. Abs. DC Bias Voltage Plot; MOM Detector: Fe-oxide-Fe, point-plane.



A mere 63 years later, S. M. Faris *et al.*, while investigating detection of optical and infrared signals using MBM (Metal-Barrier-Metal) ‘diodes’ [139] - their term for what Samuel I. Green *et al.* called MOM ‘diodes’ - rediscovered essentially the same curves when they tried to find the optimum bias voltage at which to operate their MBM structures.[140] Faris *et al.* irradiated an electrolytically etched tungsten tip, pressed against a highly polished platinum base electrode, with a chopped (880 Hz) laser beam, and ferreted out the resulting light induced voltage (V_{ϖ}) via a lock-in amplifier whose reference signal originated from the output of a photodiode exposed to part of the chopped laser beam. Provided the pressure of the tip on the base electrode was not too high,

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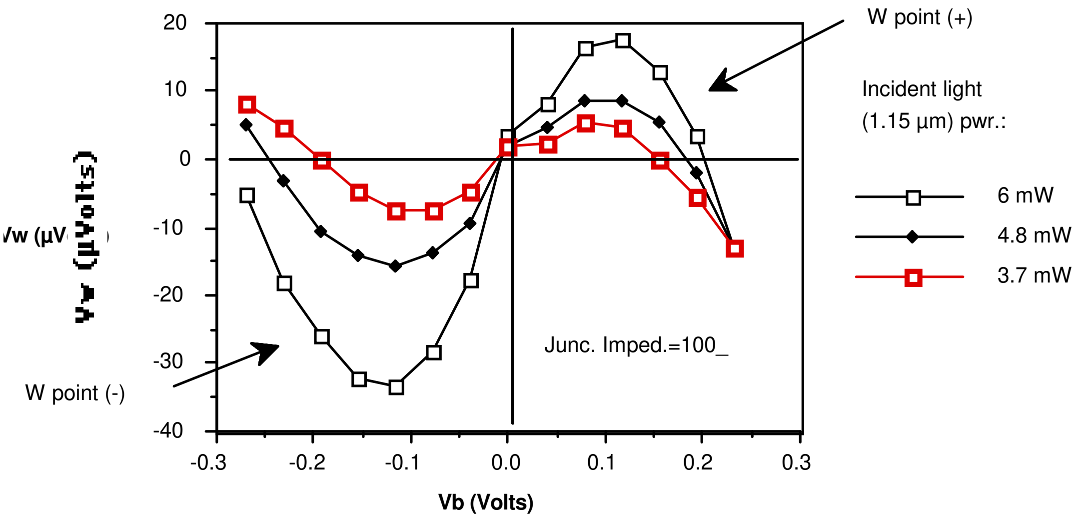
[139] The intention of Faris *et al.* not to prejudge the character of what might be separating the two metal surfaces may, in the end, turn out to be wisest strategy, especially if it turns out that the barrier is composed mainly of dirt. Where Lord Palmerston defines dirt as “…matter in the wrong place.” [Found in Lord Kelvin’s book Mathematical and Physical Papers, Vol. 6; p. 119.]

[140] S.M. Faris, T.K. Gustafson, J.C. Wiesner; Detection of Optical and Infrared Radiation with DC-Biased Electron-Tunneling Metal-Barrier-Metal Diodes; IEEE Journal of Quantum Electronics; Vol. QE-9; No. 7; July 1973; pp. 737- 745. [This was one of the very few papers dealing with optical and infrared detection or mixing using MBM ‘diodes’, which actually gave a circuit diagram of their experimental setup. For a reason or reasons unclear to me, this was and is not done by the majority of papers dealing with this topic.]

V_ϖ indicated a maximum at the intermediate values of forward and reverse DC bias, see Fig. 8.

FIGURE 8 - Faris' In-phase Voltage vs. DC Bias Voltage Plot;
MOM Detector: Pt-oxide[?]-W, plane-point.



With respect to the work of Eccles and Faris *et al.* on the bias needed for maximum sensitivity, there is a conundrum. Both groups of researchers measured the static, i.e., DC, I-V curves of their respective systems, and found the curves to be symmetrical and rather smooth. This would seem to rule out the explanation that the bias for maximum sensitivity occurs at a point of asymmetry in the I-V curve. In fact, the static I-V curves of Faris *et al.* appear to be straight lines, the small amount of nonlinearity was <u>not</u> then readily apparent at first glance. That rectification occurs at all was amazing given that the static I-V curves of Eccles and Faris *et al.* were symmetric.

After I became aware of these RF sensitivity versus DC bias curves, I wondered if the various point contact microwave diodes (1N21, 1N31, etc.) made famous by MIT's Radiation Laboratories during the early years of radar (circa

1945) exhibited such behavior? Unlike the structures of Eccles and Faris, which were MOM (Metal-Oxide-Metal) structures, these microwave diodes were MOS (Metal-Oxide-Semiconductor) arrangements or MBS (Metal-Barrier-Semiconductor) to coopt the terminology of Faris *et al.* It turned out that there was a curve called the 'current sensitivity curve', which was a plot of ß (rectified current/applied RF pwr.) versus V_f (DC forward bias voltage), that corresponds exactly to the sensitivity curves of Eccles and Faris. Note, the current sensitivity was defined as: "…the ratio of the short circuit rectified current to the absorbed r-f power…". One such ß vs. V_f curve taken by W. E. Meyerhof, *et al.* is reproduced in Fig. 9.[141] As far as I can determine, the RF power was kept constant for a given curve. The microwave diodes depicted in this figure included a silicon point contact (1N31) and a germanium welded contact diode (part number unknown).

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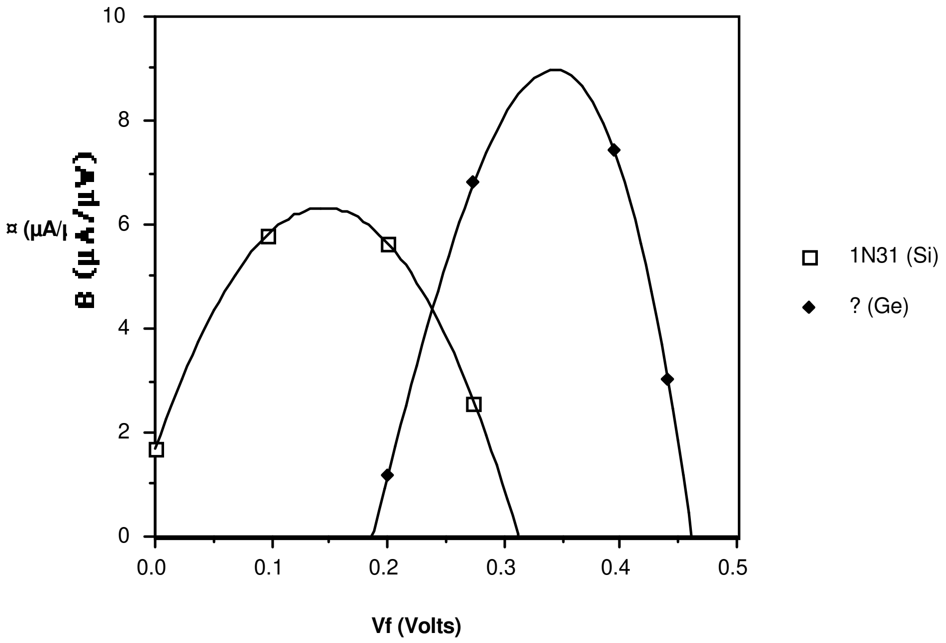
[141] Henry C. Torrey, Charles A. Whitmer; Crystal Rectifiers; McGraw-Hill Book Co.; 1948; pp. 335, 342. [Although Fig. 9 can be found in this book, it actually originated in the following National Defense Research Council (NDRC) report, whose citation is duplicated below with the same omissions and errors as found in the book,

W.E. Meyerhof, B. Serin, R.H. Vought; X-band Crystal [Video] Performance with Bias; NDRC 14-~~505~~ [456]; University of Pennsylvania; July 6, 1945; [14p.]

Note, this report was originally classified CONFIDENTIAL, but was declassified by authority of the Secretary of Defense in a memo written August 2, 1960. It was curious that Torrey and Whitmer were allowed to use this NDRC report and the data contained therein, in addition to other supposedly classified NDRC reports, in their book which was published in 1948. This practice appeared to be commonplace among all the volumes of the MIT Radiation Lab series of monographs. A copy of this particular NDRC report is on file in The University of Pennsylvania Archives, North Arcade, Franklin Field, Philadelphia, PA 19104-6320, (215)898-7024. I wish to thank Gail Pietrzyk for her help in locating all the NDRC (National Defense Research Council) reports held in the U. of P. archives. Copies of this report can also be obtained from The Library of Congress, Science and Technology Division, Washington, DC 20540, (202)707-5655. I wish to express my thanks to Charles Trew of The Library of Congress for his help in securing me a copy of this report.

As a point of interest, B. Serin in the early 1950s went on to participate in the experimental work which uncovered the isotope effect in superconductivity.]

FIGURE 9 - Meyerhof's Current Sensitivity vs. DC Forward Bias Voltage Plot; MOS diodes: point contact (Si) & welded contact (Ge)



The welded contact germanium diode were usually constructed by taking a sharpened platinum-ruthenium alloy whisker pressed against a flat piece of germanium doped with antimony and passing a large forward current through this combination for a few seconds. As one might expect this process produced diodes of varying quality and characteristics. The exact nature of the weld was, of course, not known. The reason for welding the metal catwhisker to the semiconductor was in the hope of reducing the 1/f noise which plagued all the point contact diodes.

The one thing that still needs explanation is the maximum in the sensitivity curves at intermediate biases. The explanation given by Torrey and Whitmer (1948) is neither satisfying or comprehensible:

> The rapid initial rise for germanium may be attributed to the rapid decrease in R [the diode forward resistance], which at zero bias has a value of the order of 10^6 ohms. It is clear that the current sensitivity becomes zero when the forward d-c bias voltage is greater than the contact difference of potential; in this case the barrier resistance and α [= f"(0)/f'(0); where f = I(V), i.e., f is the I-V curve of the device] become zero and the operating point is on the linear part of the d-c characteristic. [142]

Unfortunately, I do not have any better an explanation for this behavior. However, I do know that it appears to be a universal characteristic of coherer-like devices including even the electrolytic detectors (see APPENDIX B).

The sensitivity of the coherer depends on mechanical pressure, applied voltage, surface film thickness, and in the case of filings coherers the size and perhaps shape of the filings. A number of researchers have investigated the effect of mechanical pressure on the behavior of coherers and have found a correlation. Marconi's commercial coherers used beveled electrodes so that by rotating the tube about its long axis, the height of the pile of filings could be increased or decreased, and so change the coherer's sensitivity by modifying the mechanical pressure on the filings. André Eugène Blondel and Gaëtan Dobkévitch [143] state that the increase in sensitivity demonstrated by Tissot, when he employed a magnetic field in his coherer, was solely due to the increased mechanical force between the magnetic filings due to the presence of the magnetic field. The same effect was demonstrated by these two researchers by attaching a filings reservoir to their standard coherer so that they could, at will, adjust the amount of filings between the electrodes and so control the

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[142] Henry C. Torrey, Charles A. Whitmer; Crystal Rectifiers; McGraw-Hill Book Co.; 1948; p. 342.

[143] A. Blondel, G. Dobkévitch; Sur la sensibilité maxima des cohéreurs employés pratiquement dans la Telégraphie sans fils [Maximum Sensitiveness of Coherers]; Comptes Rendus Hebdomadaries des Seances de l'Academie des Sciences (Paris); Vol. 130; April 23, 1900; pp. 1123-1126. [Or see Science Abstracts, Series A; Vol. 3A; 1900; Abstract No. 1465.]

mechanical pressure experienced by the coherer filings on each other. According to Octave Rochefort [144] a nonself-restoring coherer can be made to be self-restoring by increasing the mechanical pressure on the filings, and the effect was reversible. The sensitivity of the coherer discharge alarm used by E. C. Green was adjusted by controlling the height of the filings in their A-shaped glass tube. And Bose, in his investigation of which elements made good coherers, always employed some method of applying pressure to the microphonic contacts. Finally, it should be pointed out that in modern times (circa 1973) Faris *et al.* observed a similarly strong dependence of the light wave sensitivity of their MOM structures on pressure, see Fig. 10. In this figure, the light wave sensitivity of the MOM structure lost its characteristic double extremum shape if the contact junction resistance decreased below a certain value; the contact junction resistance decreased with increasing mechanical pressure. Faris *et al.* ascribed the decrease in the contact junction resistance to a thinning of the barrier layer due to the increased mechanical pressure.

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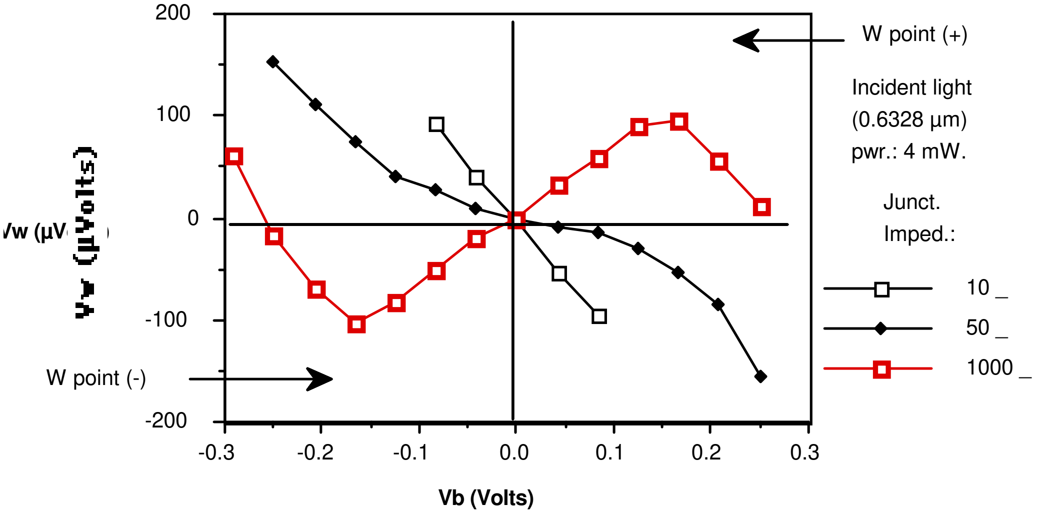
[144] O. Rochefort; Remarque sur le functionnement des cohéreurs et des autodécohéreurs [Coherers and Auto-Coherers]; Comptes Rendus Hebdomadaries des Seances de l'Academie des Sciences (Paris); Vol. 134; 1902; pp. 830-831. [Or see Science Abstracts, Series A; Vol. 6A; 1903; Abstract No. 475.]

FIGURE 10 - Faris' In-phase Voltage vs. DC Bias Voltage Plot; MOM Detector: Pt-oxide[?]-W, plane-point.



In the process of writing the section of APPENDIX E which dealt with the occurrence of coherer-like structures during the research this century into the nature of superconductivity, I came across another modern day example of a point contact structure which mimicked the behavior of Eccles' coherers.[145] In particular, these point contact structures, which were maintained at near liquid helium temperatures but above the critical or transition temperature, T_c, of the metals used, had the same rectified current (power) versus DC bias current (voltage) plot as found by Eccles for his point contact detectors. Due to time and space contraints, I cannot duplicate the relevant curves from the 1966 paper by Khaikin and Krasnopolin, but the interested reader can confirm what I am saying by looking up the paper and examining the curves in Fig. 1 along with the accompanying text. The researchers in this paper were using their low temperature point contact structures to detect modulated microwave radiation. The rectified current started out at zero at zero DC bias current, rose to a

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[145] M.S. Khaikin, I.Ya. Krasnopolin; Nonlinearity of Resistance of a Metallic Point Contact and Detection of Microwaves at Helium Temperatures; JETP Letters; Vol. 4; July-Decemeber 1966; pp. 196-199.

maximum at intermediate values of bias, and then fell back towards zero for sufficiently high DC bias currents. It was not obvious whether or not the authors of this paper tested their point contact structures for polarity reversal, in any event, they made no mention of it.

§10. NEGATIVE COHERERS: THE WASZIK EXPERIMENT. - Negative coherers responded to applied RF energy by increasing their DC resistance. Of all the coherers, those which exhibited this behavior were and are the most difficult to explain. Perhaps the best intimation of what was taking place during this behavior came by way of the rather sparse writings of one Josef Waszik. Waszik, who appeared to have only written two papers in his career - both in 1924, was investigating the phenomenon of coherers. [146] In particular, he was attempting to show that filings coherers and single contact coherers exhibited the same electrical and mechanical behavior, and that these actions were directly traceable to the presence of the thin insulating layer covering the metal filings and the contacts. One might think that at this late date - the heyday of coherers being twenty years earlier - there would not be much interest or work in this field. This assessment appears to be correct, but apparently, Waszik was inspired by a lecture given by that diehard coherer champion Édouard Branly in 1918 on the influence of the insulating surface layer on coherer behavior.

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[146] J. Waszik; Les Phénomènes Électrostatiques dans les Détecteurs a Limaille et a Contact Imparfaits [Electrostatic Phenomena in Detectors with Filings and with Imperfect Contacts].; L'Onde Electrique [The Electric Wave]; Vol. 3; November 1924; pp. 535-541.

Idem; Beitrag zur Erklärung der elektrischen Anziehung, die als Johnsen-Rahbek-Phänomen bezeichnet wird [Contribution to the eluciation of the electrical attraction, which is characteristic of the Johnsen-Rahbek phenomenon].; Zeitschrift fur Technische Physik [Journal of Applied Physics]; Vol. 5; No. 1; 1924; pp. 29-31. [A search of Science Abstracts A & B, over the time span 1918 (Vol. 21) to 1934 (Vol. 37), revealed only these two articles by Waszik.]

Waszik showed that cohering - he called it cohesion - could be provoked in two ways: 1) via RF (Radio Frequency) energy, and 2) by slowly increasing the DC bias until the 'critical voltage' was reached. Both these findings were nothing new, other workers in the field had demonstrated these same two methods of achieving cohering. What Waszik did, which was unique, was to convincingly show that there are two different types of cohering, one of which gave rise to negative coherer behavior, i.e., an increase in the DC resistance of the coherer under the influence of RF energy. According to Waszik, the two types of cohering were: 1) static cohesion, which was indicated by the conduction of a steady DC current through the detector when, for example its DC bias exceeded the 'critical voltage', and 2) vibrating cohesion, which occurred spontaneously just before static cohesion or could be induced artificially after the onset of static cohesion by carefully applying mechanical <u>tension</u> so as to pull the contacts apart ever so slightly. After artificially inducing vibrating cohesion, Waszik measured the DC resistance of the contact, and noted that this resistance <u>increased</u> significantly if RF energy were produced nearby. The significance of Waszik's finding was that it showed for the first time that one could reproducibly create a negative coherer by varying only one well defined experimental condition. It had been demonstrated by Branly, among others, that careful control of the applied mechanical <u>compression</u> was necessary for reproducible positive coherer behavior, but for some reason no one, until Waszik, apparently thought to apply a mechanical tension to a <u>cohered</u> single contact coherer. This work is probably one of the best leads we have to understanding the underlying mechanism of negative coherer behavior.

The work Waszik also did on the Johnsen-Rahbek effect has been relegated to APPENDIX D, where it more naturally contributes to the discussion of the Beilby layer.

§11. COHERERS AND COMPUTERS. - Because some types of coherers were bistable, there was a possibility of using them as memory elements. That this was and is not such a farfetched idea was shown by the U. S. government report of J. R. Bowman *et al.* [147] Bowman *et al.* were investigating the applicability of various systems for use as memory arrays and logic networks. Not surprisingly they decided to investigate whether the filings coherer could be adapted to act as a memory device. To give some perspective on this venture, I will digress for a moment and review the state of computer science at the time these reports were written, circa 1950.

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[147] J.R. Bowman, F.A. Schwertz, A. Milch, B. Moffat, R.T. Steinback, L. Nickel B.O. Marshall, Jr.; Computer Components Fellowship No. 347, Quarterly Reports Nos. 4 (July 10, 1951 - October 10, 1951) & 5 (October 11, 1951 - January 10, 1952); PB 109937 & PB 109938; U. S. Government (NTIS); October 1951 & January 1952; 83 & 85 p., respectively. [Note, copies of these reports were obtained from the Mellon Institute Library of the Carnegie-Mellon University; my contact was Cathy Bossick, (412)268-3171. A measure of the importance of this report can be appreciated from the fact that no less a leading computer designer at the time than J. P. Eckert, the co-inventor of the ENIAC computer, referenced this report in one of his papers,

J.P. Eckert; A Survey of Digital Computer Memory Systems; Proceedings of the IEEE; Vol. 41; October 1953; pp. 1393-1406.]

The first true electronic computer, the ENIAC (1945), used the Eccles-Jordan flip-flop as its memory element. [148] The flip-flops employed rather large and bulbous octal socket twin triode tubes which were arranged into arrays of ten flip-flops. The ten flip-flops in the array represented one decimal digit (0-9); the ENIAC stored numbers in their decimal representation instead of the more efficient binary form. Ten of these arrays of ten flip-flops were then grouped together to represent a ten-digit decimal number, this configuration was known as an accumulator. The disadvantages of this memory scheme were obvious: large size, significant heat production and modest, but surprisingly good for tubes, reliability. [149] The evolution of the memory element took a branching path after the ENIAC. In America, J. Presper Eckert's mercury delay line was the memory element of choice, while his Iconoscope (a modified cathode ray

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[148] Originally, when John Mauchly was first thinking about how to construct the accumulators (memories) of a electronic computer, he thought of adapting the circuitry of scalers. Scalers were and are used by particle and cosmic ray physicists to count the number of ionizing particles passing through their Geiger-Müller tubes. Because of the high cost involved in building scalers out of flip-flops using 'hard' vacuum tubes (Eccles-Jordan circuits), most scalers of that time employed gas filled tubes. Unfortunately, the maximum speed of the gas filled tubes was significantly less than that of the 'hard' vacuum tubes. It was this low operating speed which ultimately forced Mauchly and Eckert to go with the Eccles-Jordan circuit made of 'hard' vacuum tubes. A very complete description of the various gas filled tubes and their associated circuitry can be found in,

M.C. Nokes; Radioactivity Measuring Instruments, A Guide To Their And Use; William Heinemann Ltd.; 1958; chap. 7, Scalers.

[149] Anyone who thinks that vacuum tubes were reliable, circa 1945, should consult the following references to disabuse themselves of this notion,

F.R. Michael; Tube Failures in ENIAC; Electronics; Vol. 20; October 1947; pp. 116-119.

Nancy Stern; From ENIAC to UNIVAC, An Appraisal of the Eckert-Mauchly Computers; Digital Press; 1981; p. 32. [The chart on p. 32 comes from F.R. Michael's article.]

J. Presper Eckert, Jr.; Reliability of Parts; in Anon.; Theory and Techniques for Design of Electronic Digital Computers, Lectures given at the Moore School 8 July 1946 - 31 August 1946; The University of Pennsylvania; November 1, 1947; pp. 20_1-20_13, Lecture 20. [Eckert's lecture was concerned with the reliability of parts in general and not just vacuum tubes. Note, this document is not generally available, but it can be found at the library of the Moore School of the University of Pennsylvania.

Even by time of the Whirlwind computers (circa 1950), tube failures and the untimely demise of 'simpler' passive devices such as resistors, capacitors and crystals - to name just a few - were still a significant obstacle to the overall reliability of large electronic systems. See,

Kent C. Redmond, Thomas M. Smith; Project Whirlwind, The History of a Pioneer Computer; Digital Press; 1980; pp. 137-143.]

oscilloscope used as a memory element) was the dark horse entry - due to technical difficulties the Iconoscope did not see any usage in the U.S. until the construction of the Whirlwind computer, and even then these tubes only had a useful life of about one month.[150] However in England, F. C. Williams succeeded in adapting off-the-shelf cathode ray oscilloscope tubes to the task of storing data[151], while the mercury delay line found a loyal group of adherents such as M. V. Wilkes. Both the mercury delay line and the cathode ray oscilloscope memories (a.k.a. Williams tubes) were, what we call today, dynamic memories, since they required that the data contained within them be refreshed periodically. In addition, both of these memories were sequential access, as opposed to random access. The cathode ray oscilloscope memory eventually won out over the mercury delay line, because of its substantially higher bit storage/weight [or size] ratio, and its much faster access times. This led to its being incorporated into the American Whirlwind computer. By this time, circa 1950, the American version of the cathode ray oscilloscope memory had undergone substantial changes. It was, unlike the Williams tube, redesigned from scratch specifically for the purpose of storing data and so no longer resembled a conventional cathode ray oscilloscope tube.[152] One of the

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[150] Stan Augarten; <u>Bit by Bit, An Illustrated History of Computers</u>; Ticknor & Fields; 1984; pp. 195-202. [This book provides a comprehensive history of computers in general.]

J.W. Forrester; Reliability of Components; Annals of the History of Computing; Vol. 5; No. 4; October 1983; pp. 399-401.

[151] F.C. Williams, T. Kilburn; A Storage System for Use with Binary-Digital Computing Machines; Proceedings of the IEE; Vol. 96; Part III; March 1949; pp. 81-100. [This paper gives a very complete and understandable exposition of the mechanism behind the cathode ray oscilloscope's surprising ability to act as a dynamic memory device. It also includes schematics of the drive, refresh and read circuits employed with these tubes. One advantage this type of memory had over, say, the mercury delay line was that one could actual 'see' the data, i.e., the binary data appeared as dot and dashes on the fluorescent screen of the tube. During the actual running of a program the luminous dots and dashes could be observed to execute a complicated 'dance' thus providing a visual indication of the machinations of the software.]

[152] S.H. Dodd, H. Klemperer, P. Youtz; Electrostatic Storage Tube; Electrical Engineering (New York); Vol. 69; November 1950; pp. 990-995. [This journal can be found at the University of Pennsylvania's Moore School Library. Note, the current serial holdings printout for the Moore School Library does not show them having this journal at all, it is incorrect. This particular journal

improvements of the American design was the incorporation of a holding electron gun, which obviated the need to refresh the stored data, i.e., this memory was now static, not dynamic as was the case with the Williams tube.

From the proceeding retrospective, it should be apparent why there was interest in investigating all possible schemes for realizing memory capability. Among the candidates considered by Bowman *et al.* were magnetic delay lines, [153] electrolytic diodes, cold cathode diodes, Deltamax for static magnetic storage, electroluminescent material, and coherers. Note, this list may not be complete, since only four (nos. 1, 3, 4 & 5) of the seven quarterly reports were examined by me. The section on coherers in Quarterly Report No. 4 is less than one page long, and mentions that interest in using coherers as a switching device had resulted in the researchers constructing a binary-to-octal converter with fourteen filings coherers. Unfortunately, the information concerning this work is contained in the Quarterly Report No. 3, but this particular report does not appear in the NTIS (National Technical Information Service) index which contained the references to the Quarterly Reports Nos. 4 & 5. [154] Quarterly Report No. 5 devotes nineteen pages and nine figures to filings coherers. This

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went through quite a few name changes: Proceedings of the AIEE, Transactions of the AIEE, Journal of the AIEE, Electrical Engineering, and lastly (I believe) IEEE Spectrum.]

[153] The magnetic delay lines investigated by Bowman *et al.* are different from the Eckert mercury delay lines. The Eckert delay line consists of a steel tube filled with mercury with ultrasonic transducers located at either end of the tube, these two transducers must be parallel to one another to within a few minutes of arc. The electrical pulses which represent the data are converted into ultrasonic pulses by one of the transducers, and the resulting ultrasonic pulses are stored in mercury column for the length of time it takes them to propagate down the column to the other transducer where they are converted back to electrical pulses and feedback to the transmitting transducer to start the process over again. The magnetic delay line, on the other hand, works the same way as the Eckert delay line except that a magnetic wave is propagated down a length of iron wire.

[154] In an attempt to find this report I called Cathy Bossick, (412)268-3171, of the Mellon Institute Library. She checked her computer and found that the library did indeed have Quarterly Report no. 3, and that it did not have a Publication Board (PB) number; perhaps the authors of this report forgot to issue it.

report is concerned mostly with measuring the critical voltages and determining reliable methods of mechanically decohering the coherers. This report mentioned that a lot of earlier unsuccessful work was done by these same authors on using ultrasonic waves and magnetic fields to decohere the coherers. This unsuccessful work was reported in Quarterly Report No. 3.

The critical voltages of filings coherers containing different commercially available powdered metals (nickel, chromium, bismuth, iron III, iron IV, iron V, aluminum, zinc, tungsten, cobalt, copper II, antimony) were measured in various size coherers (1/16", 1/8" & 1/4" dia.). The experimental protocol was as follows. Fresh metal powder was put into a cell of a given size - the size indicating the distance between the electrodes - and a DC power supply, connected in series the coherer cell and a 56 kΩ current limiting resistor, was slowly ramped up in voltage until the coherer fired. This procedure was performed five times, each time with a fresh charge of powdered metal. The results showed that the larger the coherer cell, i.e., the farther apart the electrodes, the higher the critical voltage. Within a particular size cell and with a given metal powder, the critical voltages of the five trials agreed to within about ~15%. For the 1/4" & 1/16" dia. cells, chromium powder had the lowest critical voltage, while for the 1/8" dia. cell iron IV powder had the lowest critical voltage. This result contradicted Wolcott's assertion that nickel powder had the lowest critical voltage, but by omission did not address Strachan's assertion about cerium being the best coherer material. Bowman *et al.* also found that by increasing the DC power supply in 10 V steps and then connecting it across the coherer + current limiting resistor via a toggle switch, the critical voltage was only about half of what was determined by the slow ramping up procedure. This impulsive firing result seemed to support E. C. Green's contention that the critical voltage decreased with increasing frequency. All together, twenty-seven different metals were examined by these researchers. These metals were divided into three classes: coherable, noncoherable and conducting. Noncoherable simply meant that that particular metal powder did not coherer when placed in a 1/16” dia. cell even with a 500 V potential difference impressed across it; the label conducting was applied to any metal powder that did not exhibit the high initial resistance characteristic of filings coherers. The following Table lists the metals that fall into these three classes,

TABLE 2

COHERABLE	NONCOHERABLE	CONDUCTING
Aluminum	Arsenic	Gold
Antimony	Boron	Iridium
Bismuth	Calcium	Palladium
Chromium	Lead	Platinum
Copper	Magnesium	Rhodium
Cobalt	Selenium	Ruthenium
Manganese	Silicon	Silver
Molybdenum	Tin	
Nickel		
Niobium		
Tungsten		
Zinc		

The only outside reference cited in the coherer parts of the two reports of Bowman *et al.* was a early edition (1946) of Ragnar Holm’s book Electric Contacts. The metals which were listed under the heading CONDUCTING include most of the noble metals, i.e., those metals which allegedly do not readily form oxides when exposed to air. One of the other great controversies about coherers was whether or not you could build one out of noble metals such as gold. Branly was one of the researches who claimed that you could construct a coherer using one of the noble metals if you were careful, and to prove his point he constructed several filings coherers employing these metals. [155] The care that he exercised in building these noble metal coherers included precise control over the minuscule mechanical pressure between the filings, and equally fine control over the biasing potential. Obviously, Bowman *et al.* do not subscribe to this view, otherwise they would not have listed the noble metals in the conducting column.

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[155] E. Branly; Radioconducteurs à limailles d'or et platine [Coherers of Gold and Platinum]; Comptes Rendus Hebdomadaries des Seances de l'Academie des Sciences (Paris);Vol. 127; 1898; pp. 1206-1207. [Note, at the time Branly wrote this article, the term 'coherers' was not yet in wide use and hence Branly referred to them as 'radioconductors'.]

So, who is right? A partial answer can found in the works of Ragnar and Else Holm, in which they experimentally showed that even pure clean gold in air possesses a thin but tough - although not too tough - insulating (or, at least, semi-insulating) film, which allowed the sustaining of almost a 0.5 V DC voltage difference at the interface between two crossed gold rods pressed together with a few grams of force. Holm *et al.* have made extensive use of this crossed rod technique to investigate the influence of interfacial films on metals, including the noble metals.

Let us restrict our attention to the insulating film on gold. The first thing that needs answering is, what is the film composed of? The answer is not at all obvious. While most non-noble metals form oxides, does that also hold in the case of gold or the other noble metals? The answer, surprisingly, is that gold does form a number of oxides: Au_2O, Au_2O_3, Au_2O_2, AuO_2, etc. But the existence of an oxide does not imply that this same oxide will form directly on the surface of the metal in the presence of air. In the case of gold oxide, it is stated that the oxide cannot be formed directly by combination with oxygen. [156] The previous statement would appear to rule out a film of gold oxide on the surfaces of the base metal, but a search of the literature reveals that many researchers have evidence supporting the existence of an oxide film on most if and not all the noble metals. Because this subject is so important to our understanding of coherer behavior, we will go into it in some depth. Due to the amount of material we will need to cover to even begin to do this subject justice, this effort will be confined to APPENDIX B.

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[156] W.E. Caldwell; Gold; in the Encyclopœdia Britannica; William Benton; 1964; pp. 534-539.

While we are on the subject of which metals can function as coherers, I should like to ask the following question. With reference to the alkali metal coherers constructed by Bose, what is the insulating or semi-insulating film on these metals? These alkali metal coherers were usually constructed of lumps of the metal dispersed in some type of oil to prevent them from reacting with the water vapor in the air. The reason I am wondering about the exact nature of the insulating film between the alkali metal lumps is that it is not at all obvious what these films are composed of. The oil itself obviously contributes to isolating the metal lumps from one another, but is that all there is that serves as a barrier to electrical conduction? The short answer is, no. The long answer goes as follows. First, the solubility product of water in hydrophobic organic liquids is never identically zero, i.e., water is soluble to some extent or another in every hydrophobic liquid. This being the case, the dissolved water would preferentially react with the alkali metal lumps, thus forming a metal hydroxide layer at the metal surface and evolving hydrogen gas; in fact, a standard technique for drying hydrophobic organic liquids such as benzene is to place a couple of clean strips of sodium metal in the liquid to react with any dissolved water and then to remove the strips with their films of contamination. Another way in which a insulating film can form on the surface of alkali metal lumps immersed in hydrophobic organic liquids is via direct chemical reaction between the metal and the liquid.

When Percy W. Bridgman was investigating the effects of pressure on the electrical conductivity of alkali metals, he noticed that when he tried to store cesium under pentane (C_5H_{12}) a vigorous reaction was observed to take place between the metal and its 'protective' liquid. [157] Substitution of a higher series alkane liquid, such as iso-octane, yielded only a slightly lower reaction rate. Ultimately, Bridgman was reduced to storing the cesium under vacuum for long term storage, and working and shaping the cesium under nujol a short time before installing it in his hydraulic press. Only a thin layer of nujol remained on the cesium in the press, the rest having been removed by patting down the cesium pellet with filter paper. The reaction rate between cesium and nujol was apparently sufficiently slow that the above procedure was practical. Notice, though, that we said slow, not nonexistent; this is to be expected since nujol is a white, light mineral (paraffin) oil, [158] which according to the Merck Index (11th ed., entry #7141, Petroleum Benzin or Naphtha) [159] is principally a mixture of pentanes and hexanes; nujol, which is a very pure form of mineral oil mainly used to form mulls for infrared analysis. [160] Bridgman indicated in his article that when he mentioned the ability of cesium to react directly with various alkanes to some chemists of his acquaintance, they were surprised.

The reactivity of the alkali metals in Group IA of the Periodic Table increases as we go down the table, i.e., lithium is the least reactive while cesium is the most reactive of the nonradioactive alkalis. Since Bose mentioned that potassium coherers exhibit the property of negative coherer behavior, one naturally wonders whether the best alkali coherers would be the least reactive chemically? In other words, while some sort of film appears to be *de rigueur* for coherer action, too much reactivity on the part of the metal used in the coherer should be more detrimental than too little reactivity, e.g., gold and platinum coherers.

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[157] Percy W. Bridgman; The Resistance of 72 Elements, Alloys and Compounds to 100,000 kg/cm^2; Proceedings of the American Academy of Arts and Science; Vol. 81; 1952; pp. 167-251. [This paper can also be found in the following reference,

P. W. Bridgman; Collected Experimental Papers, Vol. VII; Harvard University Press; 1964; pp. 178-4113 - 178-4197.]

[158] Anon.; Aldrich Catalog; Aldrich Chemical Co., Inc.; 1990; nujol = mineral oil (#16,140-3).

[159] Susan Budavari (Ed.); The Merck Index; Merck & Co., Inc.; 1989.

[160] A mull is a mixture of nujol and a pure solid organic substance whose IR signature one wishes to determine. The suspension of nujol and the organic solid can be easily put between, for example, two KCl disks and the resulting sandwich inserted into an IR spectrophotometer.

A book that was frequently cited by modern researchers who were working with coherers was the one by Ragnar Holm and Else Holm. [161] This book was an exhaustively researched compendium of experimental and theoretical information regarding the operation of electric contacts such as DC motor commutators, automatic telephone switching networks, potentiometer sliding contacts, contacts between carbon microphone granules, etc. In short, Mr. and Mrs. Holm's interest lay exclusively in what happens when two conductors were brought into mechanical contact, some times repeatedly, and a current was forced to flow across the resulting junction. Examination of the index of Electrical Contacts revealed the absence of the word 'coherer' or 'coherers', so how can this book have anything to say about this subject? Like most of the other post 1910 works dealing with coherers, this particular monograph is not concerned with applying the coherer structure to the detection of RF energy. Instead, it was concerned with the effect of the coherer structure on the operation of switching systems such as the telephone system. A telephone system contains a multitude of current carrying mechanical junctions: the carbon microphone granules, the automatic switching network of Almon Brown Strowger or equivalent, terminal boxes, etc. Unlike a typical electronic circuit, where almost all the connections were soldered and all switching was done electronically via tubes or transistors, telephone systems, even modern ones, still rely on electromechanical switching. [162] Due to tarnish films formed on the switching network contacts, a coherer

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[161] Ragnar Holm, Else Holm; Electric Contacts, Theory and Application, 4th Ed.; Springer-Verlag; 1967; pp. 102-152.

[162] It will undoubtedly come as a shock to many people that telephone systems in the U.S. still have exchanges which employ the old style electromechanical relays. But it is true, nevertheless. See,

Cliff Stoll; The Cuckoo's Egg; Pocket Books; 1990; p. 52, 210.

On p.52 of Stoll's book, he explained some of the finer points of doing a telephone trace: "With luck, the trace might take a few seconds. But a few exchanges, left over from the 1950s, still use mechanical-stepping switches." And just so that no one can accuse me of U.S. bashing, consider structure was formed which had a critical voltage. When many switches appeared in series - as in the case of a telephone switching network - the effect of the summation of their respective critical voltages was significant and could degrade system performance. It was with this fact in mind that telephone engineers decided early on to use a relatively high operating voltage of 48-60 V DC, since this 'large' a voltage would be assured of exceeding the critical voltages of any reasonable number of switch contacts in series.

To give a feeling of how efficient a signaling system can be in the absence of switching networks with their attendant coherer structures due to mechanical contacts, consider this fact. After the successful laying of the second and third Atlantic telegraph cables in 1865 and 1866, respectively, Josiah Latimer Clark decided to see how small an electrochemical cell could be used to send easily readable signals through these submarine cables. To this end, he had the two Atlantic cables at Newfoundland connected together and then he sent a signal from Ireland over one cable and received it, a little more than a second later, on the other cable using a Thomson (Lord Kelvin) mirror galvanometer. What Clark was doing is what is called today a loopback test, in his case the round trip distance from Valencia (sometimes called Valentia) Island, Ireland to Heart's Content, Newfoundland and back was some 3,700 miles (statute). The

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the phone system in Hanover, Germany (formerly West Germany) described on p. 210. 'Steve replied. "But Hanover's phone lines connect through mechanical switches-noisy, complicated widgets-and these can only be traced by people. You can't trace a call with a computer."' On an episode of the Public TV series NOVA® devoted to dramatizing Stoll's book, they actually showed the Hanover telephone exchange. From what I could see, it appeared to use SXS (Step-by-Step) switches, which were invented in Kansas City, U.S.A., around 1889 by Almon B. Strowger.

Not to put too fine a point on it, but even some of the modern ESS (Electronic Switching Systems) in use by the various telephone companies utilize electromechanical switches. Examples of these electromechanical switches include: Ferreed (used in ESS #1 & #2) and Remreed (used in ESS #1, #2 & #3). See,

Bruce E. Briley; Introduction to Telephone Switching; Addison-Wesley Publishing Company, Inc.; 1983.

electrochemical cell employed by Clark was comprised of a "…very small…" silver thimble, a few drops of sulfuric acid, and a tiny piece of zinc weighing all of a gram or two; the resulting cell had an open circuit EMF of about 1.5621 V @ 25°C. That such a modest voltage could drive an intelligible signal over such a great distance is attributable to two factors. First, the excellent dielectric properties of the gutta-percha [163] insulation used to sheath the copper core, and to the fortuitous effect on this substance of the high pressure and low temperature (~37°F) found on the ocean floor, which tended to enhance its already formidable dielectric properties: if one of the cables was isolated from earth at both ends and then charged up, it took more than a half an hour before this charge leaked off to earth (the salt water of the sea surrounding the cable, which also served as the return line of the telegraph circuit). And second, the absence of mechanical junctions along the length of each of the two cables; each cable was made by splicing together shorter (1-3 mile) lengths of cable, and the

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[163] Today, gutta-percha is an almost forgotten substance. This is unfortunate given that it was the dielectric of choice on the early Atlantic submarine telegraph cables. Gutta-percha was found in the sap of the *Isonandra gutta* tree, and was obtained by 'tapping' the tree much in the same way as is done in the case of rubber trees. The method of collection was all that gutta-percha and natural rubber have in common. Their chemical and physical properties and the processing steps necessary before they can be used as an insulating covering on cables were all very different. The main advantage of gutta-percha was that it could be employed essentially in its native or raw state, it only needs to be slightly refined to rid it of its resin, absorbed water and foreign material such as pieces of bark, soil, stones, etc. Sir Charles Tilston Bright's explanation for the presence of large amounts or pieces of foreign material was quite trenchant, "Being sold by weight [the gutta-percha], the noble but enterprising savage is prone to incorporate with it all sorts of impurities, such as bark, clay, sand, and stones, or any other substance more plentiful and ready than gutta-percha itself…" [p. 285 of his book, see the next footnote]. In contrast, after natural rubber was refined, it had to undergo a chemical process called vulcanization, wherein it was mixed with sulfur and heated to no more than 300°F; vulcanization was discovered independently around 1843-44 in the United States and England by Charles Goodyear and Thomas Hancock, respectively. The introduction of sulfur during the vulcanization process had its downside in that the resulting vulcanized rubber could not be brought into intimate contact with the copper wire core of the cable lest the sulfur diffuse into the copper, thus reducing its conductivity in the long term - a buffer layer had to be located between the vulcanized rubber and the copper wire core.

Note, one of the few places gutta-percha is used today is in dentistry. Specifically in the root canal procedure where it is used to fill the canal after the nerve is removed. See,

J. Guinther; Still another health hazard heard from (Dental Division).; Welcomat; Vol. XXI; No. 51; July 8, 1992; p. 5.

splice joints were all soldered to eliminate the possibility of forming coherer-like structures with their critical voltage characteristics. The splicing operation was one of the most critical and time consuming steps in the manufacturing process, because if it was not done right the whole cable could be rendered unusable. Hence, the splicing operation was carried out in what amounted to clean room conditions and with stringent quality control proscriptions to prevent any possible failures due to infant mortality. [164] [165]

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[164] Charles Bright; Submarine Telegraphs, Their History, Construction, and Working; C. Lockwood; 1898; pp. 104-105. [Reprinted in 1974 by Arno. Sir Charles Tilston Bright was Chief Engineer of the Atlantic Telegraph Co. and it was under his stewardship that the first successful Atlantic telegraph cable was laid in 1858; Josiah Latimer Clark worked under Bright as a telegraph engineer. The first cable failed after about 700 messages were sent, most likely due to another one of Bright's engineers, Mr. Edward Orange Wildman Whitehouse. Whitehouse apparently was an ardent believer that more was always better, and used approximately 2000 V to send signals through the cable resulting in the subsequent degradation of the cable's insulation and the concomitant gradual and irreversible loss of the cable signaling ability. After the board of inquiry satisfied itself as to the cause of the cable's failure, I assume Whitehouse was encouraged to find gainful employment with some other establishment. In any event, his position as Chief Electrician was given over to Cromwell Fleetwood Varley.

Josiah Latimer Clark, besides signaling with cells constructed from thimbles, also was the first person to show experimentally that the speed of a pulse in the Atlantic cable was independent of the applied voltage at the sending end, this he did in 1863 - a result duplicated with presumably less effort by C.F. Varley in 1867 using his model cable. This result might seem obvious to us today, but it must be remembered that at the time of these experiments, James C. Maxwell's Treatise on Electricity and Magnetism had not been published - it would be published in 1873 - and even though Lord Kelvin's model of the cable explained many of the details of its functioning, there was still no overarching theory of electricity and magnetism formulated and, more importantly, disseminated to the working electricians of the time. Kelvin's electrical theories were based mainly on analogy with Jean Baptiste Joseph Fourier's theory of heat (heat being considered the dual of charge while temperature was the dual of voltage). Even when Maxwell's tome was published it did not meet with universal approbation, e.g., Lord Kelvin referred to it as "…the hiding of ignorance under cover of a formula…", see,

W.A. Atherton; Pioneers 6; Electronics & Wireless World; Vol. 93; June 1987; pp. 599-600.

[165] The term 'infant mortality' refers to those members of the population of tested components used in the next-higher-assembly which fail almost immediately upon incorporation. In the case of the Atlantic submarine telegraph cable, the components were the 1-3 mile sections of continuous (unspliced) cable, which were presumably tested to eliminate any defective or substandard individuals; the next-higher-assemble was the finished, i.e., spliced, cable. Given that the manufacturer had already culled the bad individual components at the factory, one might ask should any of the remaining components fail when they are inserted into the next-higher-assembly? The answer is that the very act of making up the final cable can introduce incipient failures due to any number of oversights: nicking the center conductor in preparation of splicing, allowing sweat from the technician's hands to get on the solder joint, improper application of the seal compound over the splice, etc. See,

Finn Jensen, Niels Erik Petersen; Burn-in; John Wiley & Sons; 1982; pp. 14-19.

CHAPTER 5 - THE RESURRECTIONS

“Everything old is new, again.”
- movie, All That Jazz, directed by Bob Fosse

§1. INTRODUCTION. - The rather arcane knowledge dredged up so far in this thesis might seem irrelevant to modern technological life. I mean, where would we find any possible use for coherers, catwhisker diodes, or any of the other superannuated detectors described so far? The answer, surprisingly, is everywhere.

The military development and use of radar during World War II and its subsequent commercialization owe a lot to the point contact diode. As the radar frequencies increased, in an effort to yield better spatial resolution, the task of heterodyning the returning radar signal (echo) down to an intermediate frequency low enough to allow substantial amplification became impossible with the vacuum tube mixers then available. The problem with the multiple grid vacuum tubes used as mixers were many: too noisy due to electron shot effect; too high an interelectrode capacitance, and hence effectively shorting the high frequency signals - both echo and the local oscillator signal - to ground; and degradation of the signal due to excessive transit time. The solution involved resurrecting the catwhisker diode.

The morphology of the resurrected catwhisker diode - sometimes called a point contact or crystal diode - was as follows,

> A small slab of silicon, containing boron or aluminum as an impurity [producing a P-type material], is mounted in the cartridge and a fine wire (catwhisker) of tungsten [typically 8 mils in diameter] is mounted in contact with it. A contact pressure of several ounces exists between the metal and crystal surfaces. The contact point is sharpened to a fine point. [The contact pressure was adjustable via a screw in the base of the cartridge. Once mechanical adjustment had yielded satisfactory electrical characteristics, a locking screw prevented movement of the adjusting screw, and the central chamber of the cartridge, housing the point contact and silicon slab, was filled with a wax that is viscous at room temperature, thus cushioning the catwhisker and so preventing mechanical shock and/or vibration or moisture from affecting the diode behavior. [166]] The contact area was small (about 10^{-6} sq cm) and the capacitance between the two surfaces, which tended to by-pass the radio frequency, is thereby minimized. [167]

Note, the silicon or germanium slab used in the point contact was initially polycrystalline, not the single crystal material we are familiar with today.

Initially, it was thought that the mechanism of rectification in point contact diodes could be explained on the basis of electron tunneling through the double layer at the surface of the metal catwhisker. Unfortunately, this theory predicted

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[166] E.G. Bowen; A Textbook of Radar; Cambridge University Press; 1954; pp. 395-397.

[167] D.G. Fink; Radar Engineering; McGraw-Hill; 1947; p. 426.

forward currents which were the reverse of those actually measured. With the realization that the semiconductor could also have a double layer at its surface, and that due to its lower carrier concentration the layer would be on the order 10^{-6} - 10^{-4} cm thick, which would preclude any tunneling because of its thickness, the tunneling theory died. The theory of Neville F. Mott and Walter Schottky [168] explained rectification in terms of the charge carriers surmounting the double layer potential barriers or layers instead of tunneling through them. [169] And while the Mott/Schottky theory does explain the DC forward bias behavior, at least in its general shape, the DC reverse bias behavior (including the negative resistance at high reverse bias voltages) and the RF mixing phenomenon, while surrounded by an incontestable amounts of empirical data, are still, in their details, pretty much cyphers. Even the details of the manufacture of the most well known point contact diode, the 1N2X [X = 1, 2, etc.], reads like some medieval necromancer's receipt for bringing back the dead. Consider the process for setting the pressure of the catwhisker. While monitoring the forward I-V characteristic of the diode at essentially DC (60 Hz), the screw setting the pressure of the catwhisker was advanced, forcing the catwhisker into the surface of the semiconductor crystal, until the electrical characteristics achieved a

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[168] N.F. Mott; The Theory of Crystal Rectifiers; Proceedings of the Royal Society (London); Vol. 171 (Series A); 1939; pp. 27-38.

W. Schottky; Zur Halbleitertheorie der Sperrschicht- und Spritzengleichrichter [Semiconductor Theory of Blocking-Layer and Point Rectifier]; Zeitschrift fur Physik [Journal of Physics]; Vol. 113; 1939; pp. 367-414. [Or see Science Abstracts, Series A; Vol. 42A; 1939; Abstract No. 4132.]

While both the preceding papers were exclusively concerned with the rectification theory for metal-semiconductor junctions, a later paper by Davydov dealt in a similar way with the rectification theory for semiconductor-semiconductor junctions, i.e., PN junctions,

B. Davydov; The Rectifying Action of Semiconductors; Technical Physics of the USSR; Vol. 5; No. 2; 1938; pp. 87-95.

[169] The tunneling through the surface potential barrier versus jumping over the barrier theories are also used to explain field emission and thermionic emission, respectively. Due to the extra energy that must be imparted to the electron in order to have it surmount the potential barrier(s), thermionic emission is always accompanied by large heat fluxes, i.e., cooling of the cathode. Field emission, on the other hand, does not involve any significant heat fluxes except I^2R contributions at large - with respect to the thermal capacity of the field emission tip - currents.

preordained criteria short of perfection, at this point "Judicious [emphasis added] tapping…" [170] with a mallet was used to coerce the recalcitrant diode's I-V curve to perfection. The effects of the multitudinous, judicious blows with the 'adjusting mallet' were significant, the forward resistance drops from 300-400 Ω to 200-300 Ω, while the reverse resistance increased from ~10 kΩ to ~ 20-100 kΩ. Another surprising bit of empirical knowledge was that good static performance (@60-120 Hz) was not a sufficient - or, as we shall see later, necessary - condition to assure the efficacy of the diode as a high frequency mixer, video detector, etc. [171] In addition, the accepted theory of the asymmetric I-V characteristic curve of the diode predicted that the work function of the catwhisker would have a pronounced affect on asymmetry of the I-V curve, but this was not observed in practice with silicon point contact diodes. [172] Consequently, any metal that was mechanically compatible with the crystal was used. Why the work function of the metal appears to be inconsequential to the basic behavior of the point contact diode was a great mystery until the concept of surface states was developed. While this concept of surface states explained away most of the observed behavior, it did not afford much relief from the problems caused by this phenomenon.

Before leaving the subject of point contact diodes, it must be mentioned that they are alive and well even today in the age of Gunn, Impatt, Schottky barrier, Esaki (tunnel or reverse), and PIN (Positive Intrinsic Negative) diodes.

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[170] Henry C. Torrey, Charles A. Whitmer; Crystal Rectifiers; MacGraw-Hill; 1948; p.324. [This book, which runs some 443 pages, was devoted to an exhaustive and exhausting exposition of everything-you-ever-wanted-to-know-about the 1N2X [1N3X] class of silicon, point contact diodes. This text was unique in that it does not just treat the diode as an entity to be analyzed only theoretically, but also took one deep into the bowels of the manufacturing process, and thus afforded the reader an uncommon view of the dichotomy between theory and practice.]

[171] Henry C. Torrey, Charles A. Whitmer; Ibid.; p. 20.

[172] Henry C. Torrey, Charles A. Whitmer; Ibid.; p. 317.

And point contact diodes are many times the standard against which the newer diodes are judged, even today.

Although I will not spend much time discussing it, the catwhisker diode also made possible the discovery of the transistor. Many people, technical and otherwise, are under the mistaken impression that the first transistor was a junction transistor, i.e., a PNP or NPN construction as is the case with modern transistors. It was not. The first transistor consisted of a slab of N-type germanium with a large-area low-resistance ohmic contact on its back surface and two metal (tungsten or phosphor bronze) point contacts spaced between 0.005-0.025 cm apart on the opposite surface; the ohmic contact served as the base terminal of the transistor while the point contacts played the *rôles* of the emitter and collector terminals (see Fig. 11a).[173] Preliminary evidence indicated that this first transistor operated by modulating the conductivity of the N-type germanium block only near the surface, i.e., conductivity modulation was thought not to be a bulk effect.

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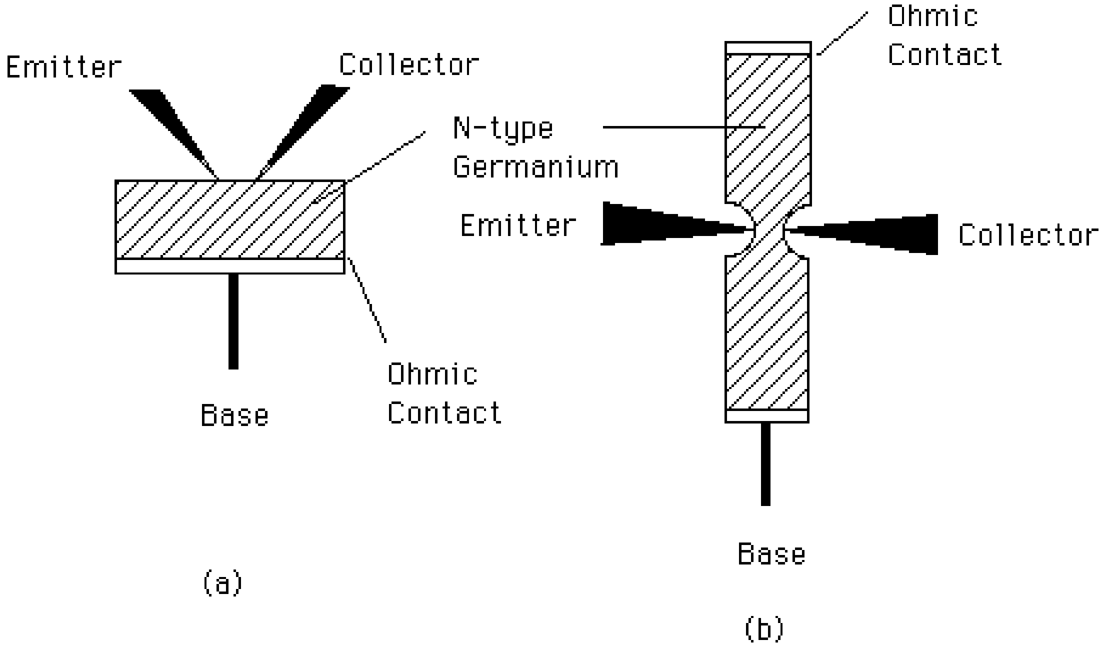
[173] J. Bardeen, W.H. Brattain; The Transistor, A Semi-Conductor Triode; Physical Review; Vol. 74; 1948; pp. 230-231.

FIGURE 11 - a) First Transistor, b) Coaxial Transistor



Unequivocal proof that conductivity modulation was indeed a bulk effect came from the coaxial point contact transistor of Winston E. Kock and R. L. Wallace, Jr., [174] who were extending the work done by John Shive on the wedge-shaped point contact transistors. The coaxial transistor consisted of a disk of doped germanium (125 mils dia. X 20 mils thk. [1 mil = 10^{-3} inch]) with a point contact located at the center of each face of the disk; the rim of the disk was the base contact and the two point contacts were the emitter and collector contact; the center of each of the two faces was dimpled inwardly, by grinding and lapping with a spherical tool followed by an electropolish operation, so that the distance between the two point contacts was only a few thousandths of an inch (see

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[174] W.E. Kock, R.L. Wallace; The coaxial transistor; Electrical Engineering; Vol. 68; March 1949; pp. 222-223.
Winston E. Kock; The Creative Engineer; Plenum Press; 1978; chapter 2: The Transistor, pp. 7-23.

Figure 11b). Note, Kock and Wallace mention in their their paper that the better the surface finish of the two dimpled areas, the higher the maximum current that the transistor could handle. Unfortunately for Kock and Wallace, the PN junction transistor [175] followed hot on the heels of the coaxial transistor, effectively shunting both types of point contact transistors into obscurity due to its superior reliability because of its lack of mechanical junctions.

After all I have just said about the point contact diode and transistor, I do not want to leave the reader with the wrong impression. No one really understood how and why they worked. [176]

With the advent of the laser, the coherer - in the form of a single contact coherer - had made a comeback of sorts. Specifically, it was used in a rather *ad hoc* manner to facilitate the heterodyning of laser and microwave sources for the purpose of "…establishing a frequency multiplier chain for comparing the frequency of short-wavelength infrared radiation with that of a standard microwave clock…". In its new capacity as a laser mixer and detector, the single contact coherer was renamed the MOM (Metal-Oxide-Metal) 'diode'. Because the course of events leading up to and including the laser heterodyning was reasonably convoluted and nonlinear, the following chronology is offered.

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[175] W. Shockley, M. Sparks, G.K. Teal; The p-n junction transistor; Physical Review; Vol. 83; July 1951; pp. 151-162.

[176] Joseph Lindmayer, Charles Y. Wrigley; Fundamentals of Semiconductor Devices; D. Van Nostrand co., Inc.; 1965; pp. 359-361.

§2. RECTIFICATION IS DISCOVERED. - In the beginning there was the crystal diode. The most common form of crystal detector consisted of piece of galena clamped in a metal holder which served as one electrode and probed with a sharp, springy metal counterelectrode, a.k.a. a catwhisker. It would be nice if I could dispose of its history that easily, but of course I can't since someone is most assuredly going to ask that bloodcurdling question: who invented or discovered it? Thankfully, the answer to that question, in this instance, is sort of simple. It was Karl Ferdinand Braun in 1874. [177] [178] Braun was investigating

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[177] Vivian J. Phillips; Early Radio Wave Detectors; Peter Peregrinus Ltd.; 1980; pp. 206-208. [Dr. Phillips also mentions the rather amazing fact that light generated by passing current through a point contact diode was observed in 1907,

H.J. Round; A Note on Carborundum; Electrical World (???); Vol. 49, 1907; p 309.

It took 78 years for SiC (carborundum)LEDs to become a commercially viable product, but as of 1985 Siemens AG of West Germany announced that it planned to market the first 'true blue' LED. This SiC based LED would have a forward voltage of 4 V @ 20 mA, and emit narrow band blue light centered at 480 nm. Because SiC has such a high sublimation point, the largest ingot that Siemens could produce was only about 15 mm dia. X 20 mm long,

J. Gorsh; Silicon Carbide Ends Long Quest for Blue Light-Emitting Diode; ElectronicsWeek; Vol. 57; October 8, 1984; p. 24, 29.

Anon.; Blue LED Uses Silicon Carbide; Laser Focus [now Laser Focus World]; Vol. 21; February 1985; p. 62.

L. Hindus; Blue, Superbright LEDs to change color-display equation; EDN (News Edition); Vol. 36; No. 3A; February 7, 1991; p. 5.

Some books refer to light emission from carborundum as the Lossew effect after O.W. Lossew,

Joachim Schubert; Dictionary of Effects and Phenomena in Physics; VCH Verlagsgesellschaft mbH; 1987; p. 46.

According to Schubert's book, Lossew observed luminescence in SiC diodes in 1923. The citation he gives to support this claim is an indirect one,

L. Bergmann, C. Schaefer; Lehrbuch der Experimentalphysik, Vol. 4; Walter de Gruyter; 1975.

I was unable to find any libraries that had Vol. 4 of this textbook. Likewise, Temple's Interlibrary Loan department could not find Vol. 4, although, they were able to locate Vols. 1-3. In an attempt to locate original source material I tried the Science Abstracts, Series A. There were no citations from 1920 (Vol. 23) to 1929 (Vol. 32). The earliest citation mentioning luminescence in SiC diodes was in 1931,

O.W. Lossew; Leuchten II des Karborundumdetektors, elektrische Leitfähigkeit des Karborundums und unipolare Leitfähigkeit der Kristalldetektoren. [Luminosity of Carborundum Detectors, …]; Physikalische Zeitschrift; Vol. 32; September 1, 1931; pp. 692-696.]

[178] [K.]F. Braun; Ueber die Stromleitung durch Schwefelmetalle [On Current Conduction through Metal Sulfides]; Annalen der Physik und Chemie; Vol. 153 (2nd Series); 1874; pp. 556-563.

Anon.; Neue Deutsche Biographie, Vol. 2; Duncker & Humblot; 1953; pp. 554-555. [This is one of the few references to use Braun's full name, Karl Ferdinand Braun. Most articles and/or books which mention Braun, invariably refer to him as Ferdinand Braun.]

the conductivity of solids, in particular, minerals such as galena and pyrite. The reason Braun was interested in the conductivity of minerals was that he was trying to verify that Ohm's law held for these substances. [179] The way he measured conductivity was to clamp the specimen to a large metal base, which also served as an electrode, and probed the sample with a thin springy wire, the catwhisker. What Braun found, which surprised him enormously, was the typical asymmetrical and nonlinear diode response; the various sulfur containing minerals he examined violated Ohm's law. The *raison d'être* of the catwhisker, as opposed to a larger electrode, was that the nonohmic behavior occurred most easily with the catwhisker, and even then it was and is highly irreproducible.

Around the same time Braun was making his discoveries of nonohmic conduction in minerals, Arthur Schuster was independently finding the same

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[179] The person <u>credited</u> with being the first to demonstrate electrical conduction, ohmic or otherwise, was an Englishman named Stephen Gray. Gray, whose name does not grace many - perhaps any - modern day physics textbooks of my acquaintance, made his seminal discovery around 1729, and later collaborated with Granville Wheler to extend his original work. See,

W.A. Atherton; Pioneers 1; Electronics & Wireless World; Vol. 92; No. 1611; January 1986; pp. 100-102.

Gray's demonstration of electrical conductivity involved, in its most sophisticated form, a brass wire 886 feet long suspended at regular intervals by fine silk threads; at one end of the wire was an ivory sphere, while the other end of the wire simply hung out in space. When a glass rod, that had been charged by rubbing, was touched to the free end of the suspended brass wire, the initially uncharged ivory sphere at the other end of the wire acquired a static charge. As a result of his researches, Gray divided all materials into two broad classes: conductors and insulators. **Note**, without taking anything away from Gray, it should be mentioned that Otto von Guericke - famous for his air pump with which he evacuated the Magdeburg spheres - had shown earlier that electricity could be conducted along a damp linen thread. Gray and Wheler's demonstration of electrical conduction was extended around 1747 by Sir William Watson when he discharged a Leyden jar via a 2 mile long wire insulated from the ground along its length and employing the Earth as a return to complete the circuit. Citations to Gary's original papers, along with citations to many other early workers in the field of electricity, can be found in the following book,

Duane Roller, Duane Henry D. Roller; <u>The Development of the Concept of Electric Charge</u>; Harvard University Press; 1954.

behavior in an entirely different system. Specifically, Schuster uncovered - without knowing it - the rectifying properties of cuprous oxide, Cu_2O, films between mechanical connections of copper wires.[180] The amazing thing about Schuster's discovery is that he correctly deduced that the nonohmic behavior was due to an air film on the copper wires jointed together at a screw terminal. This deduction is doubly amazing since it is based on the following premises. Schuster noted that if one formed a spark gap in air composed of a pointed electrode and a flat or spherical counterelectrode, the DC breakdown potential was different depending on whether the pointed electrode was positive or negative, i.e., the gap exhibited asymmetric behavior.[181] In addition, he also

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[180] A. Schuster; On Unilateral Conductivity, Philosophical Magazine [and Journal of Science]; Vol. 48 (4th series); 1874; pp. 251-258. [There are actually two oxides present when copper is oxidized: Cu_2O and CuO, known respectively as cuprous oxide and cupric oxide. Cuprous oxide gives copper a reddish sheen, and because it is a semiconductor is responsible for the nonohmic properties observed by Schuster. Cupric oxide, which usually forms on top of the cuprous oxide, gives copper a blackish sheen and being an insulator can if it is thick enough nullify the effect of the underlying cuprous oxide layer. For an excellent history of the discovery of rectification and the ensuing developments leading up to the point contact diode and transistor see,

G.L. Pearson, H. Brattain; History of Semiconductor Research; Proceedings of the IRE; Vol. 43; No. 7; 1955; pp. 1794-1806.

For a more detailed description of copper rectifiers see APPENDIX G. Another interesting source of information on copper oxide rectifiers and point contact diodes is the following book,

Heinz K. Henisch; Metal Rectifiers; Oxford University Press; 1949.]

[181] The asymmetric breakdown behavior of point-plane configurations with respect to the polarity of the impressed DC voltage was a commonly observed phenomenon during the mid-1800s. Sir William Thomson (later Lord Kelvin) remarked in his detailed description of his quadrant electrometer that the polarity of the needle (the movable, sharp surface) should be positive and the quadrants (the fixed, smooth surfaces) negative for maximum breakdown voltage. See,

Sir William Thomson; Report on Electrometers and Electrostatic Measurements; in [Henry Charles] Fleeming Jenkin (Ed.); Reports of the Committee on Electrical Standards appointed by The British Association for the Advancement of Science; E. & F.N. Spon; 1873; p. 155.

Quantitative measurements, on the asymmetrical current conduction of glow discharges with respect to the polarity of the applied DC voltage using a point and plane electrode arrangement, were made by Robert Francis Earhart and Chas. H. Lake around 1910,

R.F. Earhart, C.H. Lake; The Rectifying Effect in Point and Plane Discharge; Physical Review; Vol. 30; April 1910; pp. 460-470.

In 1922, the asymmetric discharge behavior previously alluded to was marketed as a rectifier called the S-tube. The S-tube consisted of a glass envelope filled with a gas at low pressure and having two asymmetrical cold carbon electrodes. Carbon - the exact type of carbon, they did not specify - was picked for the electrode material because of its resistance to gas clean up, which is always accompanied by disintegration (spalling) of the negative electrode (cathode) due to the occlusion of the gas and the concomitant increase in the mechanical stresses within the mentioned that it was widely known that air 'condensed' at the surfaces of metals. From these two premises, Schuster deduced that when copper wires are mechanically joined, their microscopically rough surfaces would have a thin film of air trapped between them, and so would behave like microscopic, air spark gaps with their attendant asymmetric breakdown behavior - Schuster referred to this behavior as unipolar to indicate its asymmetrical nature.

To add a bit more confusion to the priority claims surrounding the discovery of nonohmic conduction, it should be mentioned that a 1955 book on the then nascent transistor claimed that nonohmic conduction was first observed, not in 1874, but in 1835. Specifically, this book claimed that P. S. Munck, who we met earlier as perhaps the discoverer of the phenomena of cohering, wrote about nonohmic conduction in solids in the same paper which introduced the world to cohering in solids! [182] Unfortunately, I did not have the time to attempt a translation of Munck's paper in order to validate this rather startling claim.

No <u>deliberate</u> point contact structures were employed by Schuster, and it does not appear that Schuster attempted to adapt this nonohmic behavior to a useful device, e.g., as a diode detector of RF energy. However, when the British Association [for the Advancement of Science] (BA) finally decided on the creation of a standard for the Ohm (and other electrical units of measure) in order

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electrode. The secret behind the S-tube's success, according to its discoverers, was its use of the "short path principle", i.e., that below the 'critical pressure', the sparking voltage <u>in</u>creases for <u>de</u>creasing electrode separations (see the discussion of W.R. Carr's work in APPENDIX E of this thesis). For more info on the S-tube, see,

V. Bush, C.G. Smith; Control of Gaseous Conduction; Journal of the American Institute of Electrical Engineers; Vol. 41; September 1922; pp. 627-635.

[182] Thomas R. Scott; <u>Transistors and Other Crystal Valves</u>; MacDonald & Evans, Ltd.; 1955; pp. 1 & 237. [The paper by "…Munk [sic]…" that Scott referred to was,

P.S. Munck; Versuche über die Fähigkeit starrer Körper zur Leitung der Elektrizität [Experiments on the Ability of Solid Bodies to Conduct Electricity]; Annalen der Physik; Vol. 34 (2nd Series); 1835; pp. 437-463.]

to facilitate the building, testing and troubleshooting of the various submarine telegraph cables, the committee formed in the early 1870s - which was an extension of still earlier committees concerned with this same subject - besides including William Thomson (Baron Kelvin of Largs, a.k.a. Lord Kelvin), James C. Maxwell, J. D. Everett, and George Chrystal also enlisted the help of Schuster. Besides being a very competent physicist both as a theoretician and experimentalist, [183] Schuster's researches into nonohmic behavior uniquely qualified him as an expert on what not to do when trying to create an ohmic standard: all wired connections between the various pieces of electrical equipment were either soldered or the wires were cleaned and then dipped into pools of mercury to affect the connection. No twisted together or clamped connections were allowed. [184] Using an apparatus originally designed by Maxwell, Chrystal was ultimately able to show that in the metals and alloys he was examining, Ohm's law held to at least 1 part in 10^{12}.

It should be noted that the creation of a standard for the Ohm was as enormous an undertaking as the laying of the Atlantic submarine telegraph cable. The form of the standard resistor, whether it was to be a coil of wire made of some alloy as was favored by Augustus Matthiessen [185] or a column of 'pure'

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[183] Though it is not well known, Schuster actually measured the charge to mass ratio (e/m) of the electron before J. J. Thomson. In addition, Schuster was the first to recognize the effect of ions of different masses - and hence mobilities - on the spatial variation of the voltage in a glow discharge. See,

A. Schuster; The Discharge of Electricity through Gases; Proceedings of the Royal Society (London); Vol. 47; 1889-1890; pp. 526-559.

[184] P.J. Davies, J.O. Marsh; Ohm's law and the Schuster effect; IEE Proceedings; Vol. 132 (Pt. A); No. 8; December 1985; pp. 525-532.

C.A. Hempstead; The early years of oceanic telegraphy: technology, science and politics; IEE Proceedings; Vol. 136; Pt. A; No. 6; November 1989; pp. 297-305.

[185] Augustus Matthiessen (1831-1870) is famous today for what is called Matthiessen's Rule, which has to do with the effect of the minority metallic component of an alloy on the alloy's resistivity as a function of temperature. Note, there lived at same time as Augustus Matthiessen, a physicist named Heinrich Friedrich Ludwig Matthiessen who is famous today for what is called

mercury as was championed by Wilhelm Eduard Weber, was itself a very difficult decision to make - Weber's suggestion ultimately won. Matthiessen's idea of using a solid wire resistance standard suffers, then as now, from the fact that one is never sure of the exact molecular arrangement of the metal after it has been drawn into the form of a wire, even after annealing. By molecular arrangement we mean not only differences in grain structure and orientation, but also the appearance and disappearance of various allotropic and polymorphic forms, which can have diametrically opposed electrical properties, e.g., α-Tin is nonmetallic, while β-Tin is metallic. [186] Matthiessen's own results on the stability of solid wire resistance standards confirmed the metastable nature of these molecular arrangements. He found that the resistance of wires maintained under constant environmental conditions exhibited systematic changes in resistance with time. The obvious advantage in using mercury was that the molecular arrangement of a liquid was relatively invariant on average compared to that of a solid, especially a solid which has been mechanically worked or was subject to residual stress. [187]

Matthiessen's Ratio, which relates the focal length of the lens of the eye to the lens radius in fishes. In addition, around this same time period there also lived one Adolphe Matthiessen who also did vision related work. You can well imagine the confusion that results from references which give the author as either A. Matthiessen or simply Matthiessen.

[186] B.D. Sharma; Allotropes and Polymorphs; Journal of Chemical Education; Vol. 64; No. 5; May 1987; pp. 404-407.

Jerry Donohue; The Structures of the Elements; John Wiley & Sons; 1974.

[187] These same considerations about the unknown and many times unknowable influences of mechanical stress and strain caused Karl Ferdinand Braun to employ molten metal junctions in his study of thermoelectric behavior,

[K.]F. Braun; Über die Thermoelektricität geschmolzener Metalle [On the Thermoelectricity of molten Metals]; Sitzungsberichte Der Königlich Preussischen Akademie Der Wissenschaften zu Berlin [Proceedings of the Royal Prussian Academy of Science, Berlin]; Vol. 18; April 9, 1885; pp. 289-298. [Because of the great difficulty I had in differentiating this particular journal from the seeming plethora of similarly named German journals, I will include its Library of Congress call number: AS 182 .B35.]

Braun eventually used his discovery of the crystal diode in the detection of radio waves for commercial wireless telegraphy, and hence became a commercial competitor of Marconi; Braun and Marconi shared the 1909 Nobel prize for physics for the work they had done to advance the field of wireless communication. Besides the catwhisker diode, Braun also invented the oscilloscope, which we shall see employed in the hunt for the mechanism of rectification. [188]

§3. THE THERMOELECTRIC THEORY OF RECTIFICATION IS VANQUISHED, ALMOST. - Because of the crystal diode's widespread commercial applications and hence the need to optimize its behavior, the question of how it worked became more pressing, so to speak. One of the most prevalent theories was the thermoelectric theory, which postulated that the heating of the junction by the passage of current was responsible for the asymmetric and nonlinear I-V curve, since the thermally induced thermoelectric voltage would aid the current flow in one direction and impede it in the other direction. Although this theory was wrong, at the time it was eminently reasonable given that the only other asymmetrically constructed electrical junction which produced asymmetric I-V characteristics was the thermocouple. The thermocouple effect was discovered around 1821 by Thomas Johann Seebeck; I will not allow myself to get drawn into the morass concerning who actually discovered the thermocouple, itself.

Although, Karl Ferdinand Braun did <u>not</u> know why the asymmetric conduction occurred, he had correctly surmised that the mechanism was <u>not</u>

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[188] Gerald F. Tyne; <u>Saga of the Vacuum Tube</u>; Sams Publication; 1977; p. 37.

thermoelectric in nature. He reached this conclusion by satisfying himself experimentally that the observed asymmetry in the current was unchanged even if short voltage pulses, as opposed to the continuous voltages used initially, were applied to the catwhisker diode. He reasoned that this was so, because the rise in the temperature of the system, due to I^2R losses in the case of sufficiently narrow voltage pulses, would be insignificant due to the large thermal time constant of the system. Braun reached this conclusion in the paper where he first introduced the world to the phenomenon of rectification in 1874. But it would take two more papers before he thought he had provided enough evidence to convincingly refute the assertions of the thermoelectric school of rectification. [189] His last paper on the subject employed a pendulum switch interrupter to generate the voltage pulses. A pendulum switch interrupter simply has one side of the switch attached to the bottom of a pendulum bob, and the other side of the switch is connected to a pool of mercury sitting at the lowest point in the pendulum's travel. Each time the end of the pendulum bob is at the bottom of its travel, it passes through the mercury pool, closing the switch. From what I have been able to uncover, this pendulum switch interrupter idea appears to have been first thought of by Hermann von Hemholtz. All Braun's efforts notwithstanding, he never did achieve his quaesitum of quashing the thermoelectric school of thought.

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[189] [K.]F. Braun; Ueber Abweichungen vom Ohm'schen Gesetz in metallisch leitenden Körpern [On Departures from Ohm's Law in Metallic Conducting Bodies]; Annalen der Physik und Chemie; Vol. 1 (New Series, a.k.a. 3rd Series); 1877; pp.95-110.

Idem; Einige Bemerkungen über die unipolare Leitung fester Körper [Some Observations on Unipolar Conduction in Solid Bodies]; Annalen der Physik und Chemie; Vol. 19 (New Series, a.k.a. 3rd Series); 1883; pp. 340-352.

Friedrich Kurylo, Charles Susskind; Ferdinand Braun, A Life of the Nobel Prizewinner and Inventor of the Cathode-Ray Oscilloscope; The MIT Press; 1981.

It was left for George Washington Pierce, between 1907 and 1909, to try to prove experimentally, once and for all, that the thermoelectric theory of diode action was incorrect. [190] During this same time period, Pierce also became the first person to get an oscillographic record of the AC voltage across, and the resulting DC current through, a diode.

How he made the oscillograph is interesting in and of itself. He used a Braun tube (oscilloscope) with a cold cathode (no filament cathode or indirectly heated cathode), the electrons being produced by **ionization of the residual gas** in the tube. Note, it is sometimes erroneously stated that the electrons in a Braun tube are produced via field emission; the Braun tube is a linear descendant of the Hittorf-Crookes tube (gas x-ray tube), which likewise generated its electrons (cathode rays) by ionization of the residual gas in the tube. In fact, both the Hittorf-Crookes tube and the Braun tube would cease to function if the residual gas pressure was too low. For this reason, many times these tube were continuously pumped so that deliberate leaks could be employed to maintain the desired gas pressure. Present day oscilloscope tubes employ a very 'hard' vacuum, and obtain their electrons via thermionic emission. 191

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[190] G.W. Pierce; Crystal Rectifiers for Electric Currents and Electric Oscillations (Part I); Physical Review; Vol. 25; 1907; pp. 31-60.

Idem; Crystal Rectifiers for Electric Currents and Electric Oscillations (Part II); Physical Review; Vol. 28; 1909; pp. 153-187.

Idem; Crystal Rectifiers for Electric Currents and Electric Oscillations (Part III); Physical Review; Vol. 29; 1909; pp. 478-484.

[191] Today, there are serious efforts afoot to build flat panel displays using arrays of atomically sharp field emitters, i.e., so-called vacuum microelectronic technology. These vacuum microelectronic structures require only a few volts to function. See,

T. Harbert; HDTV holds promise and peril for EEs; EDN (News Edition); March 7, 1991; p. 23 & 28.

R.A. Lee; Return of the Vacuum Valve; Electronic & Wireless World; Vol. 95; May 1989; pp. 443-447.

Because the distance between the anode and cathode in the Braun tube was on the order of 10 cm, the tubes usually require tens of thousands of volts to function. G. W. Pierce employed the 20,000 V tap off a 40,000 V battery and regulated the resulting current with a running water resistor. [192] The Braun tube employed magnetic horizontal deflection (signal amplitude); there was no vertical magnetic or electrostatic deflection (signal time base), the time base was added during the photographing of the horizontally deflected trace by way of a synchronously rotating mirror; synchronous, that was, with the 60 Hz current used in the magnetic deflection circuit. Because of the thickness of the phosphor screen, it was photographed from the same side that was being bombarded by

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C.A. Spindt, I. Brodie, L. Humphrey, E.R. Westerberg; Physical properties of thin-film field emission cathodes with molybdenum cones; Journal of Applied Physics; Vol. 47; No. 12; December 1976; pp 5248-5263.

[192] According to George W. Pierce, the 40,000 V battery he used to power his Braun tube was placed at his disposal by John Trowbridge. Around 1900, Trowbridge had finished installing the 40,000 V battery in his lab at the Jefferson Physical Laboratory, Cambridge, MA, where he was the director. For those who doubt the grandeur of this battery, consider Trowbridge's own words. "I have lately completed the installation of a plant of twenty thousand storage cells in the Jefferson Physical Laboratory. This gives me over forty thousand volts and a comparatively steady current through a large resistance." See,

J. Trowbridge; The Production of the X-Rays by a Battery Current; American Journal of Science; Vol. 9 (4th Series); 1900; pp. 439-441.

Idem; Some Results Obtained with a Storage Battery of Twenty Thousand Cells; Nature; Vol. 62; No. 1605; August 2, 1900; pp. 325-327.

To be specific, John Trowbridge's gargantuan battery consisted of 20,000 Planté cells. Invented in 1859 by Gaston Planté, the Planté cell was the forerunner of the modern lead-acid storage cell, which is the mainstay of todays automobile industry. Planté got the idea for his cell from the, then commonly known, propensity of symmetrical electrochemical cells to become polarized upon the application a sufficiently large DC voltage, ~1.7 V for acids and bases. Polarization destroys the symmetry of the electrochemical cell by creating a concentration gradient (concentration polarization) in the electrolyte or by changing the surface composition of the one of the electrodes (surface polarization). For example, a cell, composed of two identical platinum electrodes dipped in a dilute acid solution, became surface polarized - the anode became covered with a thin layer of oxide - if the applied voltage was >1.7 V. If a galvanometer was substituted for the DC source, a steady current would be observed to flow from the cell indicating that it was acting as a source of EMF. This effect was first discovered in 1801 by Nicolas Gautherot, and was first applied to the construction of a secondary battery (accumulator) by Johann Wilhelm Ritter in 1803. Planté exploited this effect to construct his storage cell; he used lead because it was know to be easily polarized. Modern lead-acid batteries come from the factory with one of the lead electrodes coated with lead oxide, and so are ready to use upon addition of the sulfuric acid.

the cold cathode generated electrons, as opposed to photographing it from the opposite side as is done today.

It must be said that Pierce was not the only person whose work attempted to slay the dragon of thermoelectricity from the field of possible mechanisms of crystal detector behavior. In her PhD thesis, Paule Collet [193] mentions that in addition to Pierce, the work of Leimbach, Brandes and Flowers further supported Pierce's contention that thermoelectricity could not be the source of the behavior of crystal detector. In fact, no one experiment unequivocally proved that thermoelectricity had nothing to do with crystal diode behavior. Rather, it was evidence accumulated over many years by many people which in the end turned the tide. As Peter Galison points out in his book, modern science is usually a group effort in which different groups or people arrive at consensus by everyone taking a stab at the experimental system and the competing theories for how it 'really' works. Not until this process is over do the experiments officially end. [194] In this case, the process of 'proving the negative' actually continued unabated, even after Pierce's marathon attempts had ended. Eleven years later, a researcher in Germany named Robert Ettenreich revisited the problem of reaction times in catwhisker diodes for the purpose settling, once and for all, again, the question of whether or not the thermoelectric theory of rectification had any merit. [195] As Yogi Berra was heard to say, "It's *déjà vu*, all over again!"

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[193] Paule Collet; Les Propriétés Détectrices de la Galèna [The Detecting Properties of Galena]; Annales de Physique [Annals of Physics]; Vol. 15; Series 9; 1921; pp. 265-361.

[194] Peter Galison; How Experiments End; University of Chicago Press; 1987.

[195] R. Ettenreich; Reaktionszeit von Kontakdetektoren [Reaction Time of Contact Detectors]; Akademie der Wissenschaften in Wien Mathematisch-naturwissenschaftliche Klasse, Sitzungsberichte; Vol. 128; Pt. IIa; 1919; pp. 1169-1200. [Or see Science Abstracts, Series A; Vol. 23A; 1920; Abstract No. 1321. Note, because of the large number of similar sounding German and Austrian journals, I will include the Library of Congress call number of this journal: AS 142 V311]

Ettenreich's conclusion was that the thermoelectric theory of rectification was not supported by the facts.

The tenacity of the thermoelectric theory of diode action has its *doppelgänger* in the equally erroneous electrolytic theory of contact potential action. The electrolytic theory of contact potential held that the contact potential between metals was an artifact of moisture or some other contaminant residing on the surface of the two metals, thus forming a small electrochemical cell which was the actual seat of the measured EMF (ElectroMotive Force). This incorrect theory, which endured to as recently as 1950, [196] was not unreasonable given how difficult it was, both then and now, to produce metal surfaces which were free from absorbed or adsorbed vapors, gases, etc. Even today the phenomenon and theory of contact potentials is considered so difficult and esoteric that it is not promulgated in schools. In fact, a recent article pointed out an error propagated in a surprising number of well known and respected modern physics textbooks. The error concerned the effect of contact potential on the

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Idem; Prüfung der Trägheit von Kontaktdetektoren. [A Beat Method to Test the Reaction Lag on Contact Detectors.]; Physikalische Zeitschrift; Vol. 21; April 15, 1920; pp. 208-214. [Or see Science Abstracts, Series A; Vol. 23A; 1920; Abstract No. 1322.]

[196] Max Theodor Felix von Laue; History of Physics; Academic Press; 1950; p. 47. [von Laue, who won the Noble Prize in 1914, said the following erroneous statement about the phenomenon of contact potential between dissimilar metals, "…invariably there is a layer of moisture between the metal plates and what is actually observed is the terminal voltage of an open galvanic cell."]

Owen Williams Richardson; The Emission of Electricity from Hot Bodies; Longmans, Green and Co.; 1921; pp. 188-189. [Richardson discusses the measurement of the work function, ϕ, of a metal by means of calorimetry on a thermionic emitter. And in the course of this discussion, he mentioned H.H. Lester's calorimetric determinations of ϕ using filaments of molybdenum, carbon, tantalum and tungsten. Within experimental error, all of Lester's values of ϕ were the same, and this led Richardson to make the following statement. "If it could be established generally that ϕ is the same for all substances most important consequences would follow, amongst others the absence of contact electromotive force under good vacuum conditions." An assertion which bears a startling resemblance to what Max Theodor Felix von Laue would pontificate some thirty years later.]

proper experimental evaluation of the photoelectric effect. [197] And lest we think that, having resolved the mysteries of work functions, contact potentials, diode action, etc., we can rest easy, consider the following question. Where exactly is the seat of EMF (ElectroMotive Force) in an electrochemical battery? Even today, chemists and physicists still argue about exactly where the seat of EMF is located in a electrochemical cell, [198] and these cells have been with us from at least the time of Luigi Galvani and Alessandro Volta, circa 1791. [199]

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[197] J. Rudnick, D.S. Tannhauser; Concerning a Widespread Error in the Description of the Photoelectric Effect; American Journal of Physics; Vol. 44; No. 8; 1976; pp. 796-798. [Consider a photoelectric cell with an anode and cathode made of different metals; light is shined on the cathode, and the resulting photoelectrons are captured by the anode. The error is the assertion that this experiment yields the work function of the cathode - it doesn't, it yields the work function of the anode. The reason for this paradoxical result has to do with the contact potential difference between the two dissimilar metals used as the anode and cathode.]

[198] J. Hopkinson; Notes on the Seat of the Electromotive Forces in a Voltaic Cell; in B. Hopkinson; Original Papers by the late John Hopkinson, D.Sc., F.R.S., Vol. 2, Scientific Papers; J. and C.F. Clay; 1901; pp. 375-382.

M. DeKay Thompson; Note on the Seat of the Electromotive Force in Voltaic Cells; Transactions of the American Electrochemical Society; Vol. 63; 1933; pp. 161-166.

L.H. Fisher, R.N. Varney; Contact potential between metals: History, concepts, and persistent misconceptions; American Journal of Physics; Vol. 44; No. 5; May 1976; pp. 464-475.

Idem; Electromotive force: Volta's forgotten concept; American Journal of Physics; Vol. 48; No. 5; May 1980; pp. 405-408.

[199] Galvani was the second person to report (1791) the electrical phenomenon produced by dissimilar metals in contact - J.G. Sulzer was the first (1762). Volta was the first to extend Galvani's cell into a battery [of cells] or, as it was called back then, a Voltaic pile. Volta was also famous for having invented: the electrophore, an apparatus for making and transporting static electricity; and the eudiometric pistol, with which he discovered methane. Pictures of both these inventions can be found in,

James Burke; Connections; Little, Brown & Co.; 1978; pp. 178-179.

Note, both Galvani and Volta gave incorrect explanations of why their respective cells or batteries worked: Galvani thought the effect was due to animal electricity, while Volta believed the effect was due exclusively to the contact potential of dissimilar metals, which he also was the first to discover; the correct explanation, that the voltage (EMF, i.e., ElectroMotive Force) arose from the chemical action of the electrolyte in contact with the two dissimilar metals was provided by Giovanni Valentino Fabroni or Fabbroni, see,

Paul Fleury Mottelay; Biographical History of Electricity & Magnetism, Chronologically Arranged; Charles Griffin & Company Limited; 1922; pp. 329-330.

As a postscript to the subject of crystal detectors, I should like to mention the following factoid. According to Strachan, [200] crystal detectors employing catwhiskers were found to produce large amounts of mechanical vibration when detecting strong AM signals. In fact, the motion could sometimes be so large as to jog the catwhisker right off the crystal, thus breaking the connection and necessitating a new search for a new sensitive spot. Strachan admitted that when he first heard these claims from radio amateurs he dismissed them as being due to external vibrations, but upon investigation he was able to show unequivocally that the crystal detector was the source of the vibration and not the innocent victim of external mechanical trepidations. He was able to actually see the vibrations by attaching a long cantilever to the support arm of the catwhisker and then observing the amplified mechanical motion at the end of this cantilever via a microscope; the crystal detector was mechanically isolated from its surrounding and shielded from air currents and sounds by baffles. This effect could be effectively nullified by sturdier mechanical design of the catwhisker and employing crystals of sufficient hardness that could stand the higher contact pressures possible with the more massive catwhiskers. According to Strachan, the fact that the detector worked without the vibrations being present rules out their being somehow necessary for the proper functioning of the detector. [201] One thing Strachan did not mention was whether or not the vibrations produced by the crystal detector were related to the audio frequencies used to amplitude modulate the RF carrier of the AM radio station he was tuned to.

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[200] J. Strachan; The Crystal Detector in Theory and Practice, Part VI, Movement and Vibrations at the Loose Contact; The Wireless World and Radio Review; Vol. 14; July 9, 1924; pp. 424-426.

[201] Just so there is no lack of confusion, it must be pointed out that A. Blanc declared in a paper, penned in *Annales de Physique* [Vol. 2; November-December 1924; pp. 434-460], that the rectification at the point contact diode junction was related to the mechanical vibration produced at this junction.

§4. THE CRYSTAL DETECTOR EVOLVES INTO THE MOM 'DIODE'. - Around 1966, J. W. Dees was doing something that we've seen a lot of people doing, namely trying to find a way of detecting RF energy.[202] In particular, Dees was concerned with the portion of the electromagnetic spectrum between 30 and 1000 GHz (1 GHz $=10^9$ Hz). The main thrust of his search centered on finding a suitable point contact diode. He tried every semiconductor at his disposal: silicon (doped with aluminum), gallium arsenide (doped with zinc or tellurium), gallium antimonide (doped with zinc or tellurium), indium arsenide (doped with tin), lead sulfide, bismuth telluride, lead selenide, and magnesium stannide. The 1 mil diameter metal whiskers were of either tungsten or phosphor-bronze depending on the crystal material. Before any of the point contact diodes could be tested to see how sensitive they were to RF energy in the desired frequency range, their catwhiskers had to be adjusted for proper mechanical contact. The adjustment was made using a commercial curve tracer, which swept out the I-V curve for the diode at 120 Hz as the whisker pressure was being varied with the micrometer screw. Surprisingly, there was no correlation between the 120 Hz I-V curves and the performance of the diodes at, say, 300 GHz. In fact, some of the 'diodes' indicated <u>no</u> nonlinearity or asymmetry at 120 Hz and yet performed fine at 300 GHz with equal or better sensitivity than their counterparts which exhibited the 'proper' nonlinear and asymmetric I-V characteristics.

Because the efficacy of the diode as an RF detector did not depend on its nonlinear DC I-V characteristic, Dees decided to try a point contact structure

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[202] J.W. Dees; Detection and Harmonic Generation in the Submillimeter Wavelength Region; Microwave Journal; September 1966; pp. 48-55.

without the semiconductor. What he did was to run the tungsten catwhisker into the metal [stainless steel] post which usually held the semiconductor crystal. The results, when this ersatz point contact diode was tested at 300 GHz, indicated that it was as good as the best semiconductor point contact diodes. Other metals and graphite were tried besides the tungsten-stainless steel combination, and the results were just as good. Note, biasing and/or welding of the point contact to the post did not appear to improve the performance at 300 GHz. Just so that no one can accuse me of not stating the obvious, the ersatz point contact diode of Dees had the same construction as the single contact coherer. Its resemblance to the single contact coherer notwithstanding, it was not being used as a coherer, i.e., the voltages generated within it by the RF energy was being detected, whereas if it were utilized as a coherer a low voltage bias would be provided and the change in its resistance would be the output, a much more sensitive configuration than the former.

§5. RF DETECTION GIVES WAY TO LIGHT WAVE DETECTION: MOM 'DIODES' COME INTO THEIR OWN. - During the mid to late 1960s to the mid 1970s, a number groups were involved in trying to extend highly precise and accurate frequency measurements from the microwave into the far infrared, infrared and visible regions of the electromagnetic (EM) spectrum. Since the frequency of sinusoidal RF waveforms can be measured with both good precision and accuracy, the way to extend these measurements into the infrared and visible regions of the EM spectrum was by frequency multiplication of the secondary standard RF signal(s) up to approximately the same same frequency as that of the infrared or visible light whose frequency one wished to measure, and then heterodyning the two together to determine the difference in their respective frequencies. Since the frequency of the secondary RF standard was known to say N digits, the frequency of its *m* th harmonic was also known to the same degree, and if the heterodyning yields a difference signal in the low frequency RF range, the absolute frequency of the light signal could be determined from the frequency of this difference and the frequency of the *m* th harmonic of the secondary RF standard. The groups doing this eventually settled on using Dees' metal-to-metal diodes as the mixers for the laser heterodyning.

A detailed chronology of the laser heterodyning work using MOM (Metal-Oxide-Metal) 'diodes', together with enough experimental detail, so that the reader - and this writer - can feel comfortable with this technology, takes more space than is available in the body of this monograph. Thus, these details have been relegated to APPENDIX A.

§6. THE MOM 'DIODE' EVOLVES INTO THE STM. - With the advent of the STM (Scanning Tunneling Microscope) in the early 1980s, we again observe the resurrection of coherer like structure and behavior. In this case, the dielectric separating the two metal electrodes is vacuum, air and later on even liquids. The history of this device can be traced to the heyday of coherers, 1900. Besides temporal coincidence there are also direct links between the coherer and the early progenitors of the modern STM. The details of the history of the STM can be found in APPENDIX E.

As was the case with the coherer and MOM 'diode', the STM was enlisted as an electromagnetic wave detector and mixer. While the theoretical understanding of the normal functioning of the STM is, if not complete, at least it is generally agreed upon, and in that sense not controversial. However, the same cannot be said for its behavior as an electromagnetic wave detector or mixer. This is, in fact, the same conundrum we face with regards to the abilities of coherers and MOM 'diodes'.

The above history, spanning the interregnum between the earliest days of radio and our present silicon age, traces the evolution of the MOM 'diode' from the first point contact diode. But it should be obvious that what we really have is a case of parallel evolutions: point contact diodes -> MOM 'diodes'; coherers -> MOM 'diodes' & coherers –> STM. In fact, as pointed out by Vivian J. Phillips in his book Early Radio Wave Detectors, early workers did not and could not always distinguish clearly between coherers and point contact diodes. And as long as the diodes and, later, transistors had mechanical junctions as part of their structure, there could never be a complete separation between coherers and semiconductor devices. Today, the separation is complete, but we are now faced again with the mystery of the coherer. Like friction, coherers are everywhere and will never go away, as the next section will make abundantly clear.

CHAPTER 6 - WHAT IS KNOWN (post-1970)

> "Without theory, practice is only routine governed by the force of habit. Only theory can breed and develop the spirit of invention."
> - Louis Pasteur

One of the surprising things, already mentioned about coherers, is their ability to be rediscovered by new generations of students, scientists and engineers. This rediscovery usually takes the form of someone deliberately or accidentally being exposed to information about old fashion spark transmitters and their receivers. Invariably the term 'coherer' turns up, a search is usually then instigated to figure out what it is, and the epiphany happens - "…so this was how they detected RF energy before the advent of the vacuum tube and semiconductor diode." The proof that this process of rediscovery is an ongoing one is amply provided by the results of an online database search of the current literature.

Of the six valid citations from DIALOG® (see APPENDIX C, Part II), one was simply a history of amateur radio, and made only cursory mention of coherers, another limited its discussion to showing how to construct and use a spark gap microwave transmitter and a receiver using a filings (brass) coherer for a classroom demonstration of the light like properties of radio waves [203] , the four remaining citations provided, either directly or indirectly, modern experimental results and hypotheses. I shall now discuss each of these four citations which have some bearing on the theory of operation of the coherer.

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[203] R.R. Turtle; Microwave Demonstrations with a Coherer; American Journal of Physics; Vol. 41; No. 10; 1973; pp. 1198-1199.

The first of the four citations was the book, Early Radio Wave Detectors by Vivian J. Phillips, which was cited earlier in this monograph. This book provided indirect information about modern work on the coherer in that it referenced a paper by V. J. Phillips on some experimental work he had performed. [204] Phillips' paper was concerned with attempting to determine if positive coherer behavior, i.e., decreased DC resistance on exposure to RF energy, could be explained on the basis of any of three different theories which had been fashionable during the heyday of the coherer at the turn of the century. The three theories were: 1) Electrostatic attraction resulting in chains of filings; 2) Welding of the filings into chains; and 3) Negative temperature coefficient of the resistance of the oxide layer surrounding the filings. To this end, he examined the deportment of coherers employing nickel filings. His conclusion was, that under the conditions his coherers were subject to, their behavior was not inconsistent with all three candidate theories.

The second of the four citations was a German language paper by an author named H. Müller. [205] Müller investigated the behavior of liquid-solid coherers. The particular type of liquid-solid coherer that Müller examined was a

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[204] V.J. Phillips; Some Filings-Coherer Measurements; IEE Conference on the History Electrical Engineering (Manchester); 1975; paper 13. [This paper proved to be extremely difficult to obtain, no colleges or universities in the Philadelphia area had it, and when the Interlibrary Loan department tried to to get it they found out that no library in North America (USA, Canada and Mexico) had it. The first try at obtaining this article from the United Kingdom via the British Library (BL), which is equivalent to our Library of Congress, failed miserably when the BL refused to copy the article without Temple University first opening an account with them. I finally obtained a copy of the article through the kindness Dr. Phillips, himself.]

[205] H. Müller; Untersuchungen über den Frittvorgang in Flüssigkeitskontakten [Investigations into the Coherer Action in Liquid Contacts]; Elektrotechnik und Maschinenbau (Austria) [Electrical and Mechanical Engineering (Austria)]; Vol. 95; No. 8; 1978; pp. 373-379. [Even though this is a foreign language journal, it proved to be easier to obtain than some English language papers. In fact, Drexel's Haggerty Library and University of Pennsylvania's Van Pelt Library both carry this journal.]

copper-mercury (Cu-Hg) coherer; the insulating layer employed to achieve the coherer action was a layer of copper oxide formed by controlled heating of the copper electrodes in air.[206] Müller's interest in coherers was not for their properties as RF detectors, but rather he was interested in sliding contacts. Normal solid-solid sliding contacts have many obvious and some not so obvious disadvantages, the main drawbacks being excessive wear and high contact resistance. A logical way around these problems was to use a liquid-solid sliding contact, where the fixed contact was a metal liquid such as mercury. One possible area of application for liquid-solid sliding contacts was homopolar (unipolar) machinery.[207] This type of machinery operated at very low voltages but very high currents. Ideally, liquid-solid sliding contacts should function well under these low voltage and high current conditions, but there was a problem. In the real world, the interface between the fixed liquid contact and the rotating solid metal rotor could and most certainly does get contaminated with oil, dirt and oxide. Once the interface between the liquid and the solid contact was contaminated, the sliding contact took on the characteristics of a coherer, and one of the less desirable properties of a coherer, at least from the sliding contact standpoint, was the critical voltage phenomenon, wherein the DC resistance of the now contaminated sliding contact could exhibit large changes depending on the applied voltage and/or the presence of any RF energy.

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[206] The *récipé* H. Müller used for forming this oxide layer involved heating the polished copper base electrode in an air oven at 145-150°C for six hours. According to Ragnar & Else Holm's book, this yielded a copper oxide layer of ~10^{-8} m in thickness.

[207] Homopolar (unipolar) machines are the direct descendants of the Faraday disk (1832) and Barlow wheel (invented by Peter Barlow (1776-1862) who is also famous for the negative (double concave) lens that bears his name). In its simplest form, a homopolar generator consists of solid metal disk with a metal shaft through its center; a constant magnetic field is applied normal to the face of the disk, i.e., parallel to the shaft; the disk is rotated, and the resulting current and voltage are tapped off of sliding contacts located on the shaft and the outer edge of the disk. Today, the homopolar generator finds its main application as a source of very high current (>10^6 A) for the magnetic rail guns used in Star Wars (SDI) research, and as high current for Hall effect pumping of liquid sodium coolant in nuclear reactors.

Before going on to discuss the behavior of H. Müller's coherers, we should mention that Müller uses the German word 'Fritter' [208] for coherer, which is substantially different from 'coherer' in English or 'cohéreur' in French. As is the case with many German nouns, 'Fritter' describes, not so much the behavior of the device, as it does its construction: a loose aggregate of particles, cf. the English word 'frit' and the German word 'fritten'. Note, 'Fritter' seems to have been a slightly more recent term because many German technical articles written around, for instance, 1900 refer to 'Cohärer', 'Kohärern' and 'Antikohärer' which translate to 'coherer', 'coherers' and 'anticoherer', respectively. It turns out that the term 'Fritter' was coined by one Adolf [Adpolph] Karl Heinrich Slaby, who was an early worker in wireless. [209] Historians of science do <u>not</u> attribute any fundamental discoveries in the field of wireless to Slaby, he seems to have just been at the right places at the right times to have had his name linked with Marconi, Braun, etc. He was also the one who put the word 'Funken' [sparking] into 'Funkentelegraphie' [spark or wireless telegraphy]. By at least 1918 one can find books which employed <u>both</u> 'Kohärer' and 'Fritter'. [210] I am not exactly sure when the term 'Fritter' usurped these other terms, but I have been given a plausible explanation of why the change took place. According to a librarian at the Germany Society of Pennsylvania, [211] who is familiar with coherers and

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[208] Harold T. Betteridge; <u>Cassell's German Dictionary</u>; Macmillan Publishing Co.; 1978. [Look under the German entry for 'fritten' .]

[209] Augusto Righi, Bernhard Dessau; <u>Die Telegraphie Ohne Draht</u>; Druck and Verlag von Friedrich Vieweg und Sohn; 1907; p. 240.

[210] Franz Anderle; <u>Lehrbuch der Drahtlosen Telegraphie und Telephone [Textbook of Wireless Telegraphy and Telephony</u>]; Franz Deuticke; 1918; pp. 98-99ff.

[211] In an attempt to divine the origins and evolution of the German words for 'coherer', I have made use of the etymological resources located in the Joseph Horner Memorial Library, German Society of Pennsylvania, 611 Spring Garden St., Philadelphia, PA 19123, (215)627-4365, Hours: Tuesday, Wednesday & Thursday 10 AM - 4 PM. I wish to thank Dr. Victor Schutz, Electrical Engineering Department, Temple University, for suggesting the German Society of Pennsylvania to my adviser, Dr. Thomas E. Sullivan, who then passed this information on to me.

electronics in general and speaks French, Latin and German, the change from ‘Kohärer’ to ‘Fritter’ was most probably the result of an attempt to purify the German language. ‘Kohärer’ was the Germanisized version of the English word ‘coherer’. In 1949, an organization called the ‘Deutschen Akademie für Spräche und Dichtung’ [German Academy for Language and Literature] [212] was founded in Darmstadt, Germany, and part of its charter was that it was to be the arbiter of what were proper German words. Among the first things this organization did was to replace foreign derived words - whether they came from English, French or even Latin - with their pure German equivalent. The French, who are at least as xenophobic as any other nation in the world, have an organization called the ‘Academie Française’, one of whose main purposes was to rid the French language of such blatantly foreign words as ‘weekend’ and ‘television’. Note, the original impetus for purification of the German language had its roots in Adolph Hitler’s obsession to purify Germany from all foreign influences. Even with all this purification going on, there are still dictionaries which contain the original German word for ‘coherer’ and its proper counterpart. [213]

H. Müller performed two types of experiments on his Cu-Hg coherers. The first set of experiments involved the passage of very large currents (by coherer standards) through copper-mercury-copper systems. Because of the magnitude of the currents, the results of these tests will not concern us further. However, the apparatus used in the performance of these tests was also employed in the second set of experiments which we will closely examine, and so are of some

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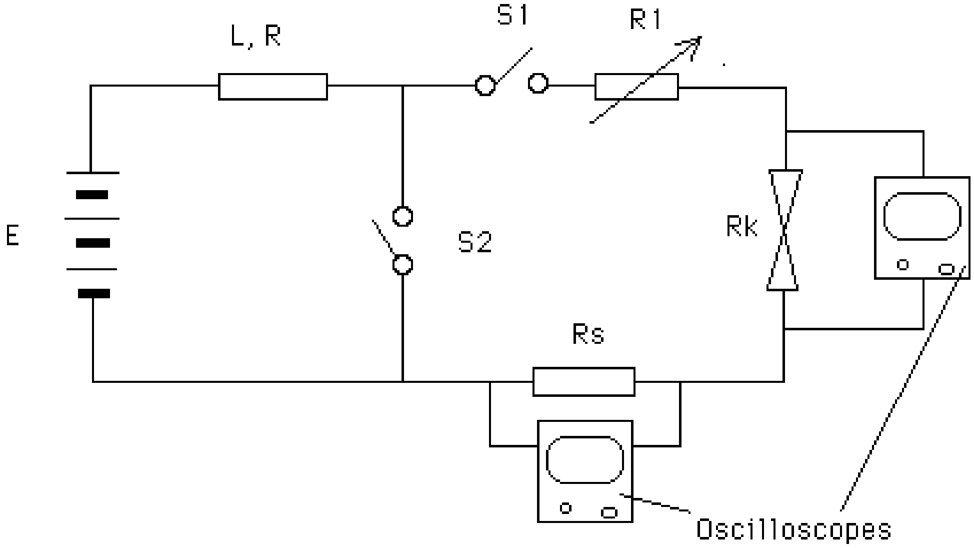
[212] Information about this organization can be obtained from either the German Information Center, 950 Third Ave., NY, NY 10022, (212)888-9840, or the Cultural Department of the German General Consul; 460 Park Ave., NY, NY, (212)308-8700.

[213] A.F. Dorian, L. Herzbruch; Dictionary of Science and Technology, English-German; Elsevier Publishing Co.; 1967; p. 179.

interest to us. Basically Müller used the same approach as the Frenchmen, G. Salmer and R. Gabillard, when they were studying the commutation (switching) time of aluminum filings coherers. That is he applied a slowly rising voltage ramp to the coherer and monitored this same voltage together with the resulting current through the coherer on a dual channel oscilloscope. Müller created the voltage ramp by way of a series RL circuit, whose time constant $\tau = L/R$ was much longer than the anticipated commutation time of the coherer structure under test, see Fig. 12. In normal operation, switches S1 & S2 were open, then S1 is closed and the exponentially rising voltage (test voltage) was applied to the contact, Rk; the test voltage was removed by closing the earthing switch, S2, and then S1 was opened. R1 was the current limiting resistor for adjusting the maximum current the contact 'sees'; Rs was the current viewing resistor, i.e., the voltage across it was proportional to the current through the contact; and L, R was the inductor plus its intrinsic series resistance, which, together with R1 and Rv, gave rise to the exponentially rising test voltage. Note , Rk < R+R1+Rv and so did not affect the time course or amplitude of the test voltage, even when it [Rk] changed in response to the applied voltage.

FIGURE 12 – H. Müller's Circuit For Investigating Contact Behavior



In the second set of experiments, essentially the same circuit was used as in the first set of experiments, but this time the critical voltage and the switching (commutation) time were measured as a function of the polarity of the bias voltage, i.e., whether the copper was positive, Cu^+Hg^-, or the mercury was positive, Cu^-Hg^+. The Cu-Hg coherer employed for these tests resembled the Walter coherer: a thin, clean copper wire dipped into a globule of mercury sitting on wide oxidized copper electrode. Upon the application of an exponentially rising voltage across the Cu-Hg junction, one observed that the junction supports this voltage until the voltage exceeded a critical value after which the junction conducted strongly reducing the voltage drop across it to close to zero. The time course of the conduction increase (a.k.a. the dwell time), after the threshold voltage was exceeded, depended strongly on the polarity of the bias voltage. Much of this behavior, I believe, can be explained based on what was known about copper oxide rectifiers (see APPENDIX A). The threshold behavior probably arose from the inevitable presence of an insulating layer of cupric oxide residing on top of the cuprous oxide layer grown next to the copper base electrode. In the manufacture of copper oxide rectifiers, after the cuprous oxide layer was grown by heating the copper base electrode in air for a suitable amount of time, the overlayer of cupric oxide was removed and so did not affect the diode's behavior. In the present case, the overlayer of insulating cupric oxide not only resulted in the system exhibiting threshold behavior, but it probably also served to create a capacitor, call it C_{insul}. Another capacitor, C_{junc}, was found at the interface between the copper and the cuprous oxide layer which was grown on it; unlike C_{insul} which was independent of the applied polarity, C_{junc} had a very distinct polarity asymmetry. C_{insul} and C_{junc} were effectively in series, which meant that the smaller of the two dominated. The sharply differing time courses of the conduction increases (dwell times) would seem to indicate that C_{junc} was the smaller of the two series capacitances.

The dwell times measured by H. Müller were on the order of 0.1-1.0 μs while G. Salmer *et al.* obtained a upper limit of 1.0 ns for their aluminum filings coherer; the systems both groups of researchers examined showed thresholds on the order of a few volts indicating the presence of thick insulating films. Presumably, the large difference in their values of dwell time could be attributed to the equally large difference in their respective contact areas. The contact area of the Müller's system as defined by its mercury drop counterelectrode might be greater or lesser than that achieved by the aluminum particles pressing up against one another in the system studied by G. Salmer *et al.*, but Salmer *et al.'s* areas and hence capacitance were in series while those of Müller's were in parallel, thus giving Müller's arrangement the bigger capacitance and concomitantly the longer dwell time. These two systems differed from MOM 'diodes' in one crucial respect. They manifested threshold behavior; MOM ‘diodes’ could possess insulating layers, but these layers were so thin, either because of the metals employed such as gold or because they were deliberately thinned by mechanical tapping, that no threshold behavior was observed.

Because the diameter of the copper base electrode was so much larger than that of the mercury counterelectrode, Müller was able to investigate the electrical characteristics of the whole surface of the copper base electrode by moving the drop of mercury over the surface of the larger electrode. What he found was that the dwell time and threshold voltage were different at different locations across this surface. This was not surprising given that, before the copper base electrode was put in the oven to grow its oxide, it was mechanically polished. Due to the inherently irreproducible nature of any polishing process, the act of polishing most likely produced inhomogeneities in the copper surface, which may have propagated through the subsequently grown oxide.

Müller’s article references the works of three authors: P. Klaudy, R. Holm and F. Freund. All three of these authors have written tracts on the properties of switches with the Holm book being undoubtedly the most famous, the other two writers seemed to be exclusively concerned with sliding contacts used in rotating machinery. Müller does not make reference to any of the work done earlier in this century on the copper oxide rectifier or the coherer.

The third and fourth citations were, respectively, a letter commenting on an article [214] that had previously been published in a journal, and the reply to this

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[214] O.F. Harbek; Electrical Conduction in Thin Lubrication Oil Films - An Explanation of the Coherer?; Radio and Electronic Engineering; Vol. 44; No. 10; 1974; p. 568.

letter.[215] The letter by Harbek, who worked for the Norwegian Defense Research Establishment at Horten in Norway, discussed the fact that the experimental and theoretical work described in a recent article[216] might provide an explanation of the workings of the Lodge-Muirhead-Robinson coherer.

For those readers who are not *aficionados* of coherers, the Lodge-Muirhead-Robinson variety of coherer[217] consisted of a slowly rotating shiny steel disk (0.5 inches in dia.) with a sharp edge, whose edge dipped into a pool of mercury, the steel disk and the mercury being insulated from one another by a drop of mineral oil on the surface of the mercury; a leather or felt pad, held by a spring, was pressed against the edge of the rotating disk ostensibly to remove dust and dirt. A voltage of between 0.03-0.5 V, steel positive, was used to bias this coherer. Note, having the steel positive with respect to the mercury gave this coherer the best sensitivity. The iron-mercury coherer of Eccles also had its greatest sensitivity when the iron was positive. The critical voltage of the Lodge-Muirhead-Robinson coherer was approximately 1 V, and like the iron-mercury coherer of Eccles, the Lodge-Muirhead-Robinson coherer was not very sensitive to vibrations. One surprising thing about the Lodge-Muirhead-Robinson coherer was that if the shiny steel disk was stationary this coherer was not self-restoring.

As was the case with all other coherers, why the Lodge-Muirhead-Robinson worked was, and is, not known. But what Anderson suggested in reply

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[215] J.C. Anderson; Electrical Conduction in Thin Lubrication Oil Films - An Explanation of the Coherer? - Reply; Radio and Electronic Engineering; Vol. 44; No. 10; 1974; p. 568.

[216] W.G. Fiennes, J. C. Anderson; Electrical Conduction in Thin Lubricating Oil Film; Radio and Electronic Engineering; Vol. 44; No. 3; 1974; pp. 141-152.

[217] A.C. Marillier; The Lodge-Muirhead Wireless Telegraph System; The Electrician (London); Vol. 50; March 27, 1903; pp. 930-934.

O. Lodge; A New Form of Self-Restoring Coherer; Proceedings of the Royal Society (London); Vol. 71; 1903; pp. 402-403.

to the letter by Harbek was that the oil film acted like an amorphous semiconductor. The work of Fiennes and Anderson was presaged by the investigations of Watson and Menon in 1929.[218] Watson and Menon noted that it was common knowledge that lubricating the wipers on potentiometers, plugs of resistance boxes, and switch contacts with vaseline or heavy paraffin oil resulted in lower contact resistances and increased stability. All this despite the fact that the lubricants were all good insulators. Even today, silicone grease is applied to the distributor terminals, rotor tip, spark plug terminals and storage battery terminals of cars for better performance. A recent edition of *EDN (Electronic Design News)* carried an article on how to reduce intermittent failures in electronic equipment by treating PCB (Printed Circuit Board) gold plated edge connectors with a mixture of mineral oil (paraffin oil) and microcrystalline wax.[219] The extraordinary everyday electrical behavior of oil impregnated electrical contacts was corroborated by the separate investigations, circa 1906, of Philip E. Shaw and Robert F. Earhart on the dielectric properties of oils as compared to air at small electrode separations.[220] What both these researchers found was that at small electrode separations air had a greater dielectric strength (i.e., higher breakdown voltage) than all the oils they tested. Note, this behavior was the

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[218] H.E. Watson, A.S. Menon; The Electrical Conductivity of Thin Oil Films. Part I. - General Nature of the Phenomenon; Proceedings of the Royal Society (London); Vol. 123 (Series A); 1929; pp. 185-202. [Note, a check of the Science Abstracts, Series A from 1929 (32A) to 1939 (42A) did not reveal the whereabouts of Part II of Watson and Menon's article. For more early information about this phenomenon see,

D.W. Mathison; Wax Lubricants; Bell Laboratories Record; Vols. 3 & 4; September 1926 - September 1927; pp. 390-391.]

[219] S.H. Leibson; Fluids vanquish intermittent contacts; EDN; Vol. 36; No. 6; March 14, 1991; pp. 59-64.

[220] P.E. Shaw; The Disruptive Voltage of Thin Liquid Films between Iridio-Platinum Electrodes. Part I; Philosophical Magazine [and Journal of Science]; Vol. 12 (6th Series); July-December 1906; pp. 317-329.

R.F. Earhart; Spark Potentials in Liquid Dielectrics; Physical Review; Vol. 23 (1st Series); 1906; pp. 358-369.

P.E. Shaw; On Spark Potentials in Liquid Dielectrics; Philosophical Magazine [and Journal of Science]; Vol. 13 (6th Series); January-June 1907; pp. 277-279.

opposite of what was found at larger electrode separations (>1 mm), where oils were in general better dielectrics than air. The deterioration of the dielectric strength of oils compared to air at small electrode separations had been predicted years earlier by Charles Proteus Steinmetz from extrapolations based on his own work on the relative dielectric strengths of oils and air. [221]

So far, we have discussed solid-solid and liquid-solid coherers, but what about a liquid-liquid coherer? To my knowledge, there were no liquid-liquid coherers in the open literature, but to be sure would require a rather extensive literature search. [222] So let me propose the following liquid-liquid coherer: a lipid bilayer separating two conducting liquids, isotonic saline solutions. The lipid bilayer is formed as follows. A beaker half filled with a saline solution is divided into two regions by lowering into the beaker a tall teflon cup with a small hole drilled in its side. Once the level of the saline equalizes on the inside and outside of the teflon cup, the bilayer is formed by 'painting' a solution of phospholipids, cholesterol [223] and a suitable hydrocarbon solvent, e.g., benzene, across the hole in the teflon cup. Hydrophobic interactions between the water and the lipid

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[221] C.P. Steinmetz; Note on the Disruptive Strength of Dielectrics; Proceedings of the AIEE; Vol. 10; 1893; pp. 85-115. [Steinmetz's original name was Karl August Rudolf Steinmetz, but when he came to America he Anglicized his first name to Charles and took his nickname of Proteus - given to him by members of the Mathematics Club at his University - as his middle name; in Greek literature, Proteus was a prophet who could take on many different nonhuman forms, such as different animals, but his human continence was always that of an old hunchback. For a more detailed look at his life, see,

Floyd Miller; <u>The Man Who Tamed Lightning, Charles Proteus Steinmetz</u> [Originally titled: <u>The Electrical Genius of Liberty Hall</u>]; Scholastic Book Services; 1965; 160 p.]

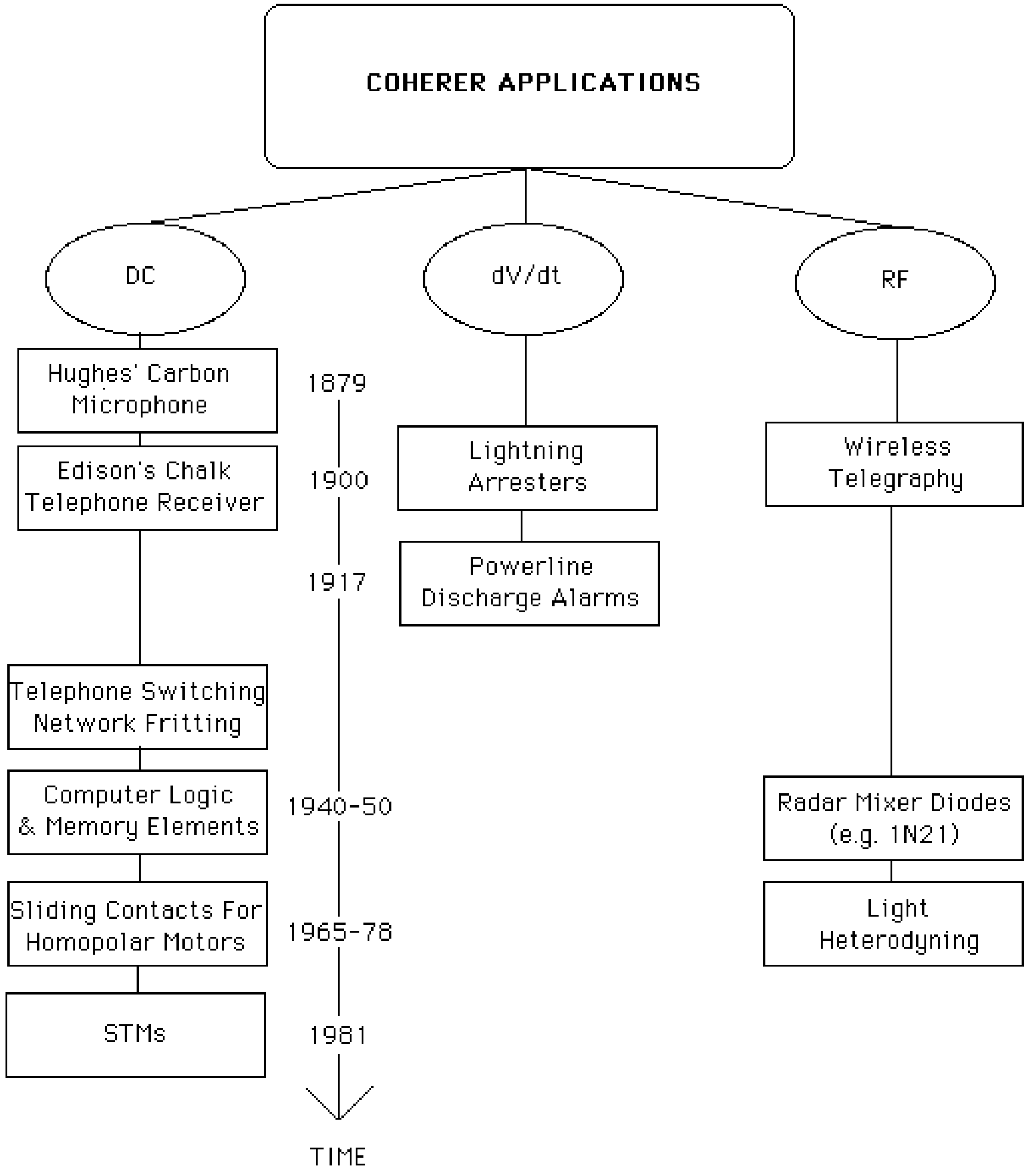
[222] A good place to start this literature search would be with the journal Bioelectromagnetics which began in 1980. The only problem with this approach is that <u>no</u> library in the Philadelphia area is listed as having this journal. The closest university library that receives this journal is Rutgers University in New Brunswick, New Jersey.

[223] Cholesterol is added to the mixture of phospholipids and organic solvent so that when the bilayer forms across the hole in the Teflon beaker its permeability to ions will be low, i.e., the membrane will be a good insulating layer. The ability of cholesterol to reduce the ion permeability of the lipid bilayer helps explain the fact that all the membranes of human and animal cells have cholesterol incorporated in them.

solution causes the drop to thin out and the lipid molecules to form a bilayer of ~60 Å thickness. Electrical connection with the inner and outer saline solutions can be achieved with clean platinum electrodes.

Although the coherer is no longer used as a detector of RF energy, the MIM (Metal-Insulator-Metal) structure that characterizes a coherer is found in many, if not most, modern day electrical and electronic systems. These modern day MIM structures, while not used as coherers, still rely on some of the same mechanisms that allowed the coherer to function. In discussing, in the previous sections, what was known about coherers, I had mentioned the numerous other applications of the coherer structure. Fig. 13 shows the various ways in which the coherer structure has insinuated its way into our technological life.

FIGURE 13 - Coherer Applications, A Chronology



CHAPTER 7 - CONCLUSIONS

"An idea isn't responsible for the people who believe it."
- Don Marquis

"…be mindful of the past…"
- Benjamin Franklin

"Just the facts, Ma'am."
-Sargent Joe Friday

The historical approach to the subject of coherers has permitted me to show in an unequivocal manner that these devices are still 'alive and well' today in the form of MOM 'diodes' and STMs. Moreover, by emphasizing the common connections among coherers, MOM 'diodes' and STMs, I hope to facilitate an understanding of the underlying mechanism behind these devices. In that sense, the esemplastic power of the historical approach is most evident: by showing that these three classes of devices share common origins and traits, the chaos of what initially appeared to be many different phenomena, was reduced to perhaps a manageable level. Unfortunately, the exact nature of the microscopic mechanism behind coherers in general still cannot be said to have been elucidated. But, at least, any further speculations along these lines will be imbued with the knowledge of what diverse device behaviors must be accounted for by any proposed mechanisms.

I must admit, though, that as work progressed on this thesis I became more and more doubtful of this unified device approach I was taking. More than worrying about being wrong, there was the sense of being utterly alone - a feeling amplified by my inability to find any modern researchers who were using this same unified device approach. Two years into the researching and writing of this thesis, with the sense of isolation growing larger daily - despite the encouragement of my advisor - I finally found proof that I was not alone. Sometime during the spring of 1992, I stumbled across an abstract of a paper by Angelika Maria Josefa Székely de Doba. In this 1924 paper, Székely compared the coherer phenomenon to the then nascent work on field emission. Further searching revealed that she had written a total of three papers on radio detectors including the one in 1924, and that these papers taken together mirrored in their approach what I was attempting to do in my thesis. The first paper, in 1918, dealt with all the then known variations of point contact detectors, including MOM structures. The second paper, in 1919, initially focused on electrolytic detectors, but later in the paper Székely realized that the point contact structures might have similar behavior with regards to the rectified current versus DC bias curves (sensitivity curves). She was right. I cannot describe the sense of relief I felt; the intellectual solitary confinement was over. Here I had finally found someone who, seventy years earlier, had taken the same approach as me.

I shall now try to summarize what I have learned:

i) Single contact, positive coherers, which after cohering, require a mechanical shock to be restored to their nominal resistance cohere by forming metal bridges. The existence of these bridges was unequivocally demonstrated by Kinsley (1905) and later Székely (1924). The mechanism responsible for creating these metallic bridges appears to be the ‘vacuum spark’ phenomenon, wherein a small field emission current rapidly transitions into a high current ‘vacuum spark’ with the attendant thermal effects. The transition from field emission to ‘vacuum spark’ which occurs in less than 10^{-7} seconds was observed by Beams (1933), using a streak camera.

ii) Single contact, positive coherers can function as RF detectors without cohering, i.e., without metallic bridge formation. In this mode of operation, they resemble MOM ‘diodes’. Pélabon (1925-26) used such structures to detect (demodulate) AM signals (voice and music). He found that the two metal contacts had to be kept in small relative motion in order for the detection to take place. My interpretation of this fact is that the minuscule relative motion served to break any metallic bridges which might inadvertently have formed and shorted out the detector.

iii) Negative coherers remain an enigma, but the work of Waszik (1924) provides us with what I consider to be a real lead: the ability to reproducibly convert a cohered coherer into a negative coherer by applying mechanical tension.

iv) Eccles (1910) showed that metallic bridge formation in positive coherers usually only happened when the radio transmitter was unusually close to the receiver or inordinately powerful at a moderate distance, i.e., in normal field operation, the coherer could detect very faint signals without forming metallic bridges. Eccles also showed that the rectified current versus DC bias curve (sensitivity curve) exhibited a peak at an intermediate value of DC bias, independent of the direction of the bias. This same type of sensitivity curve was found to hold for electrolytic detectors by Székely (1919). Faris (1973) independently rediscovered Eccles' sensitivity curves when he was studying MOM 'diodes' for use in laser detection and heterodyning.

Faris also demonstrated that these same sensitivity curves exhibited polarity reversals at sufficiently high DC bias, in both directions. Székely saw the same type of sensitivity curves with electrolytic detectors, but the magnitude of her forward and reverse biases stopped short of the values needed to observe polarity reversal in these structures, if it occurred. What is needed is an experiment to determine whether polarity reversals occur in electrolytic detectors.

v) Do coherers, which function without metal bridge formations, and electrolytic detectors detect (demodulate) in the same way? Do these structures detect in the same way as MOM 'diodes' and STMs? As was mentioned in (iv), coherers, electrolytic detectors and MOM 'diodes' have similar sensitivity curves (rectified current versus DC bias); I am not aware of anyone having measured sensitivity curves for STMs. This experiment needs to be done. Whether or not electrolytic detectors and STMs also exhibit polarity reversals awaits more experimental work.

vi) Coherers, electrolytic detectors, MOM 'diodes' and STMs all exhibit large amounts of noise at audio frequencies. In the case of STMs, this noise has been identified as 1/f noise (a.k.a. current, excess or flicker noise). What is needed is a set of experiments to quantify the audio range noise in coherers, electrolytic detectors and MOM ‘diodes’, i.e., do these devices also produce 1/f noise?

vii) Coherers, electrolytic detectors and MOM ‘diodes’, when employed as detectors, were usually adjusted for maximum sensitivity in the following manner. The adjustments were made so that the noise coming through the earphones was at its loudest, and then the adjustments were backed off slightly. Was the mechanism responsible for the noise also responsible for the detection of the radio signals? In other words, was the noise production mechanism entrained by the incoming radio waves?

viii) The surface plays a major and maybe even exclusive *rôle* in the electrical behavior of the various devices considered in this thesis. Besides their ability to detect radio waves, electrolytic cells were also shown by Braun (1898) to be able to emit light at their electrode surfaces. This behavior should be revisited experimentally. In addition, the converse effect should be searched for experimentally. That is, the biased electrolytic detector should be exposed to a chopped beam of laser light to see if it can detect this radiation, just as was done by Faris (1973) with the MOM ‘diode’.

ix) Székely (1918) examined a large class of point contact structures both MOM and MOS and came to the conclusion that they all acted like electrolytic cells due to films of water on the electrode surfaces; the water originated from the humidity of the surrounding air. The presence of these water films appeared to be directly responsible for time dependent changes in the electrical characteristics under the action of bias, either externally applied bias or internally generated bias due to demodulation of the incoming radio signals. MOM 'diodes' used in laser heterodyning were and are notorious for time dependent changes in their electrical characteristics. Do these changes arise for the same reason as postulated by Székely?

x) The nature of the electrode surfaces of the MOM 'diodes' needs to be quantified. Specifically, the nature of the Beilby layer present on the polished base electrode begs for investigation, and the influence of electrochemical etching on the tip electrode could do with much more careful scrutiny. These same admonitions also apply to all the other detectors discussed in this thesis.

xi) Finally, with respect to coherers, field emission and 'vacuum sparks' appear to be amplified by the presence of minute amounts of RF energy. Is this true? And if it is true. Why?

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APPENDIX A - MOM DEVICES

"…to an experimentalist the equations seem unsatisfactory because it is so difficult to interpret them in terms of a physical picture."
- Lars O. Grondahl

"As far as the laws of mathematics refer to reality, they are not certain; and as far as they are certain, they do not refer to reality."
- Albert Einstein

§1. INTRODUCTION, SINGLE CONTACT COHERERS ARE UNKNOWINGLY REDISCOVERED. - The history of the use of MIM (Metal-Insulator-Metal) point contact diodes employed in laser heterodyning will be told from the perspective of an outsider. Specifically, the point-of-view will be that of someone, initially unfamiliar with the technology, trying to come up to speed by reading the papers in the open literature. Before going any further, two things need to be cleared up. First, the use of these point contact diodes as mixers or detectors of laser frequencies is truly a technology and not a science. We know how to build the 'diodes' and how to couple the light and/or microwave energy to them to affect mixing, but how and why these 'diodes' work is not known even by the people who pioneered the field. Second, the nomenclature is convenient and fits the function of the physical devices, but these structures are certainly not diodes in the traditional sense and, as we shall discuss in APPENDIX B, the notion that they are MIM structures is even disputed by some workers in the field, who believe there is no insulating layer between the two metal electrodes making up this device.

The earliest attempts at absolute frequency measurements of light sources (lasers) appeared to be the work of Hocker & Javan *et al.*[224] in the mid

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[224] L.O. Hocker, A. Javan, D.R. Rao, L. Frenkel, T. Sullivan; Absolute Frequency Measurement and Spectroscopy of Gas Laser Transitions in the Far Infrared; Applied Physics Letters; Vol. 10; No. 5; March 1, 1967; pp. 147-149.

to late 1960s. Initially, their technique involved mixing the output from a far IR (InfraRed) laser with a very high harmonic of a klystron, this was called direct mixing. Examples of direct mixing involving beating higher order harmonics of a V-band klystron[225] with various CW (Continuous Wave) IR lasers are shown in the following table,

TABLE A1 - Direct Mixing Table

Lasing Mat'l	Wavelength (µm)	Klystron Harmonics (V-Band, 70-75 GHz)
CN	337 & 311	12 & 13
D_2O & C_2N_2	190 & 194	22 & 23

A commercial semiconductor microwave mixer was used for these measurements, and consisted of a crossed waveguide configuration with an adjustable catwhisker crystal diode (tungsten whisker and doped silicon wafer) in one arm. The output from the mixer was then passed through a makeshift spectrum analyzer so that the beat lines could be displayed. Once the beat lines were observed, the frequency of the V-band klystron could be determined by heterodyning it with the higher order harmonics of an X-band klystron (6.2-10.9

L.O. Hocker, A. Javan, D.R. Rao; Absolute Frequency Measurement of the 190µ and 194µ Gas Laser Transition; Physics Letters; Vol. 24A; No. 12; June 5, 1967; pp. 690-691.

L.O. Hocker, A. Javan; Absolute Frequency Measurement on New CW HCN Submillimeter Laser Lines; Physics Letters; Vol. 25A; No. 7; October 9, 1967; pp. 489-490.

L.O. Hocker, A. Javan; Absolute Frequency Measurements of New CW DCN Submillimeter Laser Lines; Applied Physics Letters; Vol. 12; No. 4; February 15, 1968; pp. 124-125. [Ali Javan, together with William R. Bennett Jr. and Donald Herriott, was most famous for creating the first gas laser, the He-Ne laser. Javan, who had obtained his PhD and done postgraduate work under the aegis of Charles Hard Townes, the guru of masers, was quite familiar with spectroscopy and masers. When he went to work for Bell Labs he decided to try to increase the maser frequencies up into the infrared or visible regions of the spectrum. He chose a gas for the lasing medium because he felt it would be easier to work with. Utilizing helium and neon, Javan enlisted the help of a spectroscopist, Bennett, to map out the energy transitions of this gas combination, and the help of an optics specialist, Herriott, to design and construct the laser optics, specifically the mirrors. On the afternoon of December 13, 1960, their efforts abruptly succeeded when, during the course of tweaking the mirrors, the sought after signal was detected. For more info see,

Joan Lisa Bromberg; The Laser in America, 1950-1970; The MIT Press; 1991.

M. Bertolotti; Maser and Lasers, An Historical Approach; Adam Hilger Ltd.; 1983.]

[225] According to Table 0-1 in Samuel Y. Liao; Microwave Devices and Circuits; Prentice-Hall, Inc.; 1985; p. 2, the V-band is characterized by the frequency range 46.0-56.0 GHz. Why Hocker & Javan called their 70 GHz klystron a V-band device I'm not sure.

GHz); [226] the X-band klystron was in turn phase locked to signal generator. Presumably, either the X-band klystron or the signal generator was a secondary frequency standard.

At approximately the same time Hocker, Javan *et al.* were doing their measurements, another group of researchers was also investigating far IR CW laser frequencies. [227] Note, this second group, while located at a different institution, was composed of two members who had worked with Hocker and Javan on their first paper on laser heterodyning.

The problem with direct mixing was that a very high harmonic of the known frequency source (the V-band klystron) needed to be utilized in order to a get a difference signal from the mixer in the frequency range of a commercial IF (Intermediate Frequency) amplifier, this tended to degrade the S/N (Signal to Noise) ratio. One way out of this dilemma was to employ a second IR laser in addition to the klystron. [228] Note, both the klystron and the second laser had to have high long term stability, since they were the standards against which the measurement was being made.

Even with this ploy of utilizing a second laser together with the klystron, there still remained the S/N problem with the output from the mixer. In a bid to improve the S/N ratio, Hocker and Javan may have decided to try what they initially called a metal-to-metal 'diode'. [229] Note, Hocker and Javan do not say why they decided to try the metal-to-metal 'diodes', I attributed it to their desire for a better S/N ratio, but they in fact don't say what motivated them. Their decision to try the metal-to-metal 'diode' was apparently inspired by the success that J. W. Dees had in using these structures to detect and mix microwave signals in the 1000 GHz range back in 1960s. [230] The main purpose of this paper by Hocker and Javan was to measure the frequency difference between five adjacent 10.6 μ P-branch transitions of a Q-switched CO_2 laser. Since the frequency difference between all five P-branch transitions is ~54 GHz, a 54 GHz klystron was mixed with the output of the CO_2 laser to generate a video beat signal. This experiment was different from Hocker and Javan's previous work in

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[226] The following table will prove helpful in keeping straight the various SI units (Système International des Unités): tera (T) = 10^{12}, giga (G) = 10^{9}, mega (M) = 10^{6}, kilo(K) = 10^{3}, milli(m) = 10^{-3}, micro (μ) = 10^{-6}, nano(n) =10^{-9}, pico(p) = 10^{-12}, femto(f) = 10^{-15}.

[227] L. Frenkel, T. Sullivan, M.A. Pollock, T.J. Bridges; Absolute Frequency Measurement of the 118.6-μm Water Vapor Laser Transition; Applied Physics Letters; Vol. 11; No. 11; December 1, 1967; pp. 344-345.

[228] L.O. Hocker, A. Javan; Laser Harmonic Frequency Mixing of Two Different Far Infrared Laser Lines up to 118μ; Physics Letters; Vol. 26A; No. 6; February 12, 1968; pp. 255-256.

[229] L.O. Hocker,D.R. Sokoloff, V. Daneu, A. Szoke, A. Javan; Frequency Mixing in the Infrared and Far-Infrared using a Metal-to-Metal Point Contact Diode; Applied Physics Letters; Vol. 12; No. 12; June 15, 1968; pp. 401-402.

[230] J.W. Dees; Detection and Harmonic Generation in the Submillimeter Wavelength Region; Microwave Journal; September 1966; pp. 48-55.

that no frequency multiplication by the mixer was needed to generate higher order harmonics, i.e., this was not a harmonic mixing experiment. The metal-to-metal 'diode' was composed of a 2 µm diameter tungsten wire whose end had been electrolytically etched to a point, and then advanced by means of a differential micrometer into contact with a flat metal base made of either silver or steel. The reception by this 'diode' was found to increase if i) the laser beam was focused onto the tungsten wire close to its point, ii) the diameter of the wire was <3 µm, iii) the polarization of the laser beam was parallel to the long axis of the tungsten wire, and iv) the klystron power was kept low in order to avoid burning out the 'diode'. As far as why the metal-to-metal point contact 'diode' works, Hocker and Javan stated that they believed that electrical contact between the two metal electrodes took place through a thin oxide layer via electron tunneling - a sort of all purpose explanation which explained nothing. The experiment with the P-branch 10.6 µm transitions did not require nonlinear behavior on the part of the metal-to-metal 'diode', i.e., higher order harmonics were not needed since the difference in frequency between adjacent transitions was at approximately the same frequency as the fundamental frequency of the klystron. Because of the preceding fact, Hocker and Javan claim that this experiment did not prove that the response of the metal-to-metal 'diodes' was as fast as the infrared frequency itself. Be that as it may, they do go on and perform an experiment which showed that the 'diode' was nonlinear enough to multiply a 54 GHz klystron fundamental frequency up to ~1000 GHz (~18th harmonic). The experiment involves beating a HCN laser's 337 µm radiation against that of the 54 GHz klystron's and getting a video beat signal.

Hocker and Javan admitted that they did not fully understand how and why the metal-to-metal 'diode' worked. They thought there was an oxide layer between the two metals which was tenuous enough that electrons could tunnel through it; as far as the coupling of the IR to the 'diode' was concerned, they indicated that they believed that standard antenna theory, customized to the 'diode' geometry and electrical parameters, would suffice. But regardless of what the explanation turned out to be, Hocker and Javan were not above using something that obviously worked, although why it worked was and still is not obvious. And so, they embarked on the first step to achieving a viable frequency multiplication chain: harmonic mixing using three known sources, a K-band klystron and an IR laser, both of whose frequencies were known, and an unknown IR laser. [231] In truth, in this experiment, which was just a feasibility study, both laser frequencies were known, I am just indicating how the protocol would be used for 'real'. The 'diode' was again composed of an electrolytically

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[231] V. Daneu, D. Sokoloff, A. Sanchez, A. Javan; Extension of Laser Harmonic-Frequency Mixing Techniques into the 9µ Region with an Infrared Metal-Metal Point-Contact Diode; Applied Physics Letters; Vol. 15; No. 12; December 15, 1969; pp. 398-401.

This technique was extended to higher frequencies in the next paper,

D.R. Sokoloff, A. Sanchez, R.M. Osgood, A. Javan; Extension of Laser Harmonic-Frequency Mixing into the 5-µ Regions; Applied Physics Letters; Vol. 17; No. 6; September 15, 1970; pp. 257-259.

sharpened 2 µm diameter tungsten wire, this time pressed against a nickel or cold-rolled steel post by another differential screw.

§2. THE RACE TO EXPLAIN IS ON. - Once the utility of metal-to-metal 'diodes' as high frequency mixers and detectors was demonstrated, everyone it seemed began to employ them in laser heterodyning experiments. In particular, there were three other groups whose work in this field involved not so much extending the mixing to higher frequencies so much as trying to understand how and why these 'diodes' worked. The first group, made up of Samuel I. Green, Paul D. Coleman and Jack R. Baird, worked in the period 1967-1971. Green *et al.* were primarily concerned with characterizing the electrical behavior of the metal-to-metal 'diode' based on the theoretical model of it being an asymmetrical tunneling structure. The second group consisted of a large group of people (K. M. Evenson, J. S. Wells, L. M. Matarrese, *et al.*) at the NIST (née NBS) who, besides wanting to employ these 'diodes' in the creation of frequency multiplier chains for speed of light metrology, tried over the years (1970-1985) to understand the exact nature of the coupling occurring between the incident IR or visible radiation and the metal-to-metal 'diode' structure. [232] The third group, composed of C. C. Bradley, G. Edwards and D. J. E. Knight and located in the United Kingdom, attempted to analyze the metal-to-metal 'diode' as lumped circuit elements, [233] assuming as a model the metal-oxide-metal tunnel structure favored by Green *et al*. Bradley *et al.* used perhaps the most unusual material of all the groups for the base electrode, a piece of pencil 'lead'; [234] the whisker

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[232] L.M. Matarrese, K.M. Evenson; Improved Coupling to Infrared Whisker Diodes by use of Antenna Theory; Applied Physics Letters; Vol. 17; No. 1; July 1, 1970; pp. 8-10.

K.M. Evenson, M. Inguscio, D.A. Jennings; Point Contact Diode at Laser Frequencies; Journal of Applied Physics; Vol. 57; No. 3 February 1, 1985; pp. 956-960.

[233] C.C. Bradley, G. Edwards, D.J.E. Knight; Absolute Measurement of Submillimetre and Far Infra-red Laser Frequencies; The Radio and Electronic Engineer; Vol. 42; No. 7; July 1972; pp. 321-327.

C.C. Bradley, G.J. Edwards; Characteristics of Metal-Insulator-Metal Point-contact Diodes Used for Two-Laser Mixing and Direct Frequency Measurements; IEEE Journal of Quantum Electronics; Vol. QE-9; May 1973; pp. 548-549. [**Warning**, the legends of the two figures in this paper have been reversed.]

[234] Pencil 'lead' starts out as a slurry of clay and graphite with an appropriate binder; the slurry is extruded through a die to give it the proper shape; it is then fired in a furnace at between 1600 and 2200°C; and finally it is impregnated with a mixture of fats and fatty acids and sometimes wax, the excess being removed chemically. The exact nature of the surface of the 'lead' is unknown. The graphite, which is the source of the 'lead's' electrical conductivity, may be oxidized at its exposed surfaces. Note, when most people think of oxidized carbon, they usually think of a gas such as CO or CO_2, but there are solid forms of oxidized graphite. In particular, there is a substance called graphite oxide, which is a yellow to dark brown solid. Graphite oxide was discovered around 1859 by Sir Benjamin C. Brodie, see,

B.C. Brodie; On the Atomic Weight of Graphite; Proceedings of the Royal Society (London); Vol. 10; 1859-1860; pp. 11-12.

Brodie discovered that he could convert graphite into graphite oxide by employing a mixture of concentrated nitric acid and potassium chlorate; amorphous carbons are not attacked by Brodie's reagent. Graphite oxide's properties are not well known even today, but it is a substance they employed was the standard electrolytically etched tungsten wire. Note, this group was not the first to use pencil lead in the construction of a MOM or MOS ‘diode’. [235]

These three groups were not the only groups investigating this phenomenon but they represented the must bountiful producers of theoretical and experimental knowledge in this field in the time period 1960-1980. Of these three groups, we will only consider the work of Samuel I. Green *et al.* since they were most directly concerned with the actual mechanism by which the MOM structure rectified and mixed.

§3. THE UNEXPECTED CONTENDER: GOLD on GOLD. - Samuel I. Green *et al.* produced three papers in this field. [236] Besides the usual harmonic mixing experiments, Green *et al.* also attempted direct rectification of a high GHz

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whose time has come: it is used in rocket propellants, lithium batteries, etc., and is the subject of ongoing research.

[235] In 1918, Angelika Székely (de Doba) published an article in which she examined various point contact diodes. See,

A. Székely de Doba; Die Kontaktdetektoren [Point Contact Detectors]; Akademie der Wissenschaften in Wien Mathematisch-naturwissenschaftliche Klasse, Sitzungsberichte; Vol. 127; Pt. 2a; No. 6; 1918; pp. 719-792.

The one type of point contact structure most exhaustively investigated by Székely was a galena-graphite arrangement, where the graphite was provided by a sharpened piece of KOH-I-NOOR® pencil lead of HB hardness (i.e., ~ the hardness of a #3 pencil). Note, Székely was probably not the first researcher to employ pencil lead in a point contact diode, but I am not sure who was the first.

[236] P.D. Coleman, S.I. Green; A Fast Room -Temperature Millimeter and Submillimeter Electric-Tunnel Effect Detector; IEEE Transactions on Electron Devices; Vol. ED-16; 1969; pp. 251-252. [Note, this was an abstract of a talk, not a full blown paper.]

S.I. Green, P.D. Coleman, J.R. Baird; The MOM Electric Tunneling Detector; in Jerome Fox (Ed.); Proceedings of the Symposium on Submillimeter Waves; Polytechnic Press of the Polytechnic Institute of Brooklyn (distributed by Wiley-Interscience); 1970; pp. 369-389.

S. I. Green; Point Contact MOM Tunneling Detector Analysis; Journal of Applied Physics; Vol. 42; No. 3; 1971; pp. 1166-1169.

[Note, an earlier Air Force final report (RADC Contract AF 30602-67-C0006) supposedly released in August of 1967 by P.D. Coleman and J.R. Baird was not generally available, if in fact it was available at all - there being no PB or AD number associated with this report as far as I was able to determine. Conversations with Jack R. Baird, LED Systems, (303)447-9998, revealed, that even though his name was listed on this report, he had in fact left the University of Illinois for the University of Colorado before the report was completed. He suggested that I get in touch with Samuel I. Green at McDonnell Douglas, St. Louis, MO, (314)233-5825, whose PhD thesis

Samuel Isaac Green; The Point Contact, Electric-Tunneling Submillimeter Wavelength Detector; University of Illinois; 1969 [see the Dissertation Abstracts International; Vol. 30; July ‘69-June ‘70; for the abstract of this thesis]

apparently contained essentially the same material as the Air Force report. Ultimately, this thesis had to be ordered from UMI (University Microfilms International), (800)521-0600, Order No. 7000-862, because the University of Illinois library, when asked by Temple’s Interlibrary Loan Dept. to loan us a copy, replied that their copy of the thesis was missing - not an uncommon occurrence, according to our Interlibrary Loan librarian. This report/thesis turned out to be an extremely difficult thing to obtain.]

signal, e.g., they were successful in detecting 75 GHz from a CW klystron, at first, then later 10,726 GHz from a pulsed H_2O laser. Quantifying the rectifying efficiency (rectified output voltage/RF input power) of 'diodes' constructed of various types and combinations of metals revealed that a gold-on-gold 'diode' had the highest efficiency. The 'diode' structure was composed of a 1 mil diameter gold wire lightly pressed against a 3000 Å thick evaporated gold film on glass. As was the case for the 1N2X class of point contact diodes, the 'diodes' of Green *et al.* usually required a judicious tap or two after they had been brought into contact in order to optimize their behavior. Gouging, presumably induced by the tapping, was thought to thin the oxide layer on the tip and base enough to allow tunneling by the electrons; detectors using gold worked on initial contact and did not require any tapping. The extraordinarily high rectification efficiency of the gold-on-gold 'diode' was thought to be due to the thinness of the insulating layer on the gold surface. However, exactly what this layer was composed of was not known *a priori* and the researchers apparently had no empirical way to find out.[237] In the case of the other metals tried, such as phosphor bronze, tungsten, beryllium copper, stainless steel and aluminum, a layer of atmospherically induced oxide was known to be present along with other chemisorped and physisorped entities.[238]

One of the most interesting behaviors observed by Green *et al.* during their measurements of rectification efficiency was the occurrence of polarity reversals of the rectified current at high applied RF powers; no DC bias was applied. Green *et al.* claimed that the existence of polarity reversals substantiated their assumption of an asymmetrical tunneling structure. It should be noted that when they were speaking about an asymmetrical tunneling structure, the asymmetry was assumed to be in the barrier heights at the two metal-oxide interfaces of the MOM structure. In the case where the two metals were the same, e.g., the gold on gold 'diode' alluded to earlier, it was not obvious that the asymmetry in the two average barrier heights could be large enough to account for the observed rectification ratio (ratio of the forward to the reverse currents).

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[237] One of the best kept secrets of Samuel I. Green's work was his method of electroetching of the gold whisker: "Gold whiskers are etched by direct current in a solution of 5 per cent [sic] by weight of both sodium cyanide and potassium ferrocyanide in water." see,

Samuel I. Green; <u>The Point Contact, Electric-Tunneling, Submillimeter Wavelength Detector</u>; UMI Dissertation Services; March 31, 1969; p. 31.

I could find no mention of this electroetching protocol, as it related specifically to gold whiskers, in any of his peer reviewed publications or conference papers. It would be truly astounding if this electrolytic process did <u>not</u> leave a layer of gold oxide and/or gold cyanide compounds on the surface of the pointed whisker, this would be in addition to the normal gold oxide passivation layer and the layer of strongly adsorbed water.

[238] The terms chemisorped and physisorped refer to the strength of the attraction between the gas (adsorbate) and the solid phase (adsorbent). One way to obtain a quantitative measure of this strength is to determine the heat of adsorption, the greater the amount of heat evolved the stronger the bond between the adsorbent and adsorbate. Chemisorped species form essentially chemical bonds with the substrate, which are stronger than the dispersion force attraction which characterizes physisorped species.

So far I have been referring to Green *et al.* as if their ideas on the mechanism behind the MOM 'diodes' were monolithic, they were not. Conversations with Samuel I. Green and Jack R. Baird - Paul D. Coleman, (217)333-2765, could not be reached - uncovered disagreements between all three men as to the mechanism and how to represent it. Baird believed that the mechanism had to do with the geometry of the MOM junction, while Coleman preferred the difference in work function or barrier height explanation. Green was a graduate student at the time and at first Baird was his PhD thesis adviser, but then Baird left to take a post at another university and Coleman took over as Green's adviser. Green, by his own admission, did not and still does not believe in Baird's geometrical model, but he also had disagreements with Coleman about the way to express the model using the assumed difference in work functions.

Baird continued to work on his geometrical explanation of the asymmetrical I-V characteristics of the MOM structures at the University of Colorado.[239] According to Baird, the physical picture of his model of why the MOM structure is capable of rectification goes as follows. With an electric field across the MOM point contact 'diode', the trajectories of electrons in the whisker are predominantly along its length, while the trajectories of the electrons in the base electrode are mainly parallel to the surface of the base. The differing trajectories of electrons in the whisker and in the base electrode result in different tunneling probabilities across the oxide layer separating the whisker and base. Thus says Baird, the electrons in the whisker approach the oxide layer head on and and so have a higher probability of surmounting this barrier than the electrons from the base electrode, which move essentially parallel to the oxide. I do not know how this model can explain the occurrence of polarity reversal.

Baird indicated, during our phone conversation, that the most stable MOM 'diodes' were those constructed with a tungsten base with the just about any metal employed as the catwhisker; the 0.040 inch diameter tungsten rod, which served as the base electrode, was cut with a diamond saw and then its end was polished with an alumina (Al_2O_3) paste. In addition, the best 'diodes' were produced during second contact, i.e., after the catwhisker was initially run into the polished tungsten base and slightly flattened, it was then lifted slightly off the base and resettled on a new spot on the base, this being the second contact.

The work of Samuel I. Green *et al.* was verified and extended by Kwok *et al.* in 1971.[240] Like the coherers, these MOM 'diodes' are very sensitive to external vibration (see page 560 of Kwok *et al.*). Another similarity between the

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[239] R.H. Havemann, P.F. Engel, J.R. Baird; Nonlinear correction to Ohm's law derived from Boltzmann's equation; Applied Physics Letters; Vol. 24; No. 8; April 1974; pp. 362-364. [I wish to thank Dr. Jack R. Baird for bringing this paper to my attention.]

[240] S.P. Kwok, G.I. Haddad, G. Lobov; Metal-Oxide-Metal (M-O-M) Detector; Journal of Applied Physics; Vol. 42; No. 2; February 1971; pp. 554-563. [I wish to thank Dr. Samuel I. Green for bringing this paper to my attention.]

MOM ‘diodes’ and the coherers was the method for adjusting them for best sensitivity. According to Kwok *et al.,* “At first the whisker is made to contact the [metal] film by adjusting the micrometer; then the whisker pressure is released slowly. The best detector performance occurs when the whisker is just about to separate from the insulating film.” Now consider what Branly in 1898 [241] had to say about adjusting his gold or platinum coherers, “…the filings are located between two metal rods; the one rod is fixed and the other moved with a screw. The filings are an element of the circuit in series with the pile [Voltaic pile or battery], one gently moves in the contact of this tube, until the point where a slight conductivity appears; one reestablishes the resistance by a suitable [mechanical] shock and one finds oneself in the best condition for operating efficiently with electric radiation.” Note, by advancing the movable electrode into the tube containing the filings, Branly was pressing the particles closer against one another by increasing the height of the pile of filings and hence the pressure they exert on one another; when he detected that he had almost broken through the insulating layers, he applied a slight mechanical shock to the coherer thus disrupting any metal to metal contacts that might have formed.

§4. THE UNEXAMINED QUANTITY: NOISE IN MOM ‘DIODES’. - In his thesis, Samuel I. Green stated that, “Initial contact between whisker and base sometimes results in an extremely noisy state of conduction which is believed due to vibration of the whisker in close proximity to the base and the contact potential between them… If this noisy state is encountered, a light tap will form the desire stable contact.” [242] When H. Pélabon was testing his metal-on-metal detectors in air, 40 years before Green’s work, he also noticed that as the two metal surfaces pressed against one another he heard a continuous rumbling sound; upon increasing the pressure further he heard the demodulated AM radio signal clearly and cleanly; increasing the pressure still further caused silence presumably due to the shorting together of the two metal surfaces via the disruption of their oxide layers. [243] Samuel I. Green thought that the ‘noisy state of conduction’ was caused by changing electrical currents in the external circuit produced by the relative motion between the two metal surfaces having different work functions, in analogy with the sound produced before balance in the Zisman method of measuring contact potentials. [244]

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[241] É. Branly; Radioconducteurs à limailles d’or et de platine [Radioconductors with Filings of Gold or Platinum]; Comptes Rendus Hebdomadaries des Seances de l’Academie des Sciences (Paris); Vol. 127; 1898; pp. 1206-1207.

[242] Samuel I. Green; The Point Contact, Electric-Tunneling, Submillimeter Wavelength Detector; UMI Dissertation Services; March 31, 1969; p. 10.

[243] H. Pélabon; Sur la détection et la stabilité de certains détecteurs [On rectification and the stability of certain detectors]; Comptes Rendus Hebdomadaries des Seances de l’Academie des Sciences (Paris); Vol. 182; January 11, 1926; pp. 124-125.

[244] W.A. Zisman; A New Method of Measuring Contact Potential Differences in Metals; Review of Scientific Instruments; Vol. 3; July 1932; pp. 367-370. [A discussion of this method can also be found in,

The Zisman method of measuring contact potentials was performed on two dissimilar vibrating electrodes separated by a small distance with the electrodes biased; one electrode was the reference metal and the other the test metal. The dissimilar electrodes were connected together through a current viewing resistor shunting the input to a multistage tube amplifier; the alternating current through the current viewing resistor was driven by the periodic variation in the value of the capacitor formed by the two electrodes as their relative distance apart varied. When the bias voltage was zero the AC current induced in the current viewing was due to the contact potential difference existing between the two vibrating electrodes. If the bias voltage was applied in such a way that it was equal and opposite the contact potential difference, the AC current went to zero. Thus, the AC null, measured with a pair of earphones at the output of the multistage amplifier, coupled with the reading of the potentiometer used to bias the vibrating electrodes, gave the contact potential difference.

However, Green does not produce any proof that there were, in fact, mechanical vibrations in his experimental setup which could be correlated with the noise he observed. Specifically, any mechanical noises coupled to his ‘diode’ would be expected to generate subsonic noise (infrasonic noise), not the audible noise that he presumably heard. What Green observed was, perhaps, noisy conduction, i.e., he applied an external voltage difference and observed that the resulting conduction current was noisy under conditions where the oxide layer was still too thick. And even in the case of Pélabon’s observations, it was not obvious that relative mechanical motion had anything to do with the noise. What the detectors of Pélabon and Green did have in common was that they both possessed mechanical contact junctions. Such junctions are well known to be sources of 1/f noise, a.k.a. excess or current noise. Perhaps the best proof of the fact that one can get 1/f noise in the absence of mechanical vibration from a MIM (Metal-Insulator-Metal) junction passing current is the 1/f noise observed in STMs (Scanning Tunneling Microscopes), see APPENDIX E. In an STM the

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Aldert van der Ziel; <u>Solid State Physical Electronics</u>; Prentice-Hall, Inc.; 1957; pp. 70-76. [Van der Ziel discussed the Zisman method, but did not provide any references to Zisman’s original paper.]

Adrianus J. Dekker; <u>Solid State Physics</u>; Prentice-Hall, Inc.; 1965; pp. 230-232. [For reasons known only to himself, Dekker did <u>not</u> list the Zisman method in his subject index - you have to look in the section of his book on contact potential, which <u>was</u> listed in the subject index. But unlike van der Ziel, Dekker did provide a reference to Zisman’s original paper.]

The Zisman method was so successful that it was eventually coopted - with suitable modifications - by biologists for the purpose of determining contact potentials differences at solid-solid and solid-liquid interfaces,

S. Rosenfeld, W.M. Hoskins; A Modified Zisman Apparatus for Measuring Contact Potential Differences in Air; Review of Scientific Instruments; Vol. 16; No. 12; December 1945; pp. 343-345.

For a more recent perspective on the Zisman method, consult the following article,

L.W. Swanson, P.R. Davis; Work Function Measurements; in Robert L. Park, Max G. Lagally (Eds.); <u>Solid State Physics: Surfaces (Vol. 22, Methods of Experimental Physics)</u>; Academic Press, Inc.; 1985; pp. 17-19.]

insulator between the two electrodes can be either a vacuum or air. Because the thickness of the insulating layer in an STM is on the order of 10 Å, the STM must be carefully isolated from mechanical vibration. This isolation is usually provided by a stack of steel plates separated by Viton® O-rings. In 1990, R. Möller *et al.* showed that a current flowing between the electrodes of an STM exhibited 1/f noise on top of the ever present Johnson noise, and that when the bias voltage across the electrodes was reduced to zero the only noise present was the Johnson noise. [245] To understand the difference between Johnson noise and 1/f noise a bit of history will be helpful.

The study of electronic noise paralleled the development of the electronics industry. Following the discovery of the audion (triode) vacuum tube, engineers finally had a simple component building block out of which to construct amplifiers. With the advent of high gain multistage amplifiers, technicians testing these amplifiers noticed the seemingly ineluctable and inescapable presence of noise at the output; the noise was probably first noticed as a audible hiss, later on it was realized that this hissing extended all the way up into the radio frequency range. No amount of shielding or interchanging of the circuit components provided substantial relief from this electronic nuisance. Eventually, as the amplifier gains continued to increase, this nuisance became a *bona fide* problem, which threatened to limit the usefulness of high gain amplifiers in certain applications.

In 1918, Walter Schottky showed that the tubes themselves were sources of noise due to a phenomenon he dubbed “Schroteffekt [shot effect]”. [246] The shot effect owed its existence to the discrete or particle nature of the ballistic electrons in electron vacuum tubes. Because of the discrete nature of the electrons impinging on the anode of the tube, the anode current oscillated in a seemingly random manner about a mean value. This variation about the mean was termed ‘shot noise’. Shot noise was of both theoretical and practical importance, theoretically it was used to make measurements of the charge on the electron and practically it explained part of the noise that appeared at the output of amplifiers. Unfortunately, shot noise turned out not to be the sole *agent provocateur* of amplifier noise.

In 1925, J. B. Johnson published a paper in which he described his attempts at measuring shot noise in a number of audion tubes of differing

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[245] R. Möller, A. Esslinger, B. Koslowski; Thermal noise in vacuum scanning tunneling microscopy at zero bias voltage; Journal of Vacuum Science and Technology A; Vol. 8; No. 1; January/February 1990; pp. 590-593.

R. Möller; New Scanning Microscopy Techniques: Scanning Noise Microscopy [&] Scanning Tunneling Microscopy Assisted by Surface Plasmons; in H. Kumar Wickramasinghe (Ed.); AIP Conference Proceedings #241: Scanning Probe Microscopy, Santa Barbara, California, 1991; American Institute of Physics; 1991; pp. 314-327.

[246] W. Schottky; Über spontane Stromschwankungen in verschiedenen Elektrizitätsleitern [On spontaneous current fluctuations in different electrical conductors]; Annalen der Physik und Chemie; Vol. 57 (4th Series); 1918; pp. 541-567.

construction.[247] He used Schottky's idea of placing an RLC parallel (tank) circuit between the plate and cathode or filament of the tube under test to peak the shot noise at the resonant frequency of the RLC network; the minute AC noise voltage of the plate circuit of the tube under test was amplified by a multistage tube amplifier and the output of the multistage amplifier was itself applied to a resistor in contact with a thermocouple; a microammeter across the thermocouple registered the mean of the voltage squared $<V^2>$, which was proportional to the noise power.

What Johnson found much to his surprise was that the shot noise power was <u>not</u> independent of frequency. As he changed the values of L & C to reduce the resonant frequency into the audio range, he noticed that the noise power increased. In fact, it increased with decreasing frequency down to the lowest frequency he was able to attain. This result clearly contradicted the theoretical predictions of Schottky's shot noise model, which demanded that the noise spectrum be flat or, what we call today, 'white'. At higher frequencies, Johnson found the flat noise spectrum expected from the shot noise model. The increased noise power in the audio range was much more pronounced with an oxide coated filament than with a bare tungsten filament. As if all this was not confounding enough, Johnson also showed that at higher frequencies, where the noise spectrum had the expect characteristics of shot noise, the magnitude of the shot noise power at all these higher frequencies was less than predicted <u>if</u> the tube was operating in a space charge limited *régime*. Note, this uniform reduction in the magnitude of the shot noise power due to the presence of space charge was, according to word-of-mouth legends, actually first discovered by Norman Campbell.

Needless to say, these 'corrections' to Schottky's original ideas about the identity and characteristics of noise in electronic vacuum tubes introduced a healthy dose of skepticism among the workers in the field. To appreciate just how much these results 'shook the temple', consider what Johnson had to say about the use of shot noise to determine the charge on the electron,

> The experimental results cited here give force to the contention of Fry that the Schottky effect is not a proper means for measuring the charge on the electron. It is rather a phenomenon which enables us, *with the aid of the already known value of e*, to determine the truth or falsity of the basic assumptions underlying the theory.[248]

Schottky, of course, was not about to take these heresies lying down. Since he could not refute the experimental findings, undoubtedly his first choice

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[247] J.B. Johnson; The Schottky Effect in Low Frequency Circuits; Physical Review; Vol. 26 (2nd Series); July-December 1925; pp. 71-85.

[248] J.B. Johnson; The Schottky Effect in Low Frequency Circuits; Physical Review; Vol. 26 (2nd Series); July-December 1925; pp. 71-85. See, in particular p. 84.

of action, he decided to do the next best thing, which was to ‘explain’ them. [249] Due to time constraints, I cannot go into his explanation of the increase in noise power at audio frequencies - what he called the ‘flicker effect’ - except to say that I am not aware of any experimental way of unequivocally confirming his model of this effect.

Having discovered even more sources of noise in electronic vacuum tubes than they ever wanted, researchers were probably not surprised to find that even the passive components, e.g., resistors, of tube amplifiers contributed to the total noise measured at the amplifier output terminals.

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[249] W. Schottky; Small-Shot Effect and Flicker Effect; Physical Review; Vol. 28 (2nd Series); July 1926; pp. 74-103.

In 1927, J. B. Johnson proposed that ordinary conductors, passing little or no current, could also be significant sources of noise.[250] Johnson's theory apparently had its genesis in the day-to-day observation that if an amplifier's input was disconnected and shielded, the noise at the amplifier's output decreased. If a resistor was then connected to the amplifier's input, the noise at the output was found to increase. This so-called 'Johnson noise' resulted from the fact that the charge distribution in a conductor fluctuated about a mean with the deviations inducing the corresponding voltage variations across the ends of the conductor. In the case where the conductor was a resistor, Johnson showed empirically that the average or mean of the square of the noise voltage, $<V^2>$ was proportional to the resistor's resistance, R, which implied that the noise power, $P_{noise} = <V^2>/R = const.*R/R = const.$, was a constant. Note, Johnson obtained the previous result by attaching different value resistors to the input of the same multistage tube amplifier. This ploy allowed him to make comparative measurements without having to determine the frequency response characteristic of the amplifier. By using a single resistor and increasing or decreasing its temperature, he was also able to divine that the noise power was proportional to the absolute temperature of the resistor. Thus, Johnson showed that the noise power of a resistor (conductor, in general) only depended on the absolute temperature and not on any other parameters such as: the value of the resistance; the type of resistor (carbon composition, wirewound, electrolyte, etc.); size of the resistor (1/4 watt, 1/2 watt, etc.); the amount of current flowing through it, provided that this current did not change the resistor temperature due to I^2R heating; or any other descriptive parameters. He also eventually verified that the noise power was the same at each frequency, i.e., the noise spectrum was 'white'.

For a short while after the work of Schottky and Johnson, it seemed as if all the sources of internal noise power in passive components had been accounted for.[251] That this was but a false hope became very obvious as early as 1934 due to the work of J. Bernamont.[252] Bernamont noticed that the

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[250] J.B. Johnson; Thermal Agitation of Electricity in Conductors.; Nature; Vol. 119; January 8, 1927; pp. 50-51.

Idem; Thermal Agitation of Electricity in Conductors.; Physical Review; Vol. 29 (2nd Series); January-June 1927; pp. 367-368, Abstract #57.

[251] Besides internal sources of noise, electronic circuits were also being buffeted by a plethora of external electrical noises, many of them natural noise sources as opposed to man made sources of noise. In 1931, Karl G. Jansky of Bell Labs, while investigating phenomena detrimental to the reliability and intelligibility of transatlantic radio telephony, discovered an extraterrestrial noise source which had qualities similar to that of Johnson noise. Note, this natural radio noise source was apparently situated in the center of our galaxy. Subsequent investigation by other researchers uncovered many other astronomical RF noise sources, and eventually gave rise to the field of radio astronomy.

[252] J. Bernamont; Fluctuations de résistance dans un conducteur métallique de faible volume [Resistance fluctuations in a metallic conductor of small volume].; Comptes Rendus Hebdomadaries des Seances de l'Acadamie des Science (Paris); Vol. 198; 1934; pp. 1755-1758.

Idem; Étude expérimentale des fluctuations de résistance dans un conducteur métallique de faible volume [Experimental study of resistance fluctuations in a metallic conductor of small

Johnson noise from certain types of resistors increased when current flowed through them. This increased noise did not appear to be due to an increase in the temperature of the resistor due to Joule heating. Wirewound resistors did not show this increased noise in the presence of current, but resistors made by depositing a thin film of metal on an insulating substrate did. In particular, Bernamont examined resistors constructed of various lengths of an extremely fine wire known as Wollaston wire (see APPENDIX B for a discussion of how this wire was made). To prevent significant heating from occurring, Bernamont submerged the Wollaston wire in petroleum ether. The unifying characteristic of Wollaston wire and thin film resistors was their significant granularity of structure.

In 1936, C. J. Christensen and G. L. Pearson [253] decided to examine the characteristics of the noise found in granular resistances such as carbon microphones and grid leak resistors. [254] For some time it had been noticed that these very granular resistances appeared to produce noise whose character was different from that of shot noise and thermal (Johnson) noise. Christensen and Pearson showed that the mean of the square of the noise voltage $<V^2>$ was, unlike the case of Johnson noise, proportional to R^β where $\beta \sim 1.25$, all other parameters held constant, which meant that the noise power increased with resistance. In addition, they also showed that $<V^2>$ was proportional to V^α where $\alpha \sim 1.85$, all other parameters held constant, which indicated that the noise power increased with increased current unlike in the case of Johnson noise where the noise power was independent of the current - provided there was no significant Joule heating. There were also two other divergences which together guaranteed that the noise observed by Christensen and Pearson was not Johnson noise: 1) an ambiguous dependence of the noise power on temperature, and 2) a power spectrum which followed a 1/f dependence, where 'f' was the frequency.

Today, this third type of internal noise is called current noise, due to its being observed to increase with increasing current, or excess noise, due to it 'on

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volume].; Comptes Rendus Hebdomadaries des Seances de l'Acadamie des Science (Paris); Vol. 198; 1934; pp. 2144-2146.

[253] C.J. Christensen, G.L. Pearson; Spontaneous Resistance Fluctuations in Carbon Microphones and Other Granular Resistances; Bell System Technical Journal; Vol. 15; 1936; pp. 197-223.

[254] Grid leak resistors were usually found connected between the signal grid and cathode of vacuum tubes. Since the cathode was also connected to ground, any current which flowed from the grid through the grid leak resistor to ground (cathode) served to bias the grid slightly negative with respect to the cathode, which was necessary for the proper operation of the circuit. This was known as self biasing.

The grid leak resistor had to be a very high value resistor in order to provide enough bias with the small amounts of current flowing from the signal grid. One way to produce such a resistor was to take a clean ceramic cylinder with electrical contact pads at either end and draw a line on the ceramic connecting the two pads using India ink. When the ink dried one had the required high value resistor. Later, grid leak resistors were made by depositing thin metallic films on glass or ceramic substrates. Both of these very different manufacturing processes apparently led to granular structures.

top' of or in excess of Johnson noise, or finally 1/f noise, due to its characteristic power spectrum. As if all these different names for the same kind of noise are not confusing enough, excess or current or 1/f noise is also known as flicker noise in tribute to the work on electronic vacuum tubes by Johnson and Schottky.

During the Second World War, the development of radar resurrected the point contact diode. Since this type of diode possessed a mechanical junction, it would be a good bet to assume that it too produced 1/f noise - and it did. The 1/f noise was found to be more intense when the point contact diode was reverse biased than when it was forward biased, but other than that the noise in the two bias directions were indistinguishable from each other and, in turn, from the 1/f noise found in a carbon button microphone. [255]

We have cataloged, so far, three types of internal noise: shot noise, Johnson noise and excess (or current or 1/f) noise. Is this list exhaustive? The answer is, no. First of all, shot noise, for example is not confined to vacuum tubes, it is also found in solid state devices such as semiconductor diodes and transistors. And second of all, there are other types of noise which are just starting to be recognized. Examples of these 'new' noise sources include popcorn noise found in ICs (Integrated Circuits) and chaotic circuit behavior, which is believed to originate in the nonlinear behavior of all real electronic components. Circuit nonlinearities can give rise to noncoherent oscillations, which though strictly speaking are not noise since they are not truly random, can nevertheless be thought of as a deterministic aperiodic signal. [256]

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[255] Henry C. Torrey, Charles A. Whitmer; Crystal Rectifiers; McGraw-Hill Book Co.; 1948; pp. 192-195. [See also,

P.H. Miller (Jr.), M.H. Greenblatt; Crystal Audio Noise; NDRC 14-387; University of Pennsylvania; January 5, 1945; 19 p.

Note, this report was originally classified CONFIDENTIAL, but was declassified by authority of the Secretary of Defense in a memo written August 2, 1960. A copy of this report is on file in The University of Pennsylvania Archives, North Arcade, Franklin Field, Philadelphia, PA 19104-6320, (215)898-7024. I wish to thank Gail Pietrzyk for her help in locating all the NDRC (National Defense Research Council) reports held in the U. of P. archives. Copies of this report can also be obtained from The Library of Congress, Science and Technology Division, Washington, DC 20540, (202)707-5655.]

[256] Perhaps the earliest descriptions of chaotic circuits was the work of B. Van der Pol. For an example see,

B. Van der Pol, J. Van der Mark; Frequency demultiplication; Nature; Vol. 120; 1927; pp. 363-364.

More recent articles on the nuts and bolts aspects of chaotic circuits can be found in the following references and their associated bibliographies,

J. Lesurf; Chaos on the circuit board; New Scientist; Vol. ???; June 30, 1990; pp. 63-66.

T.P. Weldon; An inductorless double scroll chaotic circuit; American Journal of Physics; Vol. 58; No. 10; October 1990; pp. 936-941.

§5. THE 'O' IN MOM (METAL-OXIDE-METAL) 'DIODES': THE COPPER OXIDE RECTIFIER ANALOGY. - Most of the point contact 'diodes' used in laser heterodyning had the following structure: a thin metal wire, sometimes with an S-shaped or U-shaped bend in it, electrolytically sharpened in a potassium hydroxide (KOH) solution or mechanically pointed, and then brought into contact with a flat, usually polished or lapped, metal base. The processing of the metal wire and of the base looked to be innocuous enough, but this was not the case at all. The surface of the electrolytically etched tungsten wire has been shown to possess a layer of either polycrystalline or amorphous tungsten oxide (WO_X, where X~3). [257] Biegelsen *et al.* employed a combination of TEM (Transmission Electron Microscopy) and electron diffraction to examine electrolytically etched tungsten STM (Scanning Tunneling Microscope) tips. The electron diffraction pattern was consistent with that of WO_X as found in the compilation maintained by the International Centre for Diffraction Data, Swarthmore, Pennsylvania. As a result of their findings, these researchers recommended that electrolytically etched STM tips always be ion milled before being used, a prescription endorsed by other workers in the field. [258]

The polishing of the base electrode of the point contact 'diode' was likewise not without consequence, *vis-à-vis* the Beilby layer (see APPENDIX D for a detailed explanation of the history and current thinking about the Beilby layer).

Assuming for the moment that we understand the origins of the oxide layer on the catwhisker and on the base electrode of our MOM 'diode', the question still remains as to how these layers affect the behavior of the device. The only other solid state diode which explicitly used a metal oxide was the copper oxide rectifier invented around 1930. And although the copper oxide rectifier's oxide layer was of an extravagant thickness, at least, when compared to those thought to exist on MOM structures, its behavior might still yield some insights into the operation of the MOM devices. Because the background material needed to appreciate the construction and operation of the copper oxide rectifier is rather detailed, this information has been given its own appendix (see APPENDIX G). In this appendix, we shall simply use the relevant information from APPENDIX G for the purposes of comparison.

§6. WHERE THE ANALOGY ENDS: RECTIFICATION @ 0 Hz (DC). - There was one main difference between the behavior of the copper oxide rectifier and the MOM 'diode', the copper oxide rectifier clearly rectified at or near DC with the rectification ratio decreasing to unity, i.e., no rectification, as the frequency of the applied voltage increased, while the MOM 'diodes' appeared to

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[257] D.K. Biegelsen, F.A. Ponce, J.C. Tramontana; Ion milled tips for scanning tunneling microscopy; Applied Physics Letters; Vol. 50; No. 11; March 1987; pp. 696-698.

[258] Y. Kuk, P.J. Silverman; Role of tip structure in scanning tunneling microscopy; Applied Physics Letters; Vol. 48; No. 23; June 1986; pp. 1597-1599.

rectify signals in the GHz (gigahertz) and THz (terahertz) range but completely lost their ability to rectify when the signal frequency approached DC. The reason the copper oxide rectifier could not rectify at high frequencies was that the metal-semiconductor junction introduced a capacitance in parallel with itself, which effectively shunted the applied voltage around the junction at high frequencies. The impedance of this capacitor fell monotonically as the frequency increased, and eventually the junction capacitance shorted out its own rectifying junction. The mechanical junction of the MOM 'diodes' also had a capacitance associated with it by virtue of being composed of two pieces of metal separated by an insulating or semi-insulating layer, but this junction capacitance did not appear to interfere with the ability of this structure to rectify even at light frequencies. This lack of interference due to the junction capacitance was and still is very puzzling.

Samuel I. Green *et al.* postulated that the MOM 'diodes' functioned due to asymmetrical electron tunneling because of a difference in the work function between the two pieces of metal which made up the MOM structure. Historically, this was one of the earlier models proposed to explain rectification in semiconductor diodes (see main section entitled THE RESURRECTIONS), but it failed to properly account for the observed direction of the rectified current. In this model, polarity reversal was also predicted at high electric fields. As far as I know, there are no real MOM structures which rectify at or near DC due <u>exclusively</u> to tunneling through asymmetrical barriers. In fact, Green's I-V curves of his own MOM 'diodes', done on a curve tracer at 120 Hz, were slightly nonlinear but nevertheless symmetrical. Why then did they rectify at light frequencies, but not in the neighborhood of DC (0 Hz)?

§7. POLARITY REVERSAL IN MOM 'DIODES'. - Another puzzling aspect of MOM structure behavior was the occurrence of polarity reversal at high RF power inputs with no DC bias.[259] Before trying to understand why this happened in MOM 'diodes', let's consider the root cause of this phenomenon in more traditional semiconductor rectifiers.

Polarity reversal in point contact semiconductor diodes was explained in terms of simply an asymmetry in the size of two otherwise identical rectifying interfaces. To my knowledge, Cayrel was the first person to correctly explain and

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[259] As was shown in the main body of this thesis, polarity reversal also occurred in the presence of a DC bias. Perhaps the best example of this behavior was found in the work of Faris *et al.* in 1973. See,

S.M. Faris, T.K. Gustafson, J.C. Wiesner; Detection of Optical and Infrared Radiation with DC-Biased Electron-Tunneling Metal-Barrier-Metal Diodes; IEEE Journal of Quantum Electronics; Vol. QE-9; No. 7; July 1973; pp. 737- 745.

In the presence of a DC bias, the polarity reversal occurred at a <u>fixed</u> input laser power when the DC bias voltage or current was increased beyond a certain point. Note, this type of polarity reversal did not depend on the polarity of the DC bias.

verify experimentally polarity reversals in galena point contact diodes.[260] Cayrel was trying to explain why Paule Collet had observed two types of rectification in sensitive galena point contact diodes. At low currents, Collet observed that rectification was in the normal direction, while at high currents the direction of the rectified current was in the opposite sense. This oppositely directed current was called rectification of the second species or kind. While investigating rectification in galena point contact diodes constructed of a single crystal, Cayrel noticed that rectification of the second species, i.e., polarity reversal, only occurred if the base electrode did not make firm and uniform contact with the galena. Note, in a galena point contact diode, contact was established via two electrodes: a catwhisker on one face of the crystal and a base electrode which many times was simply a flat polished metal plate pressed against the opposite face of the single crystal. Cayrel reasoned that rectification took place at both the catwhisker-crystal interface and at the base electrode-crystal interface; the rectification at the base electrode-crystal interface was thought by Cayrel to occur via asperities on the base electrode which acted like microscopic catwhiskers. At low values of alternating current, the catwhisker-crystal interface dominated, hence the rectification was in the normal direction. However at high values of alternating current, the catwhisker-crystal interfaces heated up causing a loss of rectification ability, while the base electrode-crystal interface, with its numerous asperity contacts, stayed relatively cool and so maintained its rectifying properties thus giving rise to a polarity reversal, i.e., rectification of the second kind. To prove that heat at the catwhisker-crystal interface was indeed the culprit, Cayrel cooled the catwhisker junction with a stream of dielectric fluid and observed that the rectification at high currents was in the normal direction, i.e., no polarity reversal.

Cayrel's explanation might also be valid for MOM 'diodes', but to show its relevance one would have to keep the structure cool via a stream of insulating dielectric fluid. Certainly, this experiment would be worthwhile to try.

Since no one has proposed a thermoelectric theory to explain the observed 'rectification' by the MOM devices, which is surprising given how many times in the past this idea has been taken off the shelf, dusted off and brought into service, let me propose it as another possible explanation of polarity reversal. As is mentioned in APPENDIX G, the copper oxide rectifier possesses a thermoelectric voltage as will any device having junctions made of dissimilar conductors or semiconductors. In this scheme of things, the MOM 'diodes' are not actually rectifying the incoming light energy, instead the 'diodes' are acting as thermocouples and generating a thermoelectric voltage due to nonresonant

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[260] J. Cayrel; Sur la détection des galènes [On Detection by Galenas]; Comptes Rendus Hebdomadaries des Seances de l'Academie des Sciences (Paris); Vol. 180; June 8, 1925; pp. 1728-1731.

See also,

Heinz K. Henisch; Rectifying Semi-Conductor Contacts; Oxford University Press; 1957; pp. 1-5.

absorption (conversion of light to heat) of the light energy. It is not generally appreciated that thermoelectric voltages undergo a polarity reversal at higher temperatures, i.e., the initial polarity of the thermoelectric voltage will reverse itself if the thermocouple junction temperature gets hot enough. [261] And unlike many other theories, this theory explains why the 'rectification' does not decrease rapidly at high frequencies due to the shunting of the input signal by the junction capacitance.

Recently, a physical picture of why this polarity reversal occurs was presented by J. J. Jimenez in his review of laser heterodyning work. [262] According to Jimenez's explanation, both the point and the base electrodes of the MOM 'diode' were sources of opposing unidirectional tunneling currents via the Fowler-Nordheim mechanism. However, the net tunneling current depended on which unidirectional tunneling current was larger, which in turn depended on the difference between the work function of the point electrode versus that of the base electrode. Let us designate the current density of the point and base electrodes as J_p and J_b, respectively. Initially, we shall assume that $J_p > J_b$. At zero intensity of laser illumination, the net current from the point electrode to the base electrode must be zero, otherwise the second law of thermodynamics will be violated. At this point Jimenez waved his hands and casually stated that the laser illumination caused the polarity reversal through a combination of electric field <u>and</u> thermal effects - which was different from the mechanism of R. Stratton and J. G. Simmons which was championed by S. I. Green. So much for a physical picture.

Even if my idea about the mechanism behind the rectification by MOM 'diodes' is correct, there is still the problem of how to explain the ability of these structures to perform frequency mixing. Here, I propose the following model. In place of the normally assumed linear junction capacitance, substitute a nonlinear junction capacitance. The nonlinearity of the junction capacitance allows mixing and frequency multiplication in the same manner that the nonlinear junction capacitance of a varactor diode promotes these two behaviors. This also explains the rather startling ability of the MOM 'diodes' to operate as mixers and/or heterodyners in the terahertz range, without the debilitating losses due to

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[261] Rev. J. Cumming; On some Anomalous Appearances occurring in the Thermoelectric Series; Annals of Philosophy; Vol. 6 (New Series); 1823; pp. 321-323.

[A.C.] Becquerel; Recherches sur les Effets électriques de contact produits dans les changemens de température, et application qu'on peut en faire à la détermination des hautes températures [Investigations into the electrical effects of contact produced by changes in temperature, and the applications one is able to make in the determination of high temperatures].; Annales de Chimie et de Physique; Vol. 31; 1826; pp. 371-392.

[262] J.J. Jimenez; Synthèse et mesure des fréquences optiques [Synthesis and measurement of optical frequencies]; Revue de Physique Appliquée [Review of Applied Physics]; Vol. 14; February 1979; pp. 353-367. [Even though Green *et al.* were one of the first groups, if not the first, to detect polarity reversals in MOM structures, Jimenez carefully omited any mention of their papers in his massive bibliography containing 92 citations. This omission appeared to be deliberate, since the paper by Kwok *et al.*, which was an extension of Green's work, was cited.]

the inevitable presence of parasitic shunting capacitance: the nonlinear junction capacitance, which is responsible for the mixing/heterodyning, is of the same order of magnitude as the parasitic shunting capacitances, and in fact may be larger.

§8. AN ALTERNATIVE EXPLANATION OF MOM ‘DIODES. - The term MOM ‘diode’ unconsciously makes one assume that the dominant method of electrical conduction through this structure is via electron tunneling. The researchers who have used these devices for laser heterodyning appear to have made this assumption, undoubtedly more out of convenience than scientific rigor. It turns out, though, that there is another way of accounting for the electrical conduction in these structures, and this alternative view makes no appeal, direct or indirect, to electron tunneling. If the two pieces of metal forming the MOM structure are connected by a metallic bridge or bridges, i.e., cohered, then this arrangement will certainly allow electrical conduction even in the complete absence of electron tunneling.

In a series of three papers spanning the period 1976 to 1978, three Dutch physicists, A.G.M. ‘Louis’ Jansen, F. Mueller and Peter Wyder, investigated the phenomenon of electron-phonon interactions using an apparatus which presaged the STM. [263] In this apparatus, an electrolytically etched tip, the “…spear…”, was carefully brought into contact with a larger piece of the same metal, the “…anvil…”, by a combination of differential screws for coarse approach and a piezoelectric actuator for fine adjustment. Jansen *et al.* were inspired in this enterprise by the earlier work of two experimental Russian physicists, I. K. Yanson and N. I. Bogatina, who had set out to initially investigate the nonlinear current-voltage (I-V) characteristics of thin metallic bridges or filaments. [264]

The metallic bridges were formed - in the case of the Russian work - by taking a planar MOM junction and applying a current-limited voltage of sufficient intensity, i.e., greater than the critical voltage, to cohere the junction (see

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[263] A.G.M. Jansen, F.M. Mueller, P. Wyder; Direct Measurement of α^2F in Normal Metals Using Point-Contacts: Noble Metals; in D.H. Douglass (Ed.); Superconductivity in d- and f-Band Metals; Plenum Press; 1976; pp. 607-623.

Idem; Direct measurement of electron-phonon coupling $\alpha^2F(\omega)$ using point contacts: Noble metals; Physical Review B, Solid State; Vol. 16 (3rd Series); No. 4; August 15, 1977; pp. 1325-1328.

Idem; Normal Metallic Point Contacts; Science; Vol. 199; No. 4333; March 10, 1978; pp. 1037-1040. [I wish to thank two members of my thesis committee, Dr. Vallorie Peridier and Dr. Thomas E. Sullivan, for having encouraged me to read a series of articles on heat transfer in micro-scale objects which ultimately led me to the articles of Jansen *et al.* In 1980, Jansen *et al.* wrote a review article on the subject of point contact spectroscopy, which summarized and expanded on the papers cited above,

A.G.M. Jansen, A.P. van Gelder, P. Wyder; Point-contact spectroscopy in metals; Journal of Physics C: Solid State Physics; Vol. 13; 1980; pp. 6073-6118.]

[264] N.I. Bogatina, I.K. Yanson; The nonlinearity mechanism of the volt-ampere characteristics of point junctions; Soviet Physics JETP; Vol. 36; No. 4; April 1973; pp. 692-696.

APPENDIX E for a more detailed description of the experimental protocol); bridges also formed spontaneously for reasons which were not fully understood. In fact, steps were taken to discourage the formation of such inadvertently produced metal filaments (see, again, APPENDIX E). Note, Yanson and Bogatina did not employ the terms ‘cohere’, ‘coherer’ or ‘critical voltage’, but given what we know from this thesis about coherers, the use of these terms would have certainly been appropriate.

Returning, now, to the Dutch contingent of Jansen *et al.*, we find that their results, the I-V curves, using the ‘spear and anvil’ configuration were identical to those first seen by the Russians. This was so in spite of the fact that Jansen *et al.* did not deliberately cohere their MOM junction using an electrical pulse. What they did appear to have done was to have cohered the MOM junction mechanically as a result of pressing the spear against the anvil. In their 1978 *Science* article, Jansen *et al.* hypothesized that the metallic bridges were the result of preexisting asperities on one electrode penetrating the native oxide layer on the opposing electrode and thus joining the two electrodes electrically via a short (~200 Å) narrow metallic filament.

If the aforementioned course of events accurately reflected reality, then it would not be surprising to find the same metallic bridges mediating electrical conduction and RF detection in the so-called MOM ‘diodes’ used by the laser heterodyning coterie. One might object to the whole premise of metallic bridges being able to detect RF energy, but one would then be faced with repudiating the demonstrated RF detection abilities of a whole host of metallic bridge arrangements: including bridge type Josephson junctions (see APPENDIX E for a discussion of Josephson junctions);[265] bridge configurations cooled to low temperatures, but not so low that the metals became superconducting;[266] and room temperature bridge constructs such as the modified Schäfer anticoherer depicted in Fig. B7 (APPENDIX B).

The main problem with trying to decide which mechanism, tunneling or metallic bridges, is the correct one, lies in being able to differentiate between them by some kind of experimental technique(s). The most convenient experimental data is, of course, the I-V curve at a constant temperature. Jansen *et al.* used the fact that their I-V, dV/dI-V, and d^2V/dI^2-V curves mimicked those of Yansen *et al.* as ‘proof’ that metallic bridges were behind the electrical conduction observed in their spear and anvil arrangement. This type of proof-by-imitation leaves something to be desired, but until there is an unequivocal

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[265] P.W. Anderson, A.H. Dayem; Radio-Frequency Effects in Superconducting Thin Film Bridges; Physical Review Letters; Vol. 13; No. 6; August 10, 1964; pp. 195-197.

A.H. Dayem, J.J. Wiegand; Behavior of Thin-Film Superconducting Bridges in a Microwave Field; Physical Review; Vol. 155; No. 2; March 10, 1967; pp. 419-428.

[266] M.S. Khaikin, I.Ya. Krasnopolin; Nonlinearity of Resistance of a Metallic Point Contact and Detection of Microwaves at Helium Temperatures; JETP Letters; Vol. 4; July-December 1966; pp. 196-199.

experimental test for the presence or absence of metallic bridges, the I-V curves and the derivatives thereof are the only game in town.

§9. RELIABILITY, THE ACHILLES HEEL OF MOM 'DIODES'. - One of the most irritating behaviors of homemade MOM 'diodes' was the changing of their electrical characteristics with time. This drifting of electrical characteristics - usually towards degradation - appeared to plague every researcher who worked with these devices. As far as I could tell, no one offered an explanation, backed by supporting experimental evidence, for this behavior.

In 1918, Angelika Maria Josefa Székely de Doba wrote a review and experimental article on all of the then known types of point contact 'diodes'. [267] One of the first things she noticed was that many of these 'diodes' appeared to be very weak sources of EMF (ElectroMotive Force). From her experiments with these devices she surmised that they were acting like small electrochemical cells, hence the EMFs. Where had the electrolyte come from? Her answer was, from the air, i.e., the humidity in the air deposited a microscopically thin but tenacious film of water on the surfaces making up the point contact structure. Any current flowing through such a structure produced electrolysis products which eventually changed its electrical characteristics.

I do not know if Székely's hypothesis is correct with regards to the MOM devices used in laser heterodyning work, but it is definitely possible given the way these devices are assembled and handled. Further support for Székely's hypothesis came from the early work on packaging commercial point contact diodes and transistors in the 1950s. The electrical characteristics of these devices, much to the surprise and chagrin of their manufacturers, varied with the amount of time they spent in the field. This behavior caught the manufacturers off guard because they wrongly assumed that these solid state devices were more reliable than their predecessors, the electronic vacuum tube, and hence did not use hermetic packaging due to its higher cost. Investigation of the instability of the electrical characteristics with time revealed that the main culprit was the humidity in the air. [268] Note, while this conclusion is considered 'gospel' today in the semiconductor industry, when it was first enunciated it was the subject of much controversy.

Some recent work on the question of the reliability of MOM 'diodes' has focused on the physical deformation of the tip as a means of achieving reproducible electrical behavior. Specifically, the so-called 'hooking' of the tip, when it was brought into mechanical contact with the counterelectrode, was found to improve

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[267] A. Székely de Doba; Die Kontaktdetektoren [Point Contact Detectors]; Akademie der Wissenschaften in Wien Mathematisch-naturwissenschaftliche Klasse, Sitzungsberichte; Vol. 127; Pt. 2a; No. 6; 1918; pp. 719-792.

[268] R.M. Ryder, W.R. Sittner; Transistor Reliability Studies; Proceedings of the IRE; Vol. 42; February 1954; pp. 414-419.

the reliability of the structure. [269] In order to produce the desired amount of 'hooking', the electrochemical etching of the tungsten tips had to be first optimized and standardized. The resulting tips were then carefully driven into the counterelectrode post by means of a micrometer until their pointed end had curled around sufficiently to resemble a rather tight fishhook. The counterelectrode post consisted of a quartz post onto which a thin film of nickel was sputtered and then slightly oxidized. The traditional counterelectrode post made from a cutoff and polished piece of nickel wire was found to be wanting in terms of electrical reproducibility, perhaps due to the coarse grain size according to the authors. Why this procedure was thought to work was not unequivocally demonstrated by the authors of this paper. They did hypothesize, though, that in the optimum 'hooked' configuration, the very point of the tip, while not embedded in the post, was close enough to the post to facilitate field emission due to its sharpness. However, no quantitative information was provided on the electrical longevity of these 'hooked' structures except the rather qualitative statements that "…stability is long term…" and "…; stability of this diode was observed to be long term."

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[269] C. Yu, M.A. Hemmatian, A. Niczad, Y. Taghipoor, A. Yekrangian; A systematic study of the effect of hooking upon contact on the performance of electrolytically etched point contact MOM diodes; in James C. Wiltse (Ed.); Proceedings of SPIE, Millimeter Wave Technology III, Vol. 544, April 9-10, Arlington, Virginia; The International Society for Optical Engineering; 1985; pp. 78-84.

APPENDIX B - PASSIVATION LAYERS OF NOBLE METALS

“God made solids, but surfaces were made by the Devil.”
- Wolfgang Pauli

§1. INTRODUCTION. - Of all the coherers and MOM ‘diodes’, undoubtedly the ones constructed of noble metals (gold, platinum, palladium, etc.) present the greatest challenge as far as trying to explain how they work. The main difficulty is in identifying the insulating or semi-insulating film. In fact, a controversy has raged for at least the last hundred years as to whether a film exists at all in the case of the noble elements. After all, the noble metals got their name from the fact that they appeared not to tarnish, i.e., did not react with atmospheric gases, in particular, oxygen. Since it is a fact that coherers and MOM ‘diodes’ have been built utilizing exclusively noble metals, the existence of some sort of insulating or semi-insulating film at the surface of these metals seems assured. The alternative scenario, i.e., accepting the hypothesis of no surface films whatsoever, would entail, it seems to me, a different mechanism to explain the functioning of devices made from these metals. The absence of a surface film would necessitate a dead short forming between the two pieces of metal making up the device, and it is not at all apparent how such a structure could function as a detector, mixer, etc.

One of the first people, if not the first, to champion noble metals in coherers was Édouard Branly, who constructed a number of functioning coherers using gold and platinum. Branly chided other researchers, who said that they had tried but failed to get noble metal coherers to work, by stating that a negative result does not prove that something cannot be done. Branly’s findings were confirmed a short time later by Jagadis Chandra Bose. Some 70 years later, Samuel I. Green, Jack R. Baird and Paul D. Coleman realized what they called a MOM (Metal-Oxide-Metal) 'diode' via an electrolytically etched gold wire lightly pressed against a gold film evaporated onto a piece of glass substrate. Branly, Bose and Green *et al.* commented favorably on the sensitivity of their noble metal detectors. In this same time frame we find Bowman *et al.* (see the main section entitled WHAT IS KNOWN (pre-1970)) claiming, after what they considered a suitable amount of experimentation, that noble metals would not work as coherers, this some 50 years after Branly and Bose had shown otherwise. And as recently as 1984, Riccius *et al.* in a review article on the field of laser heterodyning using MOM 'diodes', [270] while admitting that gold on gold 'diodes' worked, claimed that there could not possibly be a surface film between the two pieces of metal. Their justification for this sweeping statement was the book by O. Kubaschewski and B. E. Hopkins. [271] Since Riccius *et al.* did not specify any particular page or pages in this book, I was forced to try to find their justification by perusing the whole book. Note, I used the second edition (1967) of the book. The subject index had no listing for 'gold', although it did have the entry 'noble metals'. The 'noble metals' entries turned out to refer mostly to the platinum metals; the one mention of gold claimed that it did not react with oxygen at high temperatures. Examination of the table of contents also failed to find any mention of gold, even though chapter four listed the experimental results for a large number of metal elements. So the bottomline is this, who is right if anyone can be said to be completely right?

§2. PLATINUM BLACK, EXACTLY WHAT IS IT? - To appreciate how long this conundrum, about the existence or nonexistence of surface layers on noble metals, has bedeviled scientists and engineers, let us begin in 1820 with Edmund Davy's discovery of platinum black. [272] Davy managed to dissolve platinum metal, or more precisely to form the chloroplatinous and chloroplatinic ions ($PtCl_4^{2-}$ or $PtCl_6^{2-}$ [273]), which he then proceeded to precipitate out of solution. The resulting layer of what appeared to be finely divided metal was christened platinum black. The properties of platinum black: extremely high catalytic activity and seemingly insatiable ability to take up hydrogen and/or oxygen gas made it an almost instant commercial success. Platinum black has had a rather astounding longevity, it is still used today as a catalyst, [274] e.g., the catalytic

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[270] H.D. Riccius, K.J. Siemsen; Point-Contact Diodes; Applied Physics A, Solids and Surfaces; Vol. 35; 1984; pp. 67-74.

Idem; Experiments with Point-Contact Diodes in the 30-130 THz Frequency Region; Applied Physics A, Solids and Surfaces; Vol. 35; 1984; pp. 177-187.

[271] O. Kubaschewski, B.E. Hopkins; Oxidation of Metals and Alloys; Butterworths; 1962.

[272] E. Davy; On some Combinations of Platinum; Abstracts of the Papers Printed in the Philosophical Transactions of the Royal Society (London); Vol. 2 (II); 1815-1830; p. 124;

[273] Linus Pauling; College Chemistry; Freeman & Co.; 1964; pp. 658-660.

[274] For example, a search for the keywords 'platinum black' on the WILSONDISC® AST (Applied Science and Technology) database seven articles in the time frame 1983-1991.

converter found on most automobiles; it is the primary standard of choice for the hydrogen electrode used to determine pH (hydrogen ion concentration in solutions); and it serves as the reference electrode ($E_{ox}\{H_2\} = 0.0$ V) in the determination of the oxidation potentials of various couples.[275] It should also be noted that a layer of platinum black could also be formed by a lengthy bombardment of a piece of shiny platinum with cathode rays (electrons).[276] This effect was most likely a secondary one due to the heating of the platinum by the cathode rays and the subsequent reaction of the hot platinum with the residual air in the vacuum tube.

The first question you might think to ask concerning this substance is, what is it? Is it just platinum, and if so why is it black? Chemists, who were contemporaries of Davy, asked some of these same questions, but they were only able to investigate the chemical composition, which they found to be ~15% oxygen by weight with balance being platinum. One of the earliest and most extensive investigations into the composition and occlusive properties of platinum and palladium black was performed by Ludwig Mond, Sir William Ramsay and John Shields around 1895.[277] With respect to the composition of platinum and palladium black, these researches found that oxygen was <u>always</u> associated with them to the tune of 0.66% and 1.65% by weight, respectively. While the oxygen associated with platinum black could be completely removed by heating to a red heat in a vacuum, palladium black did not give up more than a fraction of its total occluded oxygen when subjected to this same procedure - heating the various blacks to red heat usually resulted in them transforming to the sponge form, which unlike the black form did not have as high an occlusive power. It is interesting to note that some modern day chemists describe platinum, palladium and aluminum black as colloidal suspensions of the corresponding metal. This colloidal nature is used to account for the color of these substances.[278]

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[275] For reasons which I do not understand, electrochemists now refer to ‘platinum black on platinum’ as ‘platinized platinum’.

[276] Sir J.J. Thomson, G.P. Thomson; <u>Conduction of Electricity Through Gases, Vol. 2</u>; Cambridge University Press; 1933; p. 5.

[277] L. Mond, W. Ramsay, J. Shields; On the Occlusion of Oxygen and Hydrogen by Platinum Black. Part I; Philosophical Transactions of the Royal Society (London); Vol. 186 (Series A); Pt. 2; 1895; pp. 657-693.

Idem; On the Occlusion of Oxygen and Hydrogen by Platinum Black. Part II; Philosophical Transactions of the Royal Society (London); Vol. 190 (Series A); Pt. 2; 1897; pp. 129-153.

[Note, other metals besides platinum and palladium can exist in the black form, e.g., it is possible to produce aluminum black by Joule evaporating aluminum in the presence of air or hydrogen,

W.O. Mulligan, A.B. Focke; The Crystal Structure of Aluminum Black; Journal of Chemical Physics; Vol. 45; March 1940; pp. 107-108.

R. Riesenberg, G. Schmidt; Black Aluminum Films; Vacuum; Vol. 37; No. 1-2; 1987; pp. 183-186.]

[278] The science of fine particles and solid colloidal suspensions is a ‘hot’ field today as the following articles will attest,

E. Matijevic; The World of Fine Particles; CHEMTECH; Vol. 21; No. 3; March 1991; pp. 176-181;

Present day forays at determining the composition of platinum black employ some very impressive sounding analytical techniques such as IINS (Incoherent Inelastic Neutron Spectroscopy), EELS (Electron Energy Loss Spectroscopy), IRS (Infrared Spectroscopy), etc. Udovic *et al.* [279] used IINS to divine the presence of stable OH molecules on the surface of platinum black.

William Thomson (Lord Kelvin) was another English scientist who found evidence that platinum acquires some sort of film just from standing in air or pure oxygen. He was led to the preceding conclusion as a result of the work he was doing on contact electrification between pure metals. [280] The experiment involved measuring the contact potential between two identical platinum disks, one - called the reference disk - which was always kept in the dry air of the measuring apparatus (Volta condenser), and the second disk which was exposed to either pure dry hydrogen or oxygen for a length of time and then returned to the dry air atmosphere of the measuring apparatus. The results showed that exposure to 100% hydrogen or oxygen change the contact potential, which initially was close to zero, by ~+0.11 V and ~-0.33 V, respectively; these shifts in the contact potential slowly returned to approximately zero over the course of a week.

§3. PASSIVATION LAYERS ON NOBLE METALS, THE CHEMICAL EFFECTS. - That the platinum metals (platinum, palladium, osmium, rhodium, iridium and ruthenium) do tarnish at high temperatures was asserted by W. Betteridge and D. W. Rhys. [281] They also offhandedly throw out this factoid. “At room temperature the solid metal forms a very thin, strongly adherent layer of oxide… The layer of oxide is not visible nor can it be detected by weigh change, though its presence can be inferred from the change in the gas adsorptive powers of the platinum surface if it is heated to high temperature in hydrogen to reduce the oxide film.” Support for this position also could be found in the work of the electrochemists Fred C. Anson and James J. Lingane. [282] These researchers wondered why it was that platinum behaved nobly in solutions

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[As Matijevic indicates in the above article, two whole issues (December 1990 & January 1991) of MRS Bulletin are devoted to this topic. **Warning**, do not confuse, as I did, the MRS (Materials Research Society) Bulletin with the Materials Research Bulletin, they are two different journals.]

[279] T.J. Udovic, R.R. Cavanagh, J.J. Rush; Neutron Spectroscopic Evidence for Adsorbed Hydroxyl Species on Platinum Black; Journal of the American Chemical Society; Vol. 110; 1988; pp. 5590-5591.

[280] Sir W. Thomson; On a Method of Measuring Contact Electricity; Nature; Vol. 23; April 14, 1881; pp. 567-568.

[281] W. Betteridge, D.W. Rhys; The High-temperature Oxidation of the Platinum Metals and Their Alloys; in First International Congress on Metallic Corrosion, London, April 10-15, 1961; Butterworths; 1962; pp. 186-192.

[282] F.C. Anson, J.J. Lingane; Chemical Evidence for Oxide Films on Platinum Electrometric Electrodes; Journal of the American Chemical Society; Vol. 79; 1957; pp. 4901-4904.

whose oxidation potential was higher than that of the platinum-platinum ion couple? To understand this last statement consider the following standard chemistry experiment.

A beaker contains a solution of copper sulfate ($CuSO_4$) in water, which is light blue in color; the oxidation potential, E_{ox}, of the couple $Cu \rightarrow Cu^{2+} + 2e^-$ is -0.34 V. If a number moles of powdered zinc metal, equal to the number of moles of copper in the solution, is added to this solution, the solution turns clear as the zinc is oxidized (loses electrons) to become the zinc ion (Zn^{2+}) and the copper ion (Cu^{2+}) is reduced (gains electrons) to become copper metal and precipitates out of solution. The reason for this reaction taking place is that the oxidation potential of the couple $Zn \rightarrow Zn^{2+} + 2e^-$ is +0.76 V, which is greater than the oxidation potential for the copper-copper ion couple, meaning that thermodynamically the reduction of Cu^{2+} and the oxidation Zn^{2+} proceeds spontaneously. Likewise, Anson and Lingane were wondering why platinum resists oxidation even in solutions where, thermodynamically, oxidation should be favored. They thought that a thin passivation layer of oxide, as opposed to simply an adsorbed oxygen film, might explain platinum's ability to remain noble and yet still be in electron equilibrium with the surrounding solution. Using a chronopotentiometric technique, [283] these researchers were able to satisfy themselves that indeed platinum did possess a thin oxide layer.

The question of the nobility of gold was just as perplexing, if not more so. We first note that gold <u>does</u> form oxides, many of them in fact, but according to some chemists gold cannot react directly with oxygen unless ozone (O_3) is present. Using the same logic as employed by Anson and Lingane, two electrochemists W. J. Müller and E. Löw in 1935 questioned why gold behaves nobly in solutions whose oxidation potential was greater than that of the gold-

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[283] Briefly, the chronopotentiometric method of determining the thickness of an oxide layer on a metal consists of placing the oxide-coated metal in an electrochemical cell together with an inert electrode. If the oxide-coated metal is made the cathode (-) and the inert electrode the anode (+), then the oxide layer will undergo chemical reduction and be converted to gaseous oxygen which will leave the cell or the oxide will simply be reduced to a compound which can be dissolved by the surrounding electrolyte. The electrochemical cell is powered by a constant current source. By monitoring cell potential versus time one can tell when the oxide layer has been completely dissolved by the sudden increase in the potential to that necessary to reduce hydronium ions (H_3O^+) to hydrogen gas. See the following graph, taken from Fig. 3 of,

W.E. Campbell, U.B. Thomas; Tarnish Studies, The Electrolytic Reduction Method for the Analysis of Films on Metal Surfaces; Transactions of the Electrochemical Society; Vol. 76; 1939; pp. 303-328.

The chronopotentiometric technique was originally developed by Ulick R. Evans during his investigations into the nature of oxide layers which arose as a result of tempering of metals,

U.R. Evans; The Colours Due to Thin Films on Metals; Proceedings of the Royal Society (London); Vol. 107 (Series A); 1925; pp. 228-237.

gold ion couple. [284] Their answer, after some experimentation, was that gold too had a passivation layer at its surface.

It should be mentioned that passivation also occurs in metals 'baser' than the so-called noble metals. For example, it has been known for a long time that iron can be passivated. In fact, the study of passivation of metals dates back to, at least, Michael Faraday, who was one of the first people to study the phenomena <u>and</u> provide a theoretical explanation of it. [285] His theory on this effect held sway up until, at least, the middle of this century. Briefly, Faraday espoused the idea that the passivating layer was composed of a thin oxide or film of oxygen.

So far we have examined the surface of gold from the point-of-view of the chemists, mainly the electrochemists. Another group interested in the surface interactions of gold are the surface physicists. These workers usually carry out their experiments under UHV (Ultra High Vacuum), and the metal samples they test are usually formed *in situ* by Joule evaporation, i.e., a sample of the metal is boiled and the resulting metal vapor is allowed to condense on a suitable substrate. The reason for working in a vacuum are to prevent inadvertent contamination of the newly created metal sample, the adsorbent, and to allow for precise control of the identity and quantity of the material to be adsorbed, the adsorbate. The *in situ* formation of the metal sample is done in the hope of creating a gas free metal sample. While this is a laudable goal, the subsequent experimental results will <u>only</u> be applicable to this exact type of film and its resulting surface, it will not answer the question of what occurs at a surface created by mechanically cleaving (machining), polishing, burnishing, etc. of a normal bulk sample of metal in room air. In addition, the film created by Joule evaporation is many times atypical, i.e., the crystal structure may be very

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[284] W.J. Müller, E. Löw; Passivity of Gold; Transactions of the Faraday Society; Vol. 31; 1935; pp. 1291-1299.

[285] The citations provided below are actually a series of letters between C.T. Schoenbein and Faraday.

C.T. Schoenbein, M. Faraday; On a peculiar Voltaic Condition of Iron, by Professor Schoenbein, of Bâle; in a Letter to Mr. Faraday: with further Experiments on the same Subject, by Mr. Faraday, communicated in a Letter to Mr. Phillips; Philosophical Magazine [and Journal of Science]; Vol. 9 (3rd Series); July-December 1836; pp. 53-65.

M. Faraday; Letter from Mr. Faraday to Mr. Brayley on some former Researches relative to the peculiar Voltaic Condition of Iron reobserved by Professor Schoenbein, supplementary to a Letter to Mr. Phillips, in the last Number; Philosophical Magazine [and Journal of Science]; Vol. 9 (3rd Series); July-December 1836; pp. 122-123. [By "…reobserved…" Faraday means that the original observation was made by a number of people before either Schoenbein or himself. In this letter Faraday thanked E.W. Brayley for jogging his memory as to the existence and identity of the work on passivation by earlier researchers. Among the earlier workers on passivation was the famous English astronomer Sir John Frederick William Herschel.]

C.T. Schoenbein; Remarks on Faraday's hypothesis with regard to the Causes of the Neutrality of Iron in Nitric Acid; Philosophical Magazine [and Journal of Science]; Vol. 10 (3rd Series); 1837; pp. 172-174.

M. Faraday; Note from Professor Faraday to Mr. Richard Taylor on the preceding Paper; Philosophical Magazine [and Journal of Science]; Vol. 10 (3rd Series); 1837; pp. 175-176.

different from the normal bulk metal due to the presence of a high density of imperfections. This problem is usually handled by annealing the deposited film at high temperatures, which essentially recrystallizes the film into a more normal bulk configuration. The adsorbates, usually gases, are likewise purified to as high a degree as is possible with the technology of the day. [286] This is also a laudable precaution, but the results garnered from the use of these ultra pure gases may tell us nothing about what happens in 'normal' room air with its mixture of gases, vapors and whatnots. Similarly, the adsorbents, the metals, employed are also of the highest possible purity and again this makes for good results, but it is not strictly applicable to a machined or physically worked or electrolytically etched metal part, which always suffers some contamination both at its surface and in its bulk. With all these caveats acknowledged, let us take a look at the results. According to Gerd Wedler, while platinum, palladium, rhodium and iridium all chemisorp oxygen, carbon monoxide and hydrogen, gold shows no sign of chemisorbing these three gases or nitrogen. [287]

Yet another group with an interest in the effects of gases on metals are the material technologists involved in electronic component fabrication. Consider the following situation. You are trying to sputter gold onto an oxide substrate, but find that the resulting film has poor adhesion. In a bid to improve the adhesion, you try mixing some oxygen in with the inert gas, e.g., argon, which is employed in the sputtering apparatus. The result of this ploy is better adhesion. [288] Given the conventional wisdom about the inability of gold to react directly with oxygen, why does the oxygen enhance the adhesion? Note, if the gold film on a oxide substrate prepared by the above procedure is later heated to 250°C in vacuum, it loses its adhesion; a film that has lost its adhesion from heating in a vacuum can gain some of it back if it is reheated in air. More than twenty years later, the behavior of gold sputtered in partial oxygen atmospheres is still being investigated. [289] This phenomenon of increased adhesion of gold in a partial oxygen atmosphere has also been observed for the case of melted gold on a fused silica surface. [290]

§4. PASSIVATION LAYERS ON NOBLE METALS, THE ALTERNATING CURRENT ELECTRICAL EFFECTS. - Having considered the evidence for the existence of a passivation layer on platinum and gold, I should now like to examine an RF detector, which presumably makes use of these layers.

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[286] Gerd Wedler; Chemisorption: An Experimental Approach; Butterworths; 1976; pp. 17-19.

[287] Ibid.; pp. 199-200.

[288] D.M. Mattox; Influence of Oxygen on the Adherence of Gold Films to Oxide Substrates; Journal of Applied Physics; Vol. 37; No. 9; August 1966; pp. 3613-3615.

[289] C.R. Aita; AuO^+ and AuO_2^+ gaseous ions formed during the sputter deposition of Au films in Ar-O_2 discharges; Journal of Applied Physics; Vol. 61; No. 11; June 1, 1987; pp. 5182-5184.

[290] D.C. Moore, H.R. Thornton; Effect of Oxygen on the Bonding of Gold to Fused Silica; Journal of Research, National Bureau of Standards; Vol. 62; 1959; pp. 127-135.

According to Sir John Ambrose Fleming, the electrolytic detector was invented independently and simultaneously around 1900 by Reginald A. Fessenden, Commandant Gustave Ferrié and W. Schlömilch. [291] This detector consisted of an electrolytic cell with a large platinum cathode and a very fine platinum wire anode, [292] whose depth in the electrolyte was adjusted via a micrometer screw. The depth of immersion of the fine wire anode depended on the diameter of the wire, the thinner the wire the deeper the permissible depth; the important point was to make sure that the anode surface area in contact with the electrolyte remained small. The micrometer screw and the painstaking depth adjustments could be dispensed with by the following ploy: encase the fine wire in glass, and then cut the glass tube so that the end of the wire is flush with the cut face of the tube; the glass enclosed wire could be lowered to any convenient depth, and would always have the same anode surface area in contact with the electrolyte. The electrolyte could be almost anything, but according to James E. Ives "…solutions of alkaline salts give the best results." [293] The method of connecting

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[291] [Sir] John Ambrose Fleming; The Principles of Electric Wave Telegraphy and Telephony; Longmans, Green and Co.; 1919; pp. 397-398.

Donald McNicol; Radio's Conquest of Space; Murray Hill Books, Inc.; 1946; pp. 112-119. [Besides Fessenden, Ferrié and Schlömilch there were other claimants to the title of 'Father of the electrolytic detector', including Frederick K. Vreeland and Lee de Forest. Vreeland's claim was eventually overturned in court in favor of Fessenden. de Forest gave his electrolytic detector the moniker 'responder'. It consisted of two metal electrodes spaced about 1/100 inch apart with the intervening space filled with a mixture of oil or glycerine, water, lead peroxide and metal powder. In contradistinction to the electrolytic detectors of Fessenden, Ferrié and Schlömilch, de Forest's detector responded to the presence of RF energy by increasing its resistance - it was, to pirate J. C. Bose's coherer terminology, a 'negative' electrolytic detector.

In checking out some references to electrolytic detectors in one of Angelika Székely's papers, I found that it was actually Michael I. Pupin in 1899 who first discovered this type of detector - he simply had not rushed off to patent the idea as Fessenden, Ferrié and Schlömilch would do later on. Pupin's priority in the matter of the electrolytic detector was vigorously championed by George Washington Pierce,

G.W. Pierce; The Electrolytic Detector, Studied with the Aid of an Oscillograph; Physical Review; Vol. 29 (1st Series); July-December 1909; pp. 56-70.

As proof of his contention, Pierce cited the following abstract of a talk given by Pupin to the American Physical Society,

Anon.; Electrical World and Engineer (New York); Vol. 34; No. 20; November 11, 1899; p. 743.]

[292] The extremely fine platinum wire was usually made via the Wollaston process, whereby an initially thicker platinum wire was coated with a layer of silver, then this composite wire was drawn down to the requisite diameter, and finally the silver coating was dissolved off. See,

W.H. Wollaston; A Method of drawing extremely fine Wires; Philosophical Transactions of the Royal Society; Vol. 103? (Part 1); 1813; pp. 114-118. [Wollaston measured the diameter of these wires by means of an optical comparator,

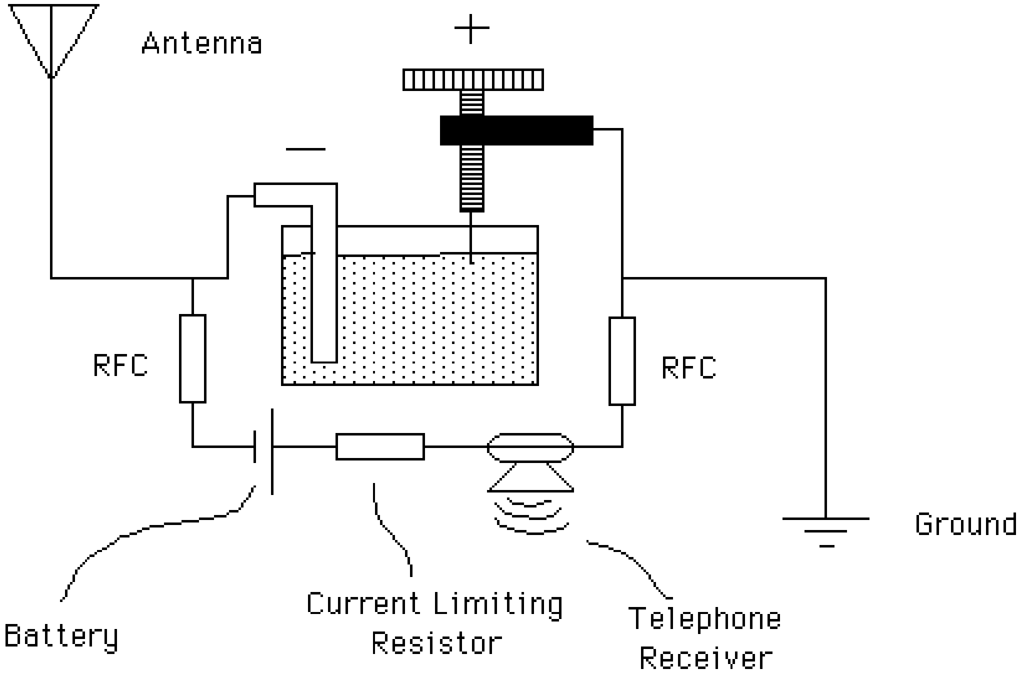
W.H. Wollaston; Description of a single-lens Micrometer; Philosophical Transactions of the Royal Society; Vol. 103? (Part 1); 1813; pp. 119-122.

Note, William Hyde Wollaston is perhaps less well known as the first person to publish an account of the dark lines found in the solar spectrum. These absorption lines were later attributed to Fraunhofer and, in fact, are known today as Fraunhofer lines.]

[293] J.E. Ives; An Electrolytic Wireless Telegraph Detector; Electrical World and Engineer (New York); Vol. 44; No. 24; December 10, 1904; pp. 995-997. [**Warning**, this article has a number of dangling and incomplete sentences and other types of discontinuous word structures,

this electrolytic detector in the receiving circuit was identical to that used with the coherer (see Fig. B1), the only caveat being that the fine wire must be the anode (connected to the positive side of the battery). Like the coherer, the electrolytic detector indicated the presence of a CW signal by lowering its DC resistance, but unlike some coherers it was self-restoring, i.e., it recovered its initial high resistance upon termination of the RF signal.

FIGURE B1 – The Electrolytic Detector and Circuitry



According to one of the earlier radio pioneers, S. M. Kintner, the electrolytic detector was "…far more sensitive and reliable than any other known type. This detector was the standard of sensitivity for years, in fact until it was displaced by the vacuum tube about 1913." In fact, according to W. Rupert Maclaurin, the U.S. Navy utilized these type of detectors in its fleet from 1908 to

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which make it unintelligible in places. There must have been some problem during proof reading or at the printer. A reasonably detailed summary of Ives' results, minus the typos, can be found in the following article and conference paper,

L. de Forest; Electrolytic Receivers in Wireless Telegraphy; The Electrician (London); Vol. 54; November 4, 1904; pp. 94-98.

L. de Forest; Electrolytic Receivers in Wireless Telegraphy; in A.E. Kennelly, W.D. Weaver; Transactions of the International Electrical Congress, St. Louis, 1904, Vol. 3; J.B. Lyon, Co.; 1905; pp. 578-601.]

1913.[294] When I related this last fact to my thesis advisor, Dr. Sullivan, he wondered how electrolytic detectors, such as that shown in Fig. B1, could be operated on the heaving, tossing and rolling deck of a warship? My answer was that the shipboard electrolytic detectors probably used an anode where the fine wire was first encased in glass and then this arrangement was broken off clean so that only very end of the wire was exposed. In this way, the anode could be dipped well under the surface of the electrolyte, and hence be immune to any sloshing of the surrounding fluid. My rather facile answer turned out to have only a small grain of truth to it. According to a 1926 book by retired U.S. Navy Lieutenant-Commander Ellery W. Stone,

> While this [electrolytic] detector was the most sensitive one in use at the time of its greatest popularity - about 1906 to 1910 - it had the disadvantage of being unsuited for work aboard ship on account of jarring imparted to the cup and the acid which it contained. In addition, it had to be frequently adjusted to keep just the point of the wire in contact with the electrolyte - in order to compensate for its evaporation, and it was easily burned out by signals from near-by stations. An attempt was made by the Massie Wireless Telegraph Company - an American concern operating on the Marconi patents - to obviate these difficulties by sealing the Wollaston wire in a glass tube which could be immersed to any depth in the solution. This procedure, however, resulted in a diminution of the sensitivity of the instrument.[295]

Stone's account appeared to me to be more reliable than those of Kintner and Maclaurin mainly because he goes into much more operational detail of the use of such detectors, which made me believe him to have had firsthand experience with them.

The passivation layer enters into the picture in terms of the possible choices of the metal used to construct the anode. Only metals which are chemically inert can be utilized for the anode of the electrolytic detector. What this means in plain English is that the anode must <u>not</u> go into solution when it is biased. Since oxidation occurs at the anode, there are two possible reactions that can take place: 1) the anode itself could be oxidized and go into solution, this is what would happen if iron was used; and 2) the water could break down with oxygen being evolved at the anode, this is the situation when platinum is used for the anode. Besides platinum, the anode had also been constructed of carbon

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[294] S.M. Kintner; Pittsburgh's Contribution to Radio; Proceedings of the IRE; Vol. 20; No. 12; December 1932; pp. 1849-1862.

W. Rupert Maclaurin; <u>Invention and Innovation in the Radio Industry</u>; Arno Press and The New York Times; 1971; pp. 60-61.

[295] Ellery W. Stone; <u>Elements of Radio Communication</u>; D. Van Nostrand Co.; 1926; pp. 299-302. [Stone's account of the operational procedures used with the electrolytic detector were corroborated by another book by a fellow navy man,

S.S. Robison; <u>Manual of Wireless Telegraphy for the use of Naval Electricians</u>; Government Printing Office; 1906; pp. 88-89.]

and aluminum, and in view of the need for the metal to possess a passivation layer, gold should also work.

§5. THE INITIAL ERRONEOUS ATTEMPTS AT EXPLAINING ELECTROLYTIC DETECTOR BEHAVIOR. - As was the case with the coherer, there were many theories of how the electrolytic detector functioned. The two top contenders were the polarization or electrolytic theory and the thermal theory. There were many variants of the polarization theory, and I shall not go into them here except to say that most posited the existence of some sort of blocking layer at the anode, which was temporarily dissolved or thinned upon application of RF energy. The thermal theory was based on the assumption of the electrolyte's resistance having a negative temperature coefficient, i.e., the RF energy would preferentially heat the electrolyte in the vicinity of the small anode, due to the high current density created by the minuscule surface area of the electrode, and the resistance of this portion of the electrolyte would drop creating a lower DC resistance.

James E. Ives performed an extensive set of experiments on the electrolytic detector, which showed that the thermal mechanism was not correct.[296] Ives presented a list of eight observations, performed on a platinum electrode electrolytic cell, which he believed refuted the claims for a thermal mechanism,

> 1) The device was not reversible with respect to the DC bias voltage, as it ought to have been if it depended for its effect solely on heating. With the fine platinum wire acting as the cathode, the detector responded to the same RF energy very faintly.
>
> 2) The fine wire anode had to be made of a metal or other conducting material which did not go into solution as a result of the oxidation taking place at the anode. Ives was implying here that a thermal effect should not depend of the chemical stability of the anode material, but this point was not all together persuasive.
>
> 3) The DC resistance of the electrolytic cell was much higher than could be accounted for in terms of the resistivity of the electrolyte unless there was some type of passivation/blocking/polarizing layer present.

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[296] Ibid.

4) The sensitivity of the detector depended on the area of the anode and not upon its shape. What this proved in terms of the two competing theories, Ives did not say.

5) Ives claimed that from field experience, the detector appeared to be a voltage operated device, and not a current operated device as one would have expected of a thermally actuated detector.

6) The detector was found to operate satisfactorily and normally even if the electrolyte was boiling. Ives contended that if the device operated via the thermal mechanism, the heat produced near the anode would have caused vapor bubbles to form at this electrode, which would then have blocked the flow of DC current instead of enhancing its flow.

7) By employing a 2-1/2% solution of hypophosphorous acid (H_3PO_2), which had a zero temperature coefficient of resistance at 60°C, a negative coefficient below 60°C and a positive one above 60°C, and operating the detector over a suitable temperature range, Ives was able to show that the temperature coefficient of resistance of the electrolyte played no significant part in its operation. This experiment unequivocally proved that the thermal mechanism based on the negative temperature coefficient of resistance of the electrolyte was incorrect. [297]

8) Electrochemists have long known that using clean platinum electrodes for measuring the specific conductance of electrolytic solutions could introduce artifacts due to polarization and other irreversible effects at the electrode surface. However, platinum electrodes could be made to act reversibly by first coating them with a thin layer of platinum black. It is not obvious to me why it is that platinum electrodes covered in platinum black act reversibly, and what is more I am not sure that electrochemists know,

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[297] I have not been able to confirm the behavior of the temperature coefficient of resistivity of hypophosphorous acid over the range of temperatures employed by Ives. The one reference I did consult did not provide sufficient information,

Edward W. Washburn (Ed.); International Critical Tables of Numerical Data, Physics, Chemistry and Technology, Vol. 6; McGraw-Hill Book Co., Inc.; 1929; p. 260.

> themselves. Nevertheless, after Ives coated the anode of his electrolytic detector with platinum black, which should not have affected the I^2R heating of the electrolyte, he found that the detector ceased to function. This, together with the previous experiment, formed the best evidence that the electrolytic detector did <u>not</u> function thermally.

A variant of the electrolytic detector was also used as an electrolytic capacitor. In 1902, Augustus Trowbridge was involved with Atlantic submarine telegraphy and wanted to build a table top model of the undersea line complete with a sending and receiving station at either end. The circuit he utilized to mimic the electrical behavior of the 1500 mile cable consisted of four RC networks in tandem. The problem was the large value needed for the capacitors; capacitors of many microfarads were very expensive and hard to obtain. Trowbridge remembered that he had read that Cromwell Fleetwood Varley had built (circa 1866-1869) a model submarine telegraph cable and employed electrolytic capacitors. The electrolytic capacitors constructed by Trowbridge closely resembled the configuration used in the electrolytic detector. Specifically, it consisted of a thin platinum wire dipping into a tube of distilled water and a sheet of platinum foil as the counterelectrode; the wire being the anode and the platinum foil the cathode. Provided that the impressed DC voltage was below the "…maximum polarization of the cell…", which it would be if the sending station (end of the cable with the telegraph key) used only a single Daniell or Leclanché cell, these electrolytic capacitors - condensers, in the parlance of the time - worked fine. With these capacitors, Trowbridge's 'cable' produced a time delay of about six seconds. [298]

Why did it work, and how might it relate to the functioning of the electrolytic detector? Varley's explanation, which I cannot improve upon, was that one or both electrodes had an exceedingly thin layer of dielectric at its surface, which served to separate the two conducting regions (e.g., the electrolyte and one of the electrodes) and thus formed a capacitor. Varley even went so far as to

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[298] A. Trowbridge; Electrolytic Condensers; Physical Review; Vol. 12; June 1901; pp. 359-362. [The proscription about keeping the applied voltage below the "…maximum polarization of the cell…" meant preventing the applied voltage from being greater than ~1.7 V. Below this voltage, the cells functioned adequately as high value capacitors (100s of µFs per cell). **Warning**, the citation to C.F. Varley's paper, in the *Philosophical Transactions*, in which he documents his measurements of his electrolytic capacitors, was incorrect. It should read,

C.F. Varley; Polarization of Metallic Surfaces in Aqueous Solutions. On a new Method of obtaining Electricity from Mechanical Force, and certain relations between Electrostatic Induction and the Decomposition of Water; Philosophical Transactions of the Royal Society (London); Vol. 161; 1871; pp. 129-136 + Plate II.

In addition, the complete citation to C.F. Varley's other paper should read,

C.F. Varley; On the Atlantic Telegraph; Notices of the Proceedings at the Meetings of the Members of the Royal Institution of Great Britain; Vol. 5; 1866-1869 (February 8, 1867); pp. 45-59.]

calculate the thickness of this dielectric, based on the assumption that it was composed of gas. The answer he got was 1/1,274,000,000 inch [0.2 Å] @ 0.2 V; at higher voltages (~1.6 V) the capacitance increased, which required, according to his model, that the thickness decreased to 2/7 of its value at the lower voltages. If we roundup the dielectric thickness to the nearest whole number, i.e., allow it to be 1 Å, then the layer appears to be composed of a monolayer of gas atoms. As we shall see in the next paragraph, this estimate is in agreement with modern observations.

In 1958, P. Kisliuk of Bell Labs attempted to ascertain the thickness of the most tenacious film of gas on a metal by observing the effect of this gas layer on the transition or crossing resistance in a crossed wire contact junction. [299] Specifically, Kisliuk used mechanically polished wires of either molybdenum or tungsten. The use of these refractory metals allowed them to be heated in a vacuum by passing a current through and thus cleaned. After the wires were heat cleaned in a vacuum, they were then exposed to either oxygen or nitrogen for a fixed length of time, they were then pressed together, crosswise, with a known force, and finally the resistance of this contact junction was measured. The most surprising result of this investigation was that it indicated that the gas layer affecting the electrical resistance of the contact junction was only 1.5 - 2.6 Å thick, i.e., one or two atomic diameters - not all that different from Varley's much earlier estimation. Implicit in Kisliuk's calculation of the thickness of the gas coverage was the assumption that the heat cleaning in a vacuum removed all foreign substances and influences from the surface of the metals. If this assumption was not, in fact, true then the calculation of the gas coverage might have been seriously flawed. For example, the wires used in this experiment "…consisted essentially of two mechanically polished crossed wires…". This polishing most certainly Beilbyized the surface of the wires and so influenced the electrical and mechanical properties of these wires (see APPENDIX D). Kisliuk got the idea for this series of experiments not from the work of Cromwell Fleetwood Varley, but rather from the crossed wire experiments of Ragnar Holm and Karl Wilheim Meissner (circa 1930), see APPENDIX E for a more detailed description of these experiments.

As a postscript to the above discussion, I should like to mention some research I uncovered just as I was about to achieve closure on this thesis. In 1924, William George Palmer, who was a chemist by training, decided to investigate the influence of different gases on the critical voltage of the coherer. What he found was that the value of the critical voltage was a strong function of the surrounding gas. As a result of the surprising repeatability of the critical voltage values versus the type of gas surrounding the coherer junction, Palmer felt confident that the coherer critical voltage could be used to investigate the phenomenon of adsorption of gases onto surfaces.

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[299] P. Kisliuk; Using Contact Resistance to Measure Adsorption of Gases on Metals; Bell System Technical Journal; Vol. 37; July 1958; pp. 925-949.

This adsorption process had been studied previously, but the usual method of ascertaining the presence of the gas was by weighing a fixed amount of finely divided metal before and after its exposure to the gas in question, i.e., the so-called gravimetric method. The main problem with this traditional approach was the rather large uncertainty in determining the surface area of the finely divided metal. Using a piece of metal foil of 'known' surface area was not the solution either because the smaller surface area of the foil required an enormous increase in the sensitivity of the weighing procedure. The foil technique assumed, of course, that the so-called 'known' surface area was really a 'known', which was a highly unlikely proposition given the roughness of most real surfaces on an atomic scale. Palmer made mention of a number of other shortcomings of the previously applied methodologies, which I shall not enumerate here.

Using his adaptation of the coherer, Palmer was able to show a correlation between the electrical energy required to cohere the junction in the presence of a specific gas and the known heat of liquefaction of that same gas. The electrical energy, W, needed to cohere the junction was calculated assuming the junction to be a capacitor whose dielectric was the gas, i.e., $W = (1/2)CV_c^2$ where V_c was the critical voltage and C was the capacitance of the coherer junction. [300] After having established the validity and repeatability of this procedure, Palmer next applied it to studying the equilibria of binary mixtures of gases condensed on the surfaces of the coherer junction. [301] Using a "…homologous series of primary alcohols, fatty acids and their ethyl esters…", Palmer demonstrated that the critical voltage increased as the length, L, of the hydrocarbon chain increased. In a homologous series (e.g., methyl, ethyl, n-propyl, and n-butyl alcohols), the functional group (in this case the CH_2OH or alcohol functional group) is always the same, but the length of the hydrocarbon chain attached to it increases in length as one progresses along the series. In addition, he showed that V_c^2/L = constant from which he deduced that the energy (heat) of desorption was proportional to the square of the electrical moment of the adsorbed molecule. [302] Finally, Palmer used his coherer technique to confirm the Langmuir isotherms for adsorbed species. [303]

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[300] W.G. Palmer; The Use of the Coherer to Investigate Adsorption Films; Proceedings of the Royal Society (London); Vol. 106 (Series A); 1924; pp. 55-68.

[301] Idem; The Adsorptive Equilibrium of Binary Gaseous Mixtures; Proceedings of the Royal Society (London); Vol. 110 (Series A); 1926; pp. 133-141.

[302] Idem; An Experimental Test of the Dipole Theory of Adsorption; Proceedings of the Royal Society (London); Vol. 115 (Series A); 1927; pp. 227-236.

[303] Idem; Some Adsorption Isothermals for a Plane Platinum Surface; Proceedings of the Royal Society (London); Vol. 122 (Series A); 1929; pp. 487-497.

§6. TOWARDS A BETTER UNDERSTANDING OF THE BEHAVIOR OF ELECTROLYTIC DETECTORS. - At the time I read the paper by James Ives, on his attempt at elucidating the mechanism behind electrolytic detectors, it seemed eminently reasonable to me. The only problem was that it was, in fact, incorrect in some of its assertions and incomplete in others. In 1919, a Moravian/Austrian experimental physicist named Angelika Maria Josefa Székely (de Doba) investigated the sensitivity of electrolytic detectors as a function of their DC bias. Specifically, she examined the Schlömilch and Jégou forms of electrolytic detectors; the Schlömilch electrolytic detector was the detector investigated by James E. Ives. [304] It turns out that even though these detectors were discovered around 1899, their behavior and properties were not characterized in any comprehensive fashion until at least 1919. This becomes clear from both Székely's paper and the references contained therein. Let me begin with a synopsis of one of the papers cited by Székely in her introduction.

In an article published in 1906, L. W. Austin of the National Bureau of Standards decided to reinvestigate the characteristics of the electrolytic detector. [305] His decision was based partially on the amount of contradictory evidence about their behavior that had accumulated since their discovery at the turn of the century. In particular, there was the controversy about whether or not the pointed platinum electrode should be positive or negative. W. Schlömilch and Lee De Forrest stated that the detector was only sensitive to radio waves when the pointed electrode was positive (anode); R. A. Fessenden and V. Rothmund & A. Lessing's acclamation was that the polarity was immaterial.

Using an electrolytic detector composed of a large platinum electrode (2 cm^2) and a fine platinum wire sealed in glass and broken off at the end to expose the very end of the wire, Austin performed two major tests of the polarity sensitivity, one at 60 Hz and the other at normal AM radio frequencies. In the course of the low frequency AC measurement, a number of different electrolytes were employed: sulfuric acid (30%), hydrochloric acid (50%), nitric acid (20%) and potassium hydroxide (50%). The AC sensitivity of this detector was measured by using a galvanometer to observe the increase or decrease in the DC current going through the detector upon its exposure to either low frequency alternating currents or radio frequency currents; the change in the DC current was relative, of course, to the leakage current that normally flowed through the biased detector in the absence of any low frequency alternating or radio

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[304] A. Székely; Beobachtungen an elecktrolytischen Detektoren [Observations on Electrolytic Detectors]; Akademie der Wissenschaften in Wien Mathematisch-naturwissenschaftliche Klasse, Sitzungsberichte [Academy of Science in Vienna, Mathematical-Natural Science Division, Proceedings]; Vol. 128; Pt. 2a; 1919; pp. 1377-1400. [**Warning**, I was unable to locate this article in the author index of the Science Abstracts, Series A even though I was able to locate all her other articles by this means.]

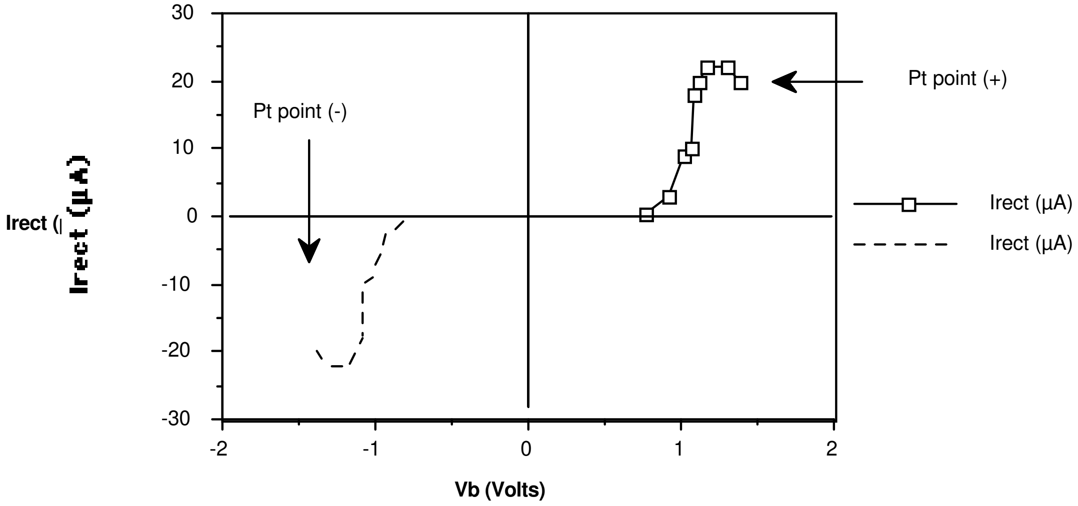
[305] L.W. Austin; On the platinum point electrolytic detector for electric waves.; Bulletin of the Bureau of Standards; Vol. 2; No. 2; 1906; pp. 261-274.

frequency currents. The results, while slightly mixed, supported the contention that the sensitivity was polarity insensitive. With DC bias (polarizing) voltage set to 1.4 V, the 60 Hz sensitivity was essentially independent of the direction of the voltage for all electrolytes tried; the sensitivity, as a function of the DC bias (polarizing) voltage, increased with increasing bias up until about 1 V where it plateaued. Once in a while, Austin would find that the 60 Hz sensitivity would actually decrease when the pointed electrode was negative, but according to him: "This effect appears only occasionally and is less regular than the more common increase in current."

The tests at radio frequencies were done using a commercially made electrolytic detector consisting of a small platinum thimble and a fine platinum wire dipping into the electrolyte contained in the thimble. There were two different sources of radio waves: 1) a table top spark transmitter utilizing a spark coil able to produce a 1 mm long spark in air, provided with two 50 cm long aerials and situated approximately 20 ft from the detector, which did not have any aerials; and 2) a commercial radio station run by the National Electric Signaling Company located some 6 miles away with the detector connected to an external aerial. The results were puzzling, because they differed depending on the radio frequency source. With the table top transmitter, the sensitivity depended on the polarity of the DC bias with the fine platinum wire as anode being far and away the most sensitive configuration. In the case of the commercial radio station, the sensitivity was independent of the direction of the DC bias voltage. The author could give no satisfactory explanation for this discrepancy.

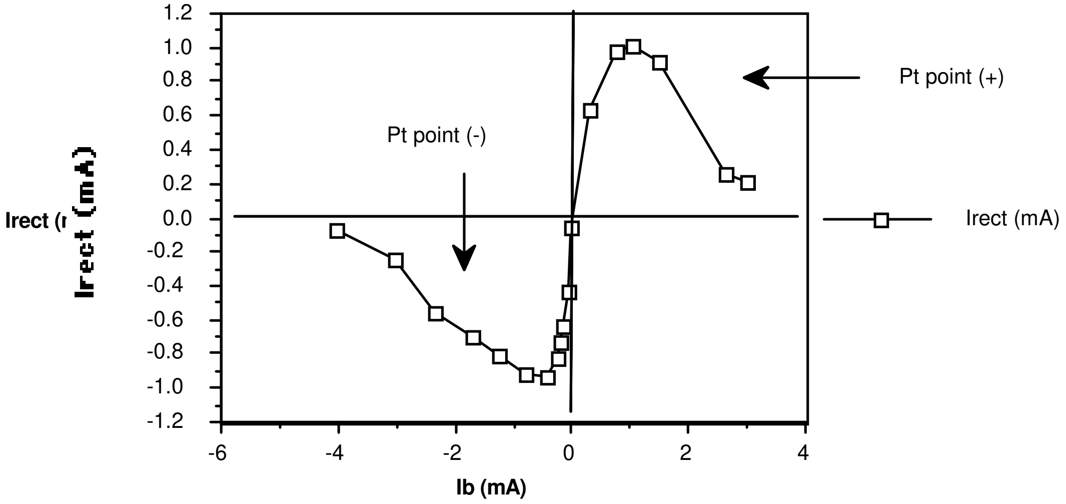
In his 1906 paper, Austin also measured the dependence of the low frequency AC (60 Hz) sensitivity on the DC bias voltage; the electrolytic detector consisted of a fine platinum wire and a large flat platinum plate in a 20% aqueous solution of nitric acid (HNO_3). His results, depicted in Fig. B2, showed that the sensitivity peaked around 1.24 V. Note, these measurements were done with the fine platinum wire being the anode (+). The dotted portion of the sensitivity versus DC bias curve corresponds to what we would expect if Austin had also made measurements with the platinum wire being the cathode (-), because of his discovery that the sensitivity was independent of the bias polarity.

FIGURE B2 - Austin's Rectified Current vs. DC Bias Voltage Plot;
Schlsmilch Detector: Pt-solu.-Pt, solu. = 20% nitric acid, 60Hz AC signal.



In 1919, Angelika Székely decided to revisit the subject of electrolytic detectors. In particular, she wished to settle once-and-for-all the question of whether or not the RF sensitivity of such detectors was dependent on the direction (polarity) of the DC bias. Fig. B3 is a plot of her data for a Schlömilch electrolytic detector similar to the one used by Austin in 1906. Within experimental error it appeared that the detector's RF sensitivity was independent of the bias polarity. In fact, the curve was an odd function (antisymmetric) - almost - of the bias, and had no zero offset, i.e., it passed through the origin.

FIGURE B3 - Sz_kely's Rectified Current vs. DC Bias Current Plot;
Schlsmilch Detector: Pt-solu.-Pt, solu. = dilute sulfuric acid.



The Schlömilch detector was an example of a symmetric - in terms of its electrode materials - type of detector. [306] Székely also examined an electrolytic detector invented by Paul Jégou, which was asymmetric with respect to its electrode materials. [307] The Jégou detector consisted of fine platinum wire just touching the surface of a concentrated sulfuric acid solution with a zinc amalgam [308] counterelectrode at the bottom of the vessel containing the acid. Because of the dissimilar electrode materials, the Jégou detector acted as its own source of EMF. One might logically expect that this type of detector would have a sensitivity curve that was an odd function, but shifted to the left or right along the bias axis, i.e., the curve would not go through the origin. This expectations is indeed satisfied as is demonstrated by Fig. B4.

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[306] Anon.; A New Detector for Hertzian Waves; The Electrician (London); Vol. 52; December 4, 1903; p. 250.

[307] P. Jégou; Dispositif pour l'étude de la sensibilité des détecteurs électrolytiques. [Apparatus for the study of the sensitivity of electrolytic detectors.]; Comptes Rendus Hebdomadaries des Seances de l'Academie des Sciences (Paris); Vol. 146; 1908; pp. 1256-1258. [**Warning**, this article does not describe Jégou's version of the electrolytic detector. It only concerns itself with the circuitry used to check the sensitivity of these types of detectors.]

Idem; Elektrolytischer Detektor ohne elektromotorische Hilfskraft. [Electrolytic Detector without an Auxiliary Voltage Source.]; Jahrbuch der drahtlosen Telegraphie und Telephphonie [Year Book of Wireless Telegraphy and Telephony]; Vol. 7; 1913; pp. 458-461. [**Note**, in her bibliography (p.1378) of her 1919 paper on electrolytic detectors, Székely erroneously referred to this journal as the Jahrb f. drahtl. Tel. u. Teleph. (Jahrbuch für drahtlosen Telegraphie und Telephphonie). This error was probably a misprint, since in her 1918 paper on contact detectors she does cite the proper title of the journal. This journal's title has undergone a number of name changes in the years since its founding in 1907: 1) Jahrbuch der drahtlosen Telegraphie und Telephphonie, 2) Zeitschrift für Hochfrequenztechnik (?), and 3) Hochfrequenztechnik und Elektroakustik. **Warning**, Fig. 1 of this article gave the erroneous impression that the fine platinum wire was continuous from the anode to the cathode.

Perusal of this article revealed that Paul Jégou had published articles on his modification of the electrolytic detector in the French journal, *Comptes Rendus Hebdomadaries des Seances de l'Academie des Sciences (Paris)*, which was both easier to find and to translate - especially for the neophyte translator. By backwards daisy chaining through these articles, the following French references were uncovered,

P. Jégou; Détecteur électrolytique très sensible fonctionnant sans force électromotrice auxiliarie. [Very sensitive electrolytic detector operating without an externally applied DC bias voltage.]; Comptes Rendus Hebdomadaries des Seances de l'Academie des Sciences (Paris); Vol. 150; May 23, 1910; pp. 1307-1308.

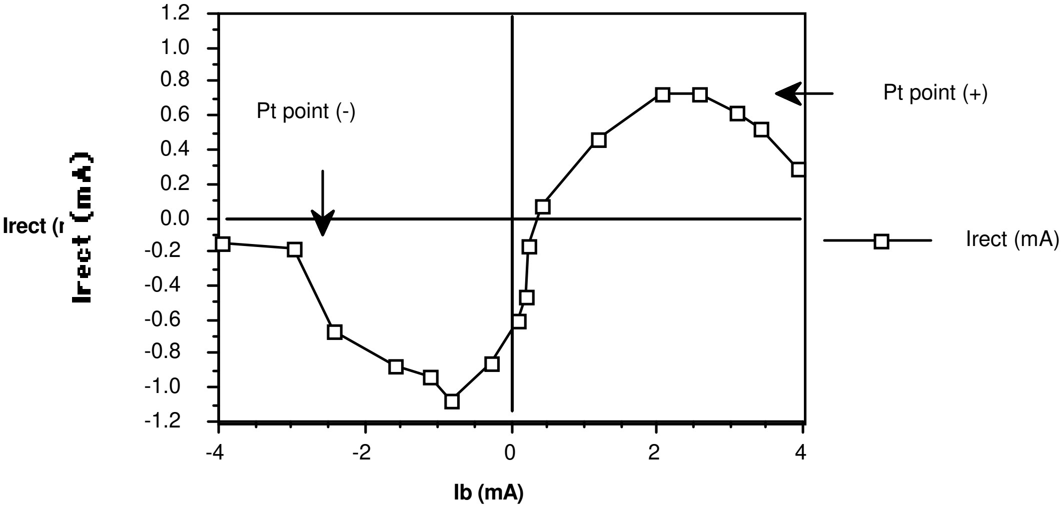
Idem; Phénomènes mis en jeu dans le détecteur électrolytique sans force électromotrice auxiliaire et considération théorique sur le fonctionnement das détecteurs électrolytiques. [Phenomena brought into play in the electrolytic detector without an auxiliary voltage source and theoretical considerations on the functioning electrolytic detectors.]; Comptes Rendus Hebdomadaries des Seances de l'Academie des Sciences (Paris); Vol. 156; February 3, 1913; pp. 385-386.

By chance, I also came across an English language description of Jégou's detector,

Anon.; A Sensitive Electrolytic Detector Without Auxiliary Electromotive Force; The Electrical Review (London); Vol. 67; No. 1,705; July 29, 1910; pp. 170-171.]

[308] An amalgam is made by dissolving a metal - in this case zinc - in mercury. The resulting alloy can have very interesting mechanical and electrical properties.

FIGURE B4 - Sz_kely's Rectified Current vs. DC Bias Current Plot;
J_gou detector: Pt-solu.-Zn/Hg, solu. = conc. sulfuric acid.



Székely appeared to be the first person to have undertaken a detailed examination of the RF sensitivity of electrolytic detectors to their DC bias. During the course of some earlier work on point contact detectors, Székely came to the conclusion that these apparently dry detectors actually functioned as small electrochemical cells due to the inevitable presence of water at the contact surface due to the humidity in the air.[309] She then wondered if these contact detectors would exhibit the same RF sensitivity curves as the wet (electrolytic) detectors? To this end, she ran a galena-graphite contact detector through the same sensitivity testing as the electrolytic detectors, and found the same type of curve (see Fig. B5).

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[309] A. Székely de Doba; Die Kontaktdetektoren [Point Contact Detectors]; Akademie der Wissenschaften in Wien Mathematisch-naturwissenschaftliche Klasse, Sitzungsberichte; Vol. 127; Pt. 2a; No. 6; 1918; pp. 719-792.

FIGURE B5 - Sz_kely's Rectified Current vs. DC Bias Current Plot;
MOM detector: PbS-C(graphite).

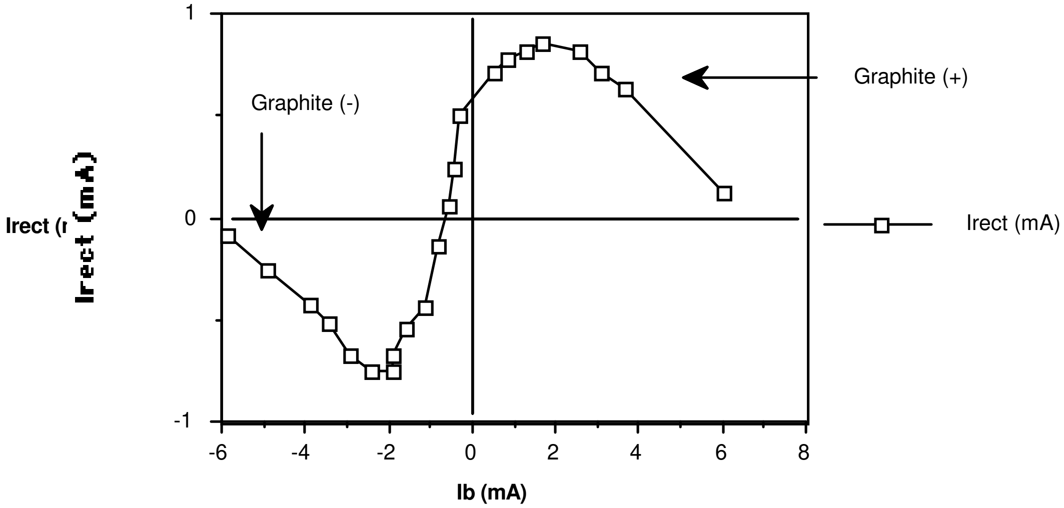

Fig. B5 points out the fact that the electrolytic detector and the MOS & MOM detectors have the same sensitivity curve. We know, from the 1973 work of Faris *et al.*, that MOM detectors undergo polarity reversal, i.e., at sufficiently high values of the DC bias, in either direction, the rectified current, instead of going in the same direction as the DC bias current, proceeds to increase in the opposite direction. All of Székely's sensitivity curves for electrolytic detectors hint at the possibility of polarity reversal, but they all terminate just before the point at which the DC bias forces the rectified current back to zero. It would be illuminating to redo Székely's sensitivity curves for electrolytic detectors with DC biases (+ & -) large enough to unequivocally to prove the existence or nonexistence of polarity reversals in these type of detectors.

Before continuing, I wish to put in my bid for the first person to have seen the phenomenon of AC modulation of DC conductivity. During the course of researching the life and work of Augustus Matthiessen, I stumbled across a recent article which discussed the origins of the standard of resistance that we call today the ohm. [310] This article mentioned that during the process of experimentally verifying Ohm's law, the researchers, charged with this duty by the British Association, had to be wary of two artifacts, both of which had been discovered by Arthur Schuster. The first artifact was the so-called unilateral conductivity (rectification), which Schuster discovered could occur at the mechanical junction between two copper wires. Today we know, of course, that this effect was due to the presence of a surface layer of cuprous oxide in intimate contact with the underlying copper, thus forming a copper oxide rectifier. The second artifact, which is the one relevant to our discussion of the electrolytic detector, was unearthed by Schuster during his sleuthing of the unilateral

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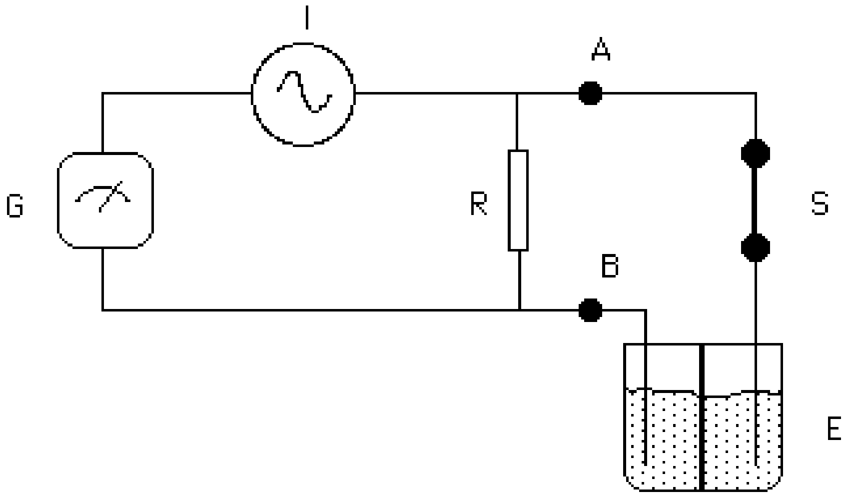
[310] P.J. Davies, J.O. Marsh; Ohm's law and the Schuster effect; IEE Proceedings; Vol. 132 (Part A); No. 8; December 1985; pp. 525-532.

conductivity effect and in it, Schuster found evidence that a superimposed AC current or voltage affects the DC conductivity of a circuit.[311]

Perhaps the best way to appreciate the second artifact is to consider the experiment employed by Schuster to detect it, see Fig. B6. G was a galvanometer; I was an AC generator (actually an air powered siren, modified to act as an AC generator by the addition of a rotating permanent magnet and a stationary coil); R was a variable resistance, whose resistance was always much less than that of the galvanometer; E was a Daniell cell, used to provide the DC current; and S was a switch, used to switch the Daniell cell into and out of the circuit. Note, Schuster took pains to make sure that the various components of his circuit were connected together in such a way as to obviate the possibility of unilateral conduction taking place.

FIGURE B6 - Schuster's Apparatus for Testing the Influence of AC Current on the DC Electrical Conductivity



The experiment consisted of measuring the galvanometer deflection due to the same DC current in the absence and then in the presence of a superimposed AC current:

1) With the siren stationary (no AC current) and switch S closed, the deflection of the galvanometer was measured. This constituted the measurement in the absence of the AC current.
2) Switch S was then opened, the siren started up and allowed to attain a steady pitch (rotational speed). Once the siren had achieved a steady speed, the

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[311] A. Schuster; Experiments on Electrical Vibrations; Philosophical Magazine [and Journal of Science]; Vol. 48 (4th Series); 1874; pp. 340-350.

> galvanometer returned to it rest position - the galvanometer being unable to sense the presence of a steady AC current. Switch S was then closed, and the galvanometer reading was noted. This constituted the measurement in the presence of the AC current.

The results of the aforementioned procedure were that the galvanometer deflection was always larger in the presence of the superimposed AC current. By varying R and repeating steps 1 & 2, Schuster was able to show that the increased deflection in the presence of AC current was proportional, within experimental error, to the magnitude of the DC current going through R. Note, since R was small compared to the galvanometer resistance, changing R did not significantly change the strength of the AC current.

Schuster's 1874 experimental setup, as depicted in Fig. B6, resembled the Jégou detector setup investigated by Székely in 1919. In Schuster's apparatus the Jégou cell was replaced by the Daniell cell, and the RF source by a low frequency AC generator - estimated by Davies and Marsh to produce a 50 Hz signal. The objection might be raised that while the Jégou cell had the expected electrode configuration for an electrolytic detector, i.e., one very small and one large electrode, the Daniell cell would not have been configured this way. This objection is specious, though, since the Schuster cell was used for detecting low frequency AC signals, which do <u>not</u> require the use of a fine wire anode.

§7. NOISE IN ELECTROLYTIC DETECTORS. - Electrolytic detectors structurally resemble single contact coherers: two conducting bodies, with either one or both having a very thin nonconducting surface layer, in mechanical contact. Note, the term 'mechanical contact' implies that the contact or interface between the two conducting bodies is <u>not</u> intimate. An example of an intimate contact or interface can be found in the copper oxide rectifier. Here, the rectifying junction occurs at the copper-cuprous oxide interface. This copper-cuprous oxide interface can be characterized as 'intimate' since the cuprous oxide is grown directly out of the underlying copper (sometimes called the 'mother copper') by taking a clean copper plate and heating it in air or oxygen to form the oxide layer. Flexing of the resulting copper-cuprous oxide interface progressively destroys its rectifying properties and, hence, denigrates its nature from intimate to mechanical. One of the electrical properties of mechanical junctions is that they produce excess, a.k.a. 1/f, noise when current flows through them. If the interface in electrolytic detectors is indeed mechanical in nature, then one would expect that these detectors would generate excess noise during normal operation. Electrolytic detectors were, in fact, known to produce noise during their operation, but the exact nature of this noise was not quantified,

> … Across the battery is shunted a variable resistance, termed a potentiometer, for varying the potential across the detector so as to keep it at a state of polarization just below the break-down

> voltage. It will be seen that when the slider of the potentiometer is at the point A, the full voltage will be impressed upon the detector, when at the point B, there will be no potential, and when at the half-way position C, the voltage will be one half that of the battery. This device thus serves as a convenient method for obtaining very minute variations in the detector potential. In operation, the slider is started at B and moved along the potentiometer until a **hissing noise** [emphasis added] is heard in the receivers. This indicates that the polarization of the detector is being broken down. The voltage is accordingly reduced until this noise ceases, in which adjustment the detector is most sensitive. [312]

From Stone's description, it appears that the electrolytic detector does produce excess or 1/f noise, since a characteristic of this type of noise is that it increases with increasing DC bias current. Thus measuring and characterizing the noise in electrolytic detectors may give some insight into the nature of the electrolyte-metal interface. While we are at it, it might prove revealing to examine the noise from another liquid-solid interface detector, the Walter detector, which consists of a tantalum wire dipped into a pool of mercury.

In an attempt to see if anyone had already looked at the production of 1/f noise in electrolytic cells, I consulted a number of bibliographies and books on the subject of noise. [313] However, I did not find any explicit mention of noise in electrochemical cells.

§8. UNEXPECTED INTERFACIAL PHENOMENA. - The site of the electrolytic detectors workings appears to be the surface of the smaller of the two electrodes. The electrical processes at the metal-solution (aqueous) interface, in general, are not understood. In fact, the same thing can be said regarding any interface. In the bulk solution, electrical conduction is ionic in character, while in the bulk metal electrodes, conduction is electronic in nature. The question arises at the interface of these two phases. How are the charges on the solvated ions transferred to the conduction electrodes of the metal electrode, and vice versa? One possible mechanism is, of course, electron tunneling. Whether this electron tunneling is elastic (lossless) or inelastic (lossy) is another question. Note, elastic electron tunneling is only lossless if we consider the electron scattering off of entities much more massive than it, i.e., atoms or molecules, but it will be lossy if the electron elastically scatters off another electron - a low probability event.

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[312] Ellery W. Stone; Elements of Radio Communication; D. Van Nostrand Co.; 1926; pp. 301-302. [See also,

S.S. Robison; Manual of Wireless Telegraphy for the use of Naval Electricians; Government Printing Office; 1906; pp. 88-89.]

[313] Aldert van der Ziel; Noise; Prentice-Hall, Inc.; 1954.

P.L. Chessin; A Bibliography on Noise; IRE Transactions on Information Theory; Vol. IT-1; September 1955; pp. 15-27.

A. van der Ziel; Flicker Noise in Electronic Devices; in L. Marton, C. Marton (Eds.); Advances in Electronic and Electron Physics; Vol. 49; 1979; pp. 225-297.

That molecules both inorganic and organic, located as fractional monolayers at metal-to-metal mechanical junctions, can influence electronic conduction due to tunneling has been amply demonstrated by the work of Jaklevic and Lambe.[314] Borrowing from the techniques used to create tunneling junctions by Ivar Giaever, who in turn borrowed them from Ragnar Holm and Karl W. Meissner, these workers constructed in a UHV (Ultra High Vacuum) chamber a sandwich of Al-Al_2O_3-inorganic or organic molecules-Pb, i.e., a tunneling junction, and upon examining their I-V curves, they detected the clear presence of inelastic electron scattering, which could be correlated with certain covalent bond modes (bending, stretching, twisting of O-H, C-H, C-C, etc.). Note, even in those tunneling structures not deliberately contaminated, the O-H modes were detected, providing proof of how hard it is to rid any system of residual water vapor. Initially, the energy lost by the tunneling electrons was detected by looking for kinks in the I-V (current-voltage) curve of the tunneling structure. In particular, the second derivative of the I-V curve was examined. Later on, this lost energy was directly observed as a broadband light output from the tunneling structure, i.e., presumably after a mode had been excited by the inelastically scattered tunneling electron, the would eventually decay back down to the ground state with the resulting emission of a photon.[315] While all this sounds very *nouveau*, it was actually first observed by Karl Ferdinand Braun in the late 1800s using our old friend the electrolytic rectifier.

Based on the 1819 observations of Theodor von Grotthuss, Braun made a study of the apparent electrolysis occurring at a constrictions or slit in a partition separating the two electrodes in an electrolytic cell. In particular, Braun noted that metal particles and gas bubbles formed at the slit in the partition made of a piece of tracing paper.[316] The electrolysis, which occurred at the slit in the partition, appeared to have a definite threshold, below a certain current there was no effect. While Braun was at a loss to explain this effect, he did give it a name, 'electrostenolysis'.[317] During the course of his investigation of this

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[314] R.C. Jaklevic, J. Lambe; Molecular Vibration Spectra by Electron Tunneling; Physical Review Letters; Vol. 17; No. 22; November 28, 1966; pp. 1139-1140.

Idem; Molecular Vibration Spectra by Inelastic Electron Tunneling; Physical Review; Vol. 165; No. 3; January 15, 1968; pp. 821-832.

Elias Burstein, Stig Lundqvist (Eds.); Tunneling Phenomena in Solids; Plenum Press; 1969; chaps. 17 & 18.

[315] J. Lambe, S.L. McCarthy; Light Emission from Inelastic Electron Tunneling; Physical Review Letters; Vol. 37; No. 14; October 4, 1976; pp. 923-925.

S.L. McCarthy, J. Lambe; Enhancement of light emission from metal-insulator-metal tunnel junctions; Applied Physics Letters; Vol. 30; No. 8; April 15, 1977; pp. 427-429.

[316] [K.]F. Braun; Ueber Electrostenolyse [On Electrostenolysis]; Annalen der Physik und Chemie; Vol. 44 (3rd Series); 1891; pp. 473-500.

[317] After reading about this, I wondered whether electrostenolysis, itself, had ever been explained. A check of a couple of dictionaries and encyclopedias of electrochemistry failed to turn up even the name, electrostenolysis. Perusal of the indexes of a well known compendium on electrochemistry was also futile,

phenomenon, Braun noted the appearance of sparks along with the metal particles and gas bubbles at the slit. Eight years later, Braun returned for a more thorough examination of the light given off by electrolytic cells.[318] Braun used an electrolytic cell composed of an aluminum electrode and a platinum electrode dipped in a dilute sulfuric acid solution. When he applied an AC voltage of 120 V through a ballast resistor to this cell, he observed an off white or yellow light being emitted from the aluminum electrode but only when it was the cathode.

§9. 'ELECTROLYTIC DETECTORS' WHOSE RESISTANCE INCREASES IN THE PRESENCE ALTERNATING CURRENTS. - Negative coherers were mentioned earlier in this thesis, and I should like to talk briefly about a very interesting form of this device known as Schäfer's coherer. According to a journal article by Erich Anselm Marx, a Schäfer coherer was constructed by taking a piece of silver coated glass, a mirror for instance, and scribing line clean across it with a diamond, the two resulting silvered areas each served as a terminal with the coherer action taking place at the scribed line, and the whole arrangement was sealed in a glass tube with a dry atmosphere.[319] Under the

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J. O'M. Bockris, *et al.* (Eds.); Comprehensive Treatise of Electrochemistry, Vols. 1-10; Plenum Press; 1980-1985.

I was ultimately able to find only a single reference to electrostenolysis in a rather outdated chemistry dictionary, and this was only a definition, not an explanation. See,

Julius Grant (Ed.); Hackh's Chemical Dictionary, 4th Ed.; McGraw-Hill Book Co.; 1969; p. 236.

[318] [K.]F. Braun; Ueber Lichtemission an einige Electroden in Electrolyten. [On Light Emission in some Electrodes in Electrolytes.]; Annalen der Physik und Chemie; Vol. 65 (3rd Series); 1898; pp. 361-364.

[319] E. Marx; Über Antikohärer [About Anticoherers]; Physikalische Zeitschrift; Vol. 2; No. 17; January 26, 1901; pp. 249-253. [Or see Science Abstracts, Series A; Vol. 4A; 1901; Abstract No. 1018. Before finding the preceding article, I was totally unaware of Erich Anselm Marx, his name not being part of the standard college level canon of scientific greats. Marx was, in fact, a very prolific and original researcher whose work included such gems as the first direct measurement of the speed of propagation of x-rays,

E. Marx; Die Geschwindigkeit der Röntgenstrahlen [Velocity of Röntgen Rays]; Physikalische Zeitschrift; Vol. 6; November 1905; pp. 768-778;

the first measurements of the Hall effect in flames, see the following retrospective,

E. Marx; Flammenleitung [Electric Conduction in Flames]; in E. Marx (Ed.); Handbuch Der Radiologie, Vol. 4; Akademische Verlagsgesellshaft M.B.H.; 1917; pp. 603-797;

extensive contributions to the then new field of x-rays,

E. Marx; Kathodenstrahlen und Röntgenstrahlen [Cathode Rays and X-Rays]; in E. Marx (Ed.); Handbuch Der Radiologie, Vol. 5; Akademische Verlagsgesellshaft M.B.H.; 1919; pp. 151-688;

and the Marx (a.k.a. Regressive) effect, which is defined in,

J. Thewlis (Ed.); Encyclopaedic Dictionary of Physics; Pergamon Press; 1961; p. 498,

as "…the reduction in the energy of photoemission [of electrons] by the simultaneous incidence of radiation of lower frequency than that producing the emission." See,

E. Marx; On a New Photoelectric Effect in Alkali Cells; Physical Review; Vol. 35; May 1, 1930; pp. 1059-1065;

E. Marx, A.E.H. Meyer; Theorie des Rückgang-Effektes des Grenzpotentials bei Zustrahlung geringerer Frequenz des einfallenden Lichtes [Theory of the Regressive Effect of the Photoelectric Limiting Potential]; Physikalische Zeitschrift; Vol. 32; February 15, 1931; pp. 153-

influence of the radio waves, the resistance of the coherer, normally about 40 ohms for a 30 mm long scratch line, increased approximately by a factor three; upon cessation of the waves, the coherer spontaneously reverted to its original resistance. Apparently the sensitivity of this device was great enough to allow reception of CW transmissions at sea over a distance of 95 km (59 statute miles). In operation, this coherer produced a rushing noise in the telephone receiver connected across it in the absence of electric waves, but upon reception of the electric waves the noise changed pitch for the length of the dot or dash. Examination of the scratch mark with the aid of a microscope revealed the presence of silver particles or bridges which disappeared upon application of the electric waves.

As usual, the question arose as to the mechanism by which this device functioned? And as usual, there was more than one school of thought. In fact, there were two main schools of thought as to the mechanism. A. Neugschwender - also known as the 'Father of the anticoherer' - maintained that the Schäfer coherer was an electrolytic detector. He based this assertion on the fact that the behavior of the Schäfer coherer under a microscope mimicked his own version of the anticoherer which was simply a mirror with a line scribed across it, and activated by the moisture from one's breath. Neugschwender associated the required presence of water with an electrolytic mechanism. As far as the Schäfer anticoherer was concerned, Neugschwender felt - and quite rightly so - that even though this anticoherer was kept in an airtight container, enough water vapor was present to cause the device to function electrolytically; the electrolysis was thought to be the process responsible for forming the silver 'trees' observed under the microscope, which were destroyed upon passage of RF energy across the gap scribed in the metal film on the mirror surface. [320] The arguing between Neugschwender and Marx about the presence or absence of water in the Schäfer anticoherer was not irrelevant, because the presence of imperceptible films of water had been shown to be responsible some otherwise unaccountable electrical behavior [321] and would later be shown to be the cause

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163. [Note, in the mid 1920s, Robert Pohl and B. Gudden were investigating the internal photoelectric effect, as opposed to the external photoelectric effect examined by Marx, and observed an antagonism between the effects of short and long wavelengths of light. I do not know if there is a connection between Marx's Regressive effect and Pohl's Antagonistic effect, but the similarities are suggestive of one. See,

B. Gudden, R. Pohl; Über den scheinbaren Antagonismus kurzer und langer Wellen bei inneren lichtelektrischen Wirkung [The Apparent Antagonism between Short and Long Waves in Interior Photoelectric Action]; Zeitschrift für Physik; Vol. 37; No. 12; 1926; pp. 881-888.]

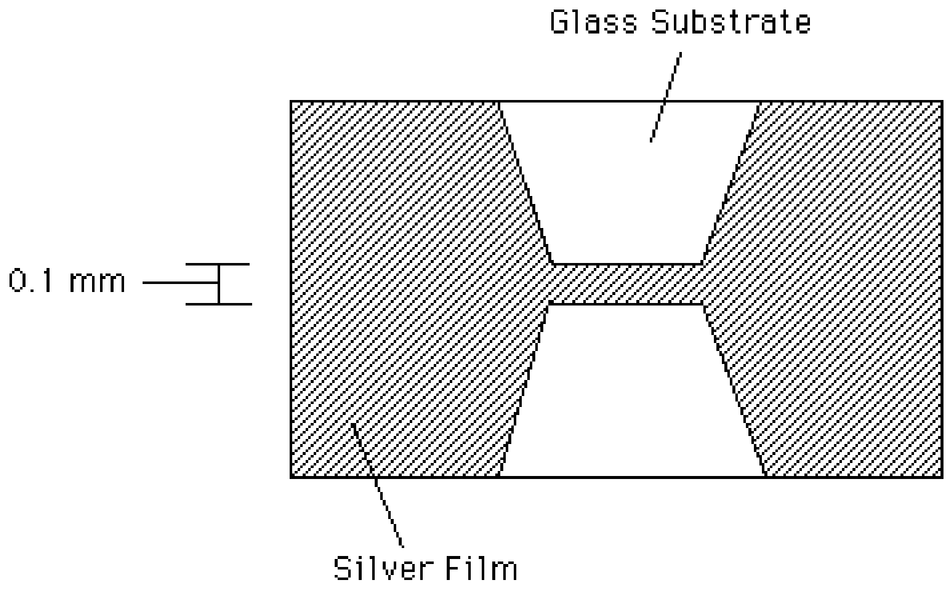
[320] A. Neugschwender; Anti-Coherers; The Electrician (London); Vol. 47; July 5, 1901; p. 396.

[321] J. Hopkinson; Certain Cases of Electromotive Force sustained by the Action of Electrolytes on Electrolytes; in B. Hopkinson; Original Papers by the late John Hopkinson, D.Sc., F.R.S., Vol. 2, Scientific Papers; J. and C.F. Clay; 1901; pp. 375-382. [John Hopkinson related how certain paradoxical conductance results seemed inexplicable to him. And that when he explained the experimental setup and their perplexing results to Lord Kelvin, Kelvin produced the correct answer immediately. The answer was the presence of an imperceptible film of water, which was providing a conductance pathway between the electrodes being used to measure the

of some often observed but unexplained non-ideal behaviors in Leyden jars and modern capacitors. [322]

E. A. Marx, on the other hand, thought the Schäfer anticoherer worked by way of a thermal mechanism. Marx based his theory on the fact that if a Schäfer coherer was constructed with a single thin bridge of metal (see Fig. B7), it functioned just like the original version. According to Marx, the anticoherer behavior of the modified Schäfer coherer was due to the RF current heating up the connecting metal bridge and so increasing its resistance due to the known positive temperature coefficient of resistivity ($1/R\ \partial R/\partial T > 0$) of metals. [323] It is interesting how when there are different mechanisms proposed for a device, there invariably is always at least one thermal mechanism among the lot. In this case, it is very difficult to determine which of these two mechanisms, if either of them, is correct.

FIGURE B7 - Modified Schäfer Anticoherer



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conductance. Note, this paper was originally published in 1876 in the *Proceedings of the Royal Society (London)*. It is surprising, given the rapidity of Kelvin's answer, that it would take another fifty years before the conundrum surrounding the results of Benjamin Franklin's experiments on the Leyden jar would be deduced by G.L. Addenbrooke, using the same explanation.]

[322] G.L. Addenbrooke; A Study of Franklin's Experiment on the Leyden Jar with Movable Coatings; Philosophical Magazine; Vol. 43 (6th Series); January-June 1922; pp. 489-493.

[323] E.[A.] Marx; Anti-Coherers; The Electrician (London); Vol. 46; October 1900-April 1901; p. 611.

One might object to Marx's theory of the Schäfer anticoherer with the following line of reasoning. The thin silver bridge depicted in Fig. B7, one might contend, was not really continuous, i.e., it was composed of individual granules of silver which appeared contiguous even to casual microscopic examination. And that the electrical conduction between these granules was actually mediated by the presence of moisture (Neugschwender's contention), which acted to bridge these particles. Against this objection, I wish to point out the work of Isabelle Stone. [324]

Stone was investigating why the measured electrical resistance of silver films was much larger that their calculated resistance based on the film's "…weight, density and dimensions…". The silver films she used were the same type of silver mirrors used to construct Schäfer anticoherers, that is the silver was deposited chemically by the reduction of a silver nitrate solution by a tartaric acid solution, the reduced (metallic) silver precipitated out of solution and deposited itself onto the glass mirror blank situated at the bottom of the tank. [325] The larger than calculated electrical resistance of these mirrors decreased spontaneously with time and/or temperatures above ambient. Stone also mentioned two other ways to cause rapid and irreversible decreases in the initial resistance: 1) by applying too high a voltage across the film, as inadvertently happened during the process of measuring the film's resistance, or 2) due to mechanical or acoustical shocks from nearby doors closing, people walking or even setting down the fresh mirror on a table too hard. In a word, these films were cohered. Note, Stone made no mention of the term 'coherer', even though she did this work during the heyday of the coherer's commercial life (circa 1898).

Stone's results suggested that the individual silver granules fused together either spontaneously over time or rapidly due to the cohering effects of either applied voltage or mechanical shock. In the case of Marx's variation of the Schäfer anticoherer, Marx most likely did <u>not</u> take any precautions against inadvertently applied voltages or mechanical shocks and so the whole film, including the bridge, was probably cohered.

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[324] I. Stone; On the Electrical Resistance of Thin Films; Physical Review; Vol. 6 (1st Series); No. 1; January 1898; pp. 1-16.

[325] S. Wein; Metallizing Non-Conductors, Part IV; Metal Finishing: Preparation, Electroplating, Coating.; Vol. 42; December 1944; pp. 736-738. [This was part IV of a review article which discussed not only the Rochelle salt process but also other silvering techniques. **Note**, the original Rochelle salt process, invented in 1855 by T. Petitjean, employed tartaric acid as the reducing agent; Draper's process, which was a modified version of Petitjean's process, actually employed a Rochelle salt (sodium potassium tartrate) solution as the reducing agent.]

Before taking leave of Mr. Marx's contribution to the study of coherers, I should like to point out that Erich Anselm Marx was <u>not</u> the inventor of the Marx generator, which is still used today to produce high voltage DC or pulses. [326]

It is interesting to note that in 1912, the famous American experimental physicist Robert Williams Wood came up with his electron atmosphere hypothesis based on his observations of the DC resistance of a diamond ruled metal film on a glass substrate - an obvious *doppelgänger* of the Schäfer coherer. Wood noticed, much to his surprise, that the DC resistance of a metal film on a glass substrate hardly changed after a checkerboard pattern was scribed into the metal film. His microscopic examinations of the ruled surface indicated to him that the ruled metal film was made up of square islands of metal separated by scribe marks marks devoid of any metal. This being the case, the only way he could explain the constancy of the DC resistance before and after the scribing was by postulating that a free electron sea, or as he puts it "…atmosphere…", extended out from the metal surface, and hence could bridge the gap between the square metal islands. The electron atmosphere was thought to extend out from the edge of the metal to a distance of something like thirty wavelengths of visible light. [327] This hypothesis anticipated the modern idea of quantum mechanical tunneling caused by the exponential spatial damping of the electron wavefunction. Unfortunately, the evidence for this notion was shown, two years later, to be faulty. In 1914, F. F. Householder, using a microscope with a 1500X oil immersion objective, found that there were invariably metallic bridges connecting the metal islands - exactly the state of affairs developed earlier by the

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[326] The inventor of the Marx generator was <u>Otto</u> Erwin Marx, who lived around the same time as Erich A. Marx.

[O.]E. Marx; Versuche uber die Prufung von Isolatoren mit Spannungsstossen [Experimental Examination of Insulators with Voltage Pulses]; Elektrotechnische Zeitschrift [Electrotechnical Journal]; Vol. 45; June 19, 1924; pp. 652-654. [Note, German researchers have an irritating habit of <u>not</u> using their full complement of Christian names, e.g., Otto Erwin Marx always signed his papers as E. Marx, Karl Wilheim Meissner signed his papers as W. Meissner, etc. - the amount of confusion arising from this practice is enormous. One of the best sources for the complete name of German scientists and engineers are the various editions of <u>J.C. Poggendorff's Biographisch-Literarisches Handwöterbuch Der Exakten Naturwissenschaften</u>.]

Idem; Erzeugung von verschiedenen Hochspannungsarten zu Versuchs- und Prüfzwecken [Generation of different high voltage species for experimental and testing purposes]; Elektrotechnische Zeitschrift; Vol. 46; 1925; pp. 1298-1299. [Otto Erwin Marx is best known, and by too many people only known, for his circuits for creating high voltage pulses, the Marx's generator, which is the mainstay of many high voltage labs, particle accelerators, EMP (ElectroMagnetic Pulse) facilities, etc. In this respect, Marx shares the same fate as Alan Dower Blumlein who also is only remembered for his circuit for creating high voltage pulses, the Blumlein switch. For more information on Marx's other inventions see

Frank B.A. Frügel; <u>High Speed Pulse Technology, Vols. 1-4</u>; Academic Press; 1965.]

[327] R.W. Wood; Preliminary Note on the Electron Atmospheres of Metals; Philosophical Magazine [and Journal of Science]; Vol. 24 (6th Series); July-December 1912; pp. 316-322.

people working on the Schäfer coherer.[328] Additional evidence against Wood's interpretation can be found in the work of F. C. Brown.[329]

§10. MORE UNLIKELY INTERACTIONS: NOBLE GASES WITH NON-NOBLE SURFACES. - In this appendix we have tried to understand how normal, i.e., non-noble, atoms and molecules interact with so-called noble metal surfaces, this enterprise has its mirror image in the study of how noble gases, in particular helium, interact with non-noble surfaces. It turns out that, contrary to popular belief, helium <u>does</u> interact strongly with solid surfaces, which may make the proposed presence of oxide layers on gold and platinum surfaces less hard to swallow. A little history is in order here.

Around 1926, a group of researchers working at the University of Berlin and later Cornell University attempted to transmute hydrogen into helium by saturating finely divided palladium, in the form of palladium black, sponge[330] or platinized asbestos, with hydrogen gas.[331] The experimental protocol was as follows. The glass apparatus containing the finely divided palladium was filled with helium-free hydrogen, which the palladium rapidly sequestered; after 12 hours, any residual condensable gases were removed with liquid air and activated charcoal, helium-free oxygen was admitted into the glass system to combine with any remaining hydrogen and the water that formed together with any excess oxygen was removed by heating and passage over activated charcoal; the residual gas, which was inured to these procedures, was passed through a capillary tube surrounded with electrodes, which ionized this gas and allowed its spectra to be read. The upshot of all this activity was that these researchers measured a significant amount of helium in the residual gas; a test for the ingress of atmospheric air with its significant load of helium was the presence of neon lines of which there was only one, indicating no helium contamination from the atmosphere. The amount of helium found by the foregoing procedure was proportional to the length of time the hydrogen was incubated, at room temperature, with the finely divided palladium.

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[328] F.F. Householder; Note on Evidence for Electron Atmospheres; Physical Review; Vol. 4 (2nd Series); No. 1; July-December 1914; p. 47.

[329] F.C. Brown; A Practical Electrical Method of Measuring the Distance Between Parallel Conducting Plates, with Application to the Question of the Existence of Electron Atmospheres.; Physical Review; Vol. 2 (2nd Series); No. 4; July-December 1913; pp. 314-322.

[330] Palladium sponge is formed by sintering palladium black.

[331] F. Paneth, K. Peters; Über die Verwandlung von Wasserstoff in Helium [On the Transformation of Hydrogen into Helium]; Berichte der Deutschen Chemischen Gesellshaft [Report of the Germany Chemical Society]; Vol. 59; 1926; pp. 2039-2048.

F. Paneth, K. Peters, P. Günther; Über die Verwandlung von Wasserstoff in Helium [On the Transformation of Hydrogen into Helium]; Berichte der Deutschen Chemischen Gesellshaft ; Vol. 60; 1927; pp. 808-809. [An English language report of this work can be found in *Nature*,

Anon.; The Reported Conversion of Hydrogen into Helium; Nature; Vol. 118; October 9,1926; pp. 526-527.

Because of concern for the validity of their results, these workers were very careful to prevent any artifact due to atmospheric helium. They even went so far as to surround the glass chamber with a vacuum mantle and then immerse this combination in a water bath to prevent any diffusion of atmospheric helium through the glass walls of the chamber. And, of course, they performed the requisite blanks (controls) to guarantee that the glass chamber and finely divided palladium were not the source of the helium due to their previous exposure to the atmosphere. The blank for the glass chamber simply involved heating the empty chamber, while the blank for the palladium involved introducing it into the chamber without the hydrogen and then turning on the heat. All of these precautions would appear to be sufficient to assure that the measured effect was real - they were not, the effect was an artifact. [332] What these same researchers discovered later, undoubtedly to their dismay, was that if they filled the glass chamber, minus its normal load of palladium, with helium-free hydrogen and then turned on the heat, the glass released significant amounts of helium. That this helium was not due to the hydrogen being transmuted by the glass itself was proved by repeated applications of hydrogen, heating and gas removal until no helium was detected, upon exposure of the inside of the glass chamber to the atmosphere for one day and reapplication of the hydrogen, heating, etc., more neon-free helium was detected. Why glass should sequester helium is still a mystery as far as I can tell.

As if the problem of why glass takes up helium was not confusing enough, consider the following. Around 1978, three Russian scientists discovered that commercially pure metals, when heated to sufficiently high temperatures in a vacuum, gave off helium. [333] When this helium was examined more carefully, it was found to contain He^3 and He^4 , which was not unusual given that small amounts of the rarer isotope, He^3, were always present together with the more abundant form. What was inexplicable was that the He^3/He^4 ratio had values from 10^{-3} to 1, which was at least three orders of magnitude <u>larger</u> than was found in the atmosphere.

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[332] F. Paneth; The Transmutation of Hydrogen into Helium; Nature; Vol. 119; May 14, 1927; pp. 706-707.

[333] B.A. Mamyrin, L.V. Khabarin, V.S. Yudenich; Anomalously high isotope ratio $^3He/^4He$ in technical-grade metals and semiconductors; Soviet Physics, Doklady; Vol. 23; No. 8; August 1978; pp. 581-583. [A description of their apparatus can be found in the following reference,

B.A. Mamyrin, L.V. Khabarin; Multiposition Metallic reactor for Liberation of Noble Gases; Instruments and Experimental Techniques; Vol. 20; No. 2; 1977; pp. 586-587.

The authors indicated that they excluded glass and quartz from the construction of their vacuum oven for what, by now, should be obvious reasons. Their crucible was made of corundum, which is a trade name for fused alumina, Al_2O_3; artificial corundum is made by fusing the mineral bauxite (hydrated alumina, silica and iron hydroxide), see

William Gardner, Edward I. Cooke, Richard W.I. Cooke (Eds.); <u>Chemical Synonyms and Trade Names</u>; Technical Press; 1978.]

The currently inexplicable behavior of helium - the noblest of the noble gases [334] - with respect to glass and other conventional materials, and the questions raised by the evidence of a passivation layer on noble metals belies how little we know about the interactions at the surface of all materials.

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[334] One measure of the nobleness of helium as compared to neon, argon, krypton, xenon and radon is the smallness of its Critical Temperature: He, T_c = -267.9°C; Ne, T_c = -228.7°C; Ar, T_c = -122.3°C; Kr, T_c = -63.8°C; Xe, T_c = +16.6°C; Rn, T_c = +104.04°C. Note, absolute zero is -273.15°C. The Critical Temperature is the temperature above which a gas cannot be condensed into a liquid no matter how high the pressure. The above Critical Temperature information was obtained from,

Robert C. Weast (Ed.); CRC Handbook of Chemistry and Physics, 50th Ed.; The Chemical Rubber Co.; 1969; pp. F-63-F-64, Tables of Critical Temperatures and Pressures.

Warning, one sometimes hears the following statement being made in support of helium being the noblest of the nobles gases. “Helium is so noble that it does not even form compounds with itself.” If by this statement, the speaker means that helium, unlike all the other noble gases, is monatomic, then they are incorrect. The fact is that none of the noble gases is polyatomic.

APPENDIX C - LITERATURE SEARCH STRATEGY

“Things don’t turn up in this world until somebody turns them up.”
- James A. Garfield

§1. PRE-1970. - A literature search was undertaken covering the period from _1884 to 1969; the criterion for the upper limit was that citations from 1970 onwards could usually be accessed via computer online searches and will be considered in the next section. All citations before 1970 had to be looked up manually, this involved using the various long term indexes such as the Engineering Index (1884 - present) [335] ; Science Abstracts, Series B, a.k.a. the Electrical and Electronic Abstracts (1903 - present) and the Science Abstracts, Series A, a.k.a the Physics Abstracts (1898 - present) [336] ; Applied Science and Technology Index (1958 - present) [337] ; and the General Science Index (1978 - present) [338] . A complete set of these indexes was found in, for example the Haggerty Library of Drexel University.

The search strategy was very simple, I looked for the words ‘coherer’ or ‘coherers’ in the Alphabetic Subject Index section of each year of a given index. This search strategy worked very well with the more recent indexes, 1950 and up, which used an Alphabetic Subject Index. Unfortunately, the Alphabetic Subject Index is a rather recent addition to the Engineering Index and Science Abstracts, as you go further back in time the various indexes begin to employ the Alphabetic Subject Index to Subject Categories. For example, from 1941 to 1942 the Physics Abstracts divided all possible subjects into four general categories: Chemistry, Physics, Mathematics and Astronomy with the entries under each of these categories organized alphabetically. For my search this was not a problem since the subject ‘coherer’ or ‘coherers’ should only be found under the category Physics. Pre-1941, though, the Physics Abstracts have subjects partitioned into

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[335] The Engineering Index is published by: Engineering Information, Inc., United Engineering Center, 345 East 47th St., NY, NY 10017.

[336] The Science Abstracts (Series A & B) are published by: INSPEC (The Institute of Electrical Engineers), 445 Hoes Lane, Piscataway, NJ 08855-1331.

[337] The Applied Science and Technology Index is published by: The H. W. Wilson Co., 950 University Ave., Bronx, NY 10452, [Customer Service](800)367-6770.

[338] The General Science Index is published by: The H. W. Wilson Co., 950 University Ave., Bronx, NY 10452, [Customer Service](800)367-6770.

many more categories (or subcategories - over 100 in all), and the job of deciding which categories to search became progressively harder. Although I have only mentioned the Physics Abstracts, this trend towards the use of subject categories and subcategories can be found in all indexes. The following table lists the various subcategories that were searched in the various indexes,

TABLE C1 - Abstract categories and subcategories

INDEX	YEARS	[SUB]CATEGORIES
Engr. Index	1969 - 1918	-
Engr. Index	1917 - 1906	Communications
Engr. Index	1905 - 1884	
Physics Abstracts	1972 - 1943	-
Physics Abstracts	1942 - 1941	Physics
Physics Abstracts	1940 - 1899	Oscillation & Waves, Electric
Physics Abstracts	1898	Radiant Waves, Oscillations
Elec. & Elctrn. Abs.	1971 - 1929	-
Elec. & Elctrn. Abs.	1928 - 1903	Telegraphy + Telephony (Wireless)

Besides the use of an Alphabetic Subject Index, the more recent years of the indexes also included Cumulative Author and Subject Indices which covered a block of years, e.g., the Physics Abstracts for the period from 1958 - 1972 organized their Cumulative Indexes in blocks of four years. Besides the three indexes already mentioned, a manual search was also done of the Science Citation Index [339] from 1961 - 1974; from 1974 onwards, this index can be accessed by an online computer search using the database called SciSearch, which can be found on the DIALOG online search service (see the next section). The manual search of the Science Citation Index was done using the PermuTerm® Subject Indexes over the years 1965 - 1974. Thankfully, there existed 5-Year Cumulations, 1965 - 1969 and 1970 - 1974, over the years of interest, which made the search less arduous than it otherwise might have been. This manual search turned up four 'hits', three of which were duplicates from the DIALOG online search, and one which was new. Note, Drexel has the Science Citation Index going back to 1961, but before 1964 these indexes do not contain a PermuTerm® Subject Index.

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[339] The Science Citation Index is published by: ISI (Institute for Scientific Information, Inc.), 3501 Market St., Philadelphia, PA 19104, [Technical Support #](800)336-4474. Note, although the Science Citation Index covers the period 1945-present, only the issues from 1965 onwards have a Subject Index (called a PermuTerm Index). A call to the Technical Support department has confirmed that there is no way to do a subject search of the Science Citation Index before 1965.

Another index which was searched was the Government Reports Announcements & Index [340] which covered the period 1946 (Vol.1) - present. This index was manually searched from 1946 - 1963; after 1963, the entries were accessible with the DIALOG online service using the NTIS database (see the next section). Note, the NTIS does not keep very old government reports, i.e., those reports with a PB (Publication Board) number less than 150,000. Reports with PB number less than 150,000, can be obtained from the Library of Congress [341] , but be warned that it takes a long time to get anything from the Library of Congress. In order to just find out whether they [Library of Congress], in fact, have the government report, you must first submit a written request for a search and an estimate of the cost to photocopy the document, once they reply to this initial request it takes another 6-8 weeks for them to fill the order for the photocopied material.

The results (citations, abstracts, etc.) of all these searches are presented in the following table,

TABLE C2 - Literature Search Results

Engineering Index

1901-1905 (Vol. 4): 16 citations.
1896-1900 (Vol. 3): 16 citations.

Science Abstracts, Series B (Electrical & Electronic Abstracts)

[Signalling & Telegraphy + Telephony (Wireless)]
1910 (Vol. 13B): 1134A
1908 (Vol. 11B): 468
1904 (Vol. 7B): 381
1903 (Vol. 6B): 475A, 476A, 1062A

Science Abstracts, Series A (Physics Abstracts)

[Oscillation & Waves, Electric]
1928 (Vol. 31A): 2814
1916 (Vol. 19A): 115B

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[340] The Government Reports Announcements & Index is published by: National Technical Information Service (NTIS), 5285 Port Royal Rd., Springfield, VA 22161, [General Information](703)487-4600. If you wish to place an order - they accept major credit cards - use the following phone number: (800)336-4700. In the event that the ID# of the document does not come up on their electronic database when you are trying to place your order, you can call the following number to check whether the Library of Congress should have it: [Title ID](703)487-4780.

[341] Library of Congress, Photoduplication Service, Washington, DC 20540, (202)707-5655 or 5640; for future reference, the main number is (202)707-5000, and the number for the reference desk is (202)707-5522.

1912 (Vol. 15A): 1431
1910 (Vol. 13A): 1133, 1134
1908 (Vol. 11A): 468B
1907 (Vol. 10A): 1214
1906 (Vol. 9A): 361
1905 (Vol. 8A): 1038, 1271, 1923, 2248, 2280
1904 (Vol. 7A): 157, 370, 371, 618, 1135, 1136, 1174, 1501, 1750, 1767, 2011, 2271, 2273, 2682, 2962, 3253
1903 (Vol. 6A): 475, 476, 1061, 1062, 1063, 1440
1902 (Vol. 5A): 718, 1106, 2091, 2092
1901 (Vol. 4A): 384, 385, 634, 855, 1312, 1313, 1314, 1337, 1345, 1515,1516, 1715, 2000, 2377, 2378, 2404
1900 (Vol. 3A): 125, 126, 127, 128, 667, 1295, 1462, 1464, 1465, 2028, 2034, 2209, 2245
1899 (Vol. 2A): 105, 292, 293, 457, 458, 692, 693, 1023, 1106, 1164, 1165, 1166, 1716, 1717, 1718, 1719, 1380
[Radiant Waves, Oscillations]
1898 (Vol. 1A): 39,166, 640, 792, 1363,1364

Applied Science and Technology Index

None.

General Science Index

None.

Science Citation Index

1966: 1 citation.
1961: 1 citation, this was found indirectly, i.e., via the first citation.

Government Reports Announcements & Index

1953 (Vol. 20): PB-109937, PB-109938

Note, this strategy of employing the keyword ‘coherer#’, where “#’ was the wild card symbol, did not ensnare all the articles and/or books having to do with this subject. The problem was that for a long time coherers and crystal rectifiers were treated as different realizations of the same physical phenomena, and so some important and informative information about coherers was sequestered in articles whose titles, while mentioning the term ‘crystal diode, detector or rectifier’, did not allude to the fact that the articles were also about coherers.

Due to the possibility of the article, document or book being in a foreign language, I needed to know how to find if there was a translation readily available. There were three indexes which listed translations,

i) World Translation Index (1967 - present) [342]
ii) Transdex Index (1962 - present) [343]
iii) Translations Register-Index (1967 - 1982) [344]

All these indexes can be found in Temple's Paley Library. Part of the effort of this thesis involved trying to find translations of foreign language papers having to do with the major interests of this monograph. To this end, the National Translation Center (NTC) was asked to search for translations of the following eighteen articles,

1) Walther Schottky; Über kalte und warme Elektronentladungen.; Zeitschrift für Physik; Vol. 14; 1923; pp. 63-106.

2) G. Hoffmann; Elektrizitätsübergang durch sehr kurze Trennungastrecken; Physikalische Zeitschrift; Vol. 11; 1910; pp. 961-967. [**Note**, the article is pp. 961-966, and the discussion is pp. 966-967.]

3) Franz Rother; Der Elektrizitätsübergang bei sehr kleinen Kontaktabständen; Physikalische Zeitschrift; Vol. 12; 1911; pp. 671-674.

4) Franz Rother; Der Elektrizitätsübergang bei sehr kleinen Kontaktabständen und die Elektronenatmosphären der Metalle; Annalen der Physik; Vol. 44 (4th Series); 1914; pp. 1238-1272.

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[342] The World Translation Index is published by: International Translations Centre, Schuttersveld 2, 2611 WE Delft, The Netherlands.

[343] The Transdex Index is published by: University Microfilms International, 300 N. Zeeb Rd., Ann Arbor, MI 48106-1346, (800)521-0600.

[344] The Translations Register-Index **was** published by: National Translations Center, The University of Chicago, 5730 S. Ellis Ave., Chicago, IL 60637, (312)962-7060. In 1983, the Translation Register-Index was adsorbed into the World Translation Index. **As of January 1989**, the National Translations Center (NTC) has a new address: NTC, Library of Congress, Washington, DC 20541, (202)707-0100. The NTC charges a $10.00 fee per citation to check if it has a translation of the article, this search is usually completed within 24 hours and, if directed to do so, they will call you with the results. If they indeed have the translation, it can be purchased from them for $35.00.

Postscript: On about June 11, 1993, I received a letter from the head of the NTC informing me that due to its inability to succeed as a cost recovery service (i.e., to be self supporting solely from the sale of its services), the Library of Congress will be terminating its support for the NTC no later than October 1, 1993. In the meantime, the NTC will try to find another sponsor, but failing this it will be disbanded.

5) Franz Rother; Über den Austritt von Elektronen aus kalten Metallen; Annalen der Physik; Vol. 81 (4th Series); No. 20; 1926; pp. 317-372.

6) Ragnar Holm, Karl Wilheim Meissner; Messungen mit Hilfe von flüssigem Helium. XIII. Kontaktwiderstand zwischen Supraleitern und Nichtsupraleitern; Zeitschrift für Physik; Vol. 74; 1932; pp. 715-735.

7) G. Todesco, Bruno Benedetto Rossi; Contributo allo studio dei contatti imperfecti metallici; Accademia Nazionale dei Lincei. Atti. Classe di Science Fisiche, Mathematiche, e Naturali. Rendiconti; Vol. 7; April 1, 1928; pp. 568-573.

8) Ferdinand Braun; Über die Thermoelektricität geschmolzener Metalle; Sitzungberichte der Königlich Preussischen Akademie der Wissenschaften; Vol. 18; April 9, 1885; pp. 289-298.

9) Ferdinand Braun; Einige Bemerkungen über die unipolare Leitung fester Körper; Annalen der Physik und Chemie; Vol. 19 (New Series, a.k.a. 3rd Series); 1883; pp. 340-352.

10) Ferdinand Braun; Ueber die Stromleitung durch Schwefelmetalle; Annalen der Physik und Chemie; Vol. 153 (2rd Series); 1874; pp. 556-563.

11) Emil Gabriel Warburg; Ueber die Verzögerung bei der Funkenentladung; Annalen der Physik und Chemie; Vol. 62 (New Series, a.k.a. 3rd Series); No. 11; 1897; pp. 385-395.

12) Felix Bloch; Über die Quantenmechanik der Elektronen in Kristallgittern; Zeitschrift für Physik; Vol. 52; 1928; pp. 555-600.

13) Emil Gabriel Warburg; Ueber eine Methode, Natriummetall in Geissler'sche Röhren einzuführen und über das Kathodengefälle bei der Glimmentladung; Annalen der Physik und Chemie; Vol. 40 (New Series); No. 5; 1890; pp. 1-17.

14) E. Plessing; Zur Struktur polierter Metallflächen; Physikalische Zeitschrift; Vol. 39; August 15, 1938; pp. 618-620.

15) S. Dobinski; Zur Struktur polierter Metallflächen, Bemerkung zur Arbiet von E. Plessing; Physikalische Zeitschrift; Vol. 40; April 1, 1939; pp. 232-233.

16) E. Plessing; Bemerkung zur vorstehenden Notiz von S. Dobinski; Physikalische Zeitschrift; Vol. 40; April 1, 1939; pp. 233-234.

17) E. Plessing; Untersuchung bearbeiteter Metalloberflächen mittels Elecktroneninterferenzen; Zeitschrift fur Physik; Vol. 113; No. 1-2; 1939; pp. 36-55.

18) Josef Waszik; Beitrag zur Erklärung der elektrischen Anziehung, die als Johnsen-Rahbek-Phänomen bezeichnet wird.; Zeitschrift fuur Technische Physik; Vol. 5; No. 1; 1924; pp. 29-31.

The result of this search was that translations were found for only two of the eighteen articles. The items which were translated included #1 & #13, which were cataloged by the NTC using the following designations: TT-123-82 & 77-22546, respectively.

Transdex Index was <u>not</u> consulted for the following reason. The Transdex Index originally started as a U.S. government publication funded by the CIA (Central Intelligence Service) for the purpose of gathering, in a timely manner, strategic information on adversaries and/or economic rivals of the United States. To this end, Transdex Index concentrated its translational efforts on the following countries or regions of the world in order of importance: U.S.S.R., Asian, Eastern Europe, Western Europe, The Near East, and Africa. In addition, because of its concern to provide this translated material in a timely fashion, the journals, newspaper articles, etc. were all translated within a year of their original appearance. The articles I was interested for this thesis were usually older articles, and so they would be outside the sphere of interest of the Transdex Index.

§2. POST-1970. - An online search using DIALOG [345] (search service) on TYMNET (telecommunications vendor), and employing a single search word ‘coherer’, yielded the following results,

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[345] For more information on the DIALOG service call 1-800-3-DIALOG and request a copy of the DIALOG Database Catalog 1990. The address is: DIALOG, 3460 Hillview Ave., Palo Alto, CA 94304, Attn. Publication Distribution; enclose a check or money order for $13.00 ($3.00 for the catalog plus a $10.00 handling charge) - sometimes they will send the catalog for free.

TABLE C3 - Online science, engineering and technical databases

DIALOG Services[346]	No. of Citations
Compendex (USA, 1970 - present) [Compendex = Engineering Index Monthly]	3
INSPEC (UK, 1969 - present) [INSPEC = Science Abstracts, Series A & B]	6
SciSearch (1974 - present) [SciSearch = Science Citation Index]	2
Conference Paper Index (1973 - present) [Conference Papers Index]	0
Soviet Science & Technology (1975 - present) [-]	0

Of these eleven 'hits', six were valid references to coherers, the other five citations either used the term coherer to mean something else (four instances) or dredged up a citation that had nothing to do with the term 'coherer' (one instance). The amazing thing about the results of this search was that it uncovered <u>any</u> citations at all. The fact that it did supports my contention that the subject continues to fascinate people. The cost of this enterprise came out to exactly $41.71 for a 15 minute online session.

In addition to checking to above online searches, an online search was also done of U.S. government documents using the NTIS online database (see Table C4),

TABLE C4 - Online databases of U.S. government reports

DIALOG Services	No. of Citations
National Technical Information Service (1964 - present)[347] [NTIS = Government Reports Announcements & Index]	1

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[346] Most online search services of my acquaintance do not go back much further than 1970. This was confirmed by our librarian, Mrs. Betsy Tabas, Temple University, College of Engineering, Computer Science and Architecture Library.

[347] NTIS is published by: National Technical Information Service, 5285 Port Royal Rd., Springfield, VA 22161, [General Information](703)487-4600.

The one 'hit' found in the NTIS online database turned out to be bogus. We searched for occurrences of the word 'coherer#' in the titles and abstract, where # is a wild card character representing other letters or groups of characters, and found a citation with the misspelled word 'coherernt' in its abstract; the article was concerned with partially coherent light sources, not coherers.

Another government documents database that would be worthwhile scrutinizing is the Technical Reports Database (1953 - present) [TRD = Technical Reports Awareness Circular], [348] which can be accessed via the Defense Gateway Information Service (DGIS). Unfortunately, this is a restricted database only available to U.S. government agencies, defense contractor, grantees and universities doing defense work. This reference database contains citations and abstracts to unclassified work and partial citations and abstracts to classified work. Although I cannot access this database, all is not lost because the NTIS database does contain <u>some</u> of the recent unclassified defense technical reports.

Since this is a thesis, I decided to check to see if there were any databases that had citations to either PhD dissertations or Masters theses. I came up with the following database,

TABLE C5 - Online databases of theses

BRS Services [349]	No. of Citations
Dissertations Abstracts Online (PhDs,1861 - present, Masters, 1962 - present) [350] [DISS = Dissertations Abstracts International, American Doctoral Dissertations & Comprehensive Dissertation Index]	0

The search strategy was the same as for the other databases, i.e., search for a occurrence of the words 'coherer' OR 'coherers' in either the title or, where available, the abstract of the dissertations. Considering how far back this database goes, it was surprising to find not even one reference to coherers. Note, recently, Temple University has acquired the complete Dissertations

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[348] The Technical Reports Database is published by: Defense Technical Information Center (DTIC), Cameron Station, Alexandria, VA 22314, (202)274-7633 or 6847 or 7791.

[349] For more information on the BRS service call (800)955-0906.

[350] Dissertation Abstracts Online is published by: University Microfilms International (UMI), 300 North Zeeb Rd., Ann Arbor, MI 48106, (800)521-0600. By the way, this database does go back to 1861, I double checked this by calling up UMI and speaking with the supervisor in charge of this database, (800)521-0600, X708.

Abstracts Index covering the time span 1861 to 1991 on CD-ROM (Compact Disk-Read Only Memory).

In addition to the previously mentioned citation services, I used the WILSONDISC™, Version 2.2, [351] CD ROM at Drexel's Haggerty library. This free service has the following database: Applied Science and Technology Index (10/83 - 07/04/90) [352] ; there were no 'hits' using the WILSONDISC. Also, the main branch of the Philadelphia Free Library has a free CD ROM service called InfoTrac™, Version 5.14i [353] ; there were no 'hits' on this service on either of its two databases: General Periodicals or Academic Index. Even though there were no 'hits' on InfoTrac™, one of the two databases did have the word 'coherer' in it, but without any citations.

Due to the possibility that a citation may turn out to be an article, document or book in a foreign language, there is an online service for determining whether or not a English translation exists,

TABLE C6 - Online translation databases

DIALOG Services

World Translation Index (1984 - present)
[WTI = World Translation Index]

Note, the articles listed in a given year of this index do not necessarily correspond to articles from that particular year, e.g., the 1970 Index might have listed articles which had been written in 1950, but were not translated until 1970. It should also be noted that this database was not particularly extensive, comprising as it did only about a quarter of a million records. Actual experience shows just how circumscribed this database was. Of the following eleven foreign language citations, none of them was found in the WTI database.

1) G. Hoffmann; Elektrizitätsübergang durch sehr kurze Trennungastrecken; Physikalische Zeitschrift; Vol. 11; 1910; pp. 961-967. [**Note**, the article is pp. 961-966, and the discussion is pp. 966-967.]

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[351] WILSONDISC™ is published by: The H. W. Wilson Co., 950 University Ave., Bronx, NY 10452, [Customer Service](800)367-6770. The WILSONDISC Guide, which gives detailed information about both how to use the CD ROM and what databases it contains, can be obtained directly from the company - I got it for free.

[352] All told, there are twelve (12) databases that can be accessed via the WILSONDISC. Of these twelve databases, only two (2) are relevant to my search for coherers: Applied Science and Technology Index (AST) and General Science Index (GSI). Drexel only owns the AST database.

[353] InfoTrac™ is published by: Information Access Co., 11 Davis Drive, Belmont, CA 94002, (800)227-8431.

2) Franz Rother; Der Elektrizitätsübergang bei sehr kleinen Kontaktabständen; Physikalische Zeitschrift; Vol. 12; 1911; pp. 671-674.

3) Franz Rother; Der Elektrizitätsübergang bei sehr kleinen Kontaktabständen und die Elektronenatmosphären der Metalle; Annalen der Physik; Vol. 44 (4th Series); 1914; pp. 1238-1272.

4) Franz Rother; Über den Austritt von Elektronen aus kalten Metallen; Annalen der Physik; Vol. 81 (4th Series); No. 20; 1926; pp. 317-372.

5) Ragnar Holm, Karl Wilheim Meissner; Messungen mit Hilfe von flüssigem Helium. XIII. Kontaktwiderstand zwischen Supraleitern und Nichtsupraleitern; Zeitschrift für Physik; Vol. 74; 1932; pp. 715-735.

6) G. Todesco, Bruno Benedetto Rossi; Contributo allo studio dei contatti imperfecti metallici; Accademia Nazionale dei Lincei. Atti. Classe di Science Fisiche, Mathematiche, e Naturali. Rendiconti; Vol. 7; April 1, 1928; pp. 568-573.

7) Ferdinand Braun; Über die Thermoelektricität geschmolzener Metalle; Sitzungberichte der Königlich Preussischen Akademie der Wissenschaften; Vol. 18; April 9, 1885; pp. 289-298.

8) Ferdinand Braun; Einige Bemerkungen über die unipolare Leitung fester Körper; Annalen der Physik und Chemie; Vol. 19 (New Series, a.k.a. 3rd Series); 1883; pp. 340-352.

9) Ferdinand Braun; Ueber die Stromleitung durch Schwefelmetalle; Annalen der Physik und Chemie; Vol. 153 (2rd Series); 1874; pp. 556-563.

10) Emil Gabriel Warburg; Ueber die Verzögerung bei der Funkenentladung; Annalen der Physik und Chemie; Vol. 62 (New Series, a.k.a. 3rd Series); No. 11; 1897; pp. 385-395.

11) Felix Bloch; Über die Quantenmechanik der Elektronen in Kristallgittern; Zeitschrift für Physik; Vol. 52; 1928; pp. 555-600.

If a translation of a foreign language article cannot be found and purchased from one of the translation services, one is usually stuck with having to translate it themselves or paying someone to do it (minimum $15-20/page). Because of the availability of small computers such as the IBM PC and the Apple Macintosh™, it might seem reasonable to assume that translation software exists, at least, for the case of the standard European languages such as French, German and Spanish. It turns, though, that there are very few translation programs and those that exist are of dubious efficacy. In addition, translation of a long foreign language article is a two step process, each step of which is frought with peril for the unwary.

The first step is not the translation but rather getting the article ‘into’ the computer. Typing a 30 or 40 page article into a word processor is an onerous task to put it mildly, and it is also subject to transcriptional errors. The only other alternative is to use a scanner together with OCR (Optical Character Recognition) software to ‘capture’ the text. This approach is heir to two major disadvantages: cost, the scanner is about $1500 and good OCR software runs around $1000; and efficacy, even the best OCR software is not error proof, and this shortcoming becomes more acute in the presence of diacritical marks (umlauts: ü, accents acute: é & grave: è, cedilla: Ç, caret: â, etc.), foreign punctuations (¿, << >>, …), nonstandard characters (ß, œ, etc.), different fonts (a, a, a, a, a, a, a, a), different sizes of fonts (a, a, a), and photocopies of old journals with their attendant noisy images.

The second step is the actual translation. Perhaps the biggest single impediment to machine driven translation is the requirement that a language be logical, i.e., that every facet of it be defined and set out in rules, and that the people using this language scrupulously follow said rules - which assumes, of course, that they are, in fact, aware of the rules. Unfortunately, language, being a human endeavor, is far from being logical in its construction or application. Add to this the use of jargon, e.g., scientific terminology, and you have the receipt for disaster, at least as far as machine driven translations are concerned. Note, even a person doing a translation by hand can end up with an unreadable clear text if the article is scientific and the translator is a layman. Another stumbling block to getting a good translation is the fact that every word has multiple meanings based on context. [354]

§3. PRE-SCIENCE ABSTRACTS, SERIES A & B INFORMATION. - An area I deliberately glossed over, at the start of this appendix, was the locating of articles on coherers pre-1896-8. Because the Science and Engineering Abstracts did not exist before this time, there was no systematic way for me to search for articles related to coherer research in the 1800s, other than the hit-or-miss approach of backwards daisy chaining of references from articles and/or

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[354] A very interesting series of articles on the topics of MT (Machine Translation) and MAT (Machine Assisted Translation) can be found in a recent issue of *BYTE* magazine,

M. Vasconcellos; Machine Translation; BYTE; January 1993; pp. 153-156, 160-162, 164.
E. Hovy; How MT Works; BYTE; January 1993; pp. 167-168, 171-172, 174-176.
L.C. Miller; Babelware for the Desktop; BYTE; January 1993; pp. 177-178, 180, 182-183.
Idem; Machine-Translation Software; BYTE; January 1993; pp. 185-186.

These articles deal not only with MT and MAT from a theoretical point-of-view, but also enumerate and discuss commercially available translation software packages. I wish to thank Howard Fox of Fox Cleaners for making me aware of these articles.

books. In the course of just such a paper chase, I happened upon a series of three articles which contained extremely detailed bibliographies of journal papers and/or books affiliated with the topic, coherers.[355] These bibliographies covered the time frame from the early 1900s all the way back to 1800. That I found this information was a matter of luck, on my part, coupled with the excellent library resources provided by Temple University, University of Pennsylvania and the Philadelphia Consortium of Special Collections Libraries.[356]

As I was winding up my research, I also stumbled over the fact that the Royal Society of London published what amounted to an index of scientific papers covering the period 1800 to 1900 called, Royal Society of London Catalogue of Scientific Papers, 1800-1900. This publication contained both an author and subject index, and covered most of the important journals of the time. Due to time constraints and exhaustion on my part, this material was not accessed.

§4. POSTSCRIPT. - In what can only be classified as a stroke of luck, I happened on a series of three articles by Angelika Maria Josefa Székely de Doba which mirrored the approach used in this thesis of treating coherers, MOM 'diodes' and STMs in a unified manner.[357] The bibliographies contained in her

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[355] K.E. Guthe; Coherer Action; in A.E. Kennelly, W.D. Weaver (Eds.); Transactions of the International Electrical Congress, St. Louis, 1904, Vol. 1 of 3; J.B. Lyon Co.; 1905; pp. 242-255.

Augusto Righi, Bernhard Dessau; Die Telegraphie ohne Draht [Wireless Telegraphy]; Druck und Verlag von Friedrich Vieweg und Sohn; 1907; pp. 228-274.

G. Schlabach; Der heutige Standpunkt der Kohärerfrage [The Current Thinking on the Coherer Question]; Physikalische Zeitschrift; Vol. 2; No. 26; 1901; pp. 383-387.

[356] In 1985, the Philadelphia Consortium of Special Collections Libraries was formed to promote better utilization of the city's impressive collection of research and archive libraries. The consortium is currently composed of sixteen libraries and includes the following libraries specializing in collections of materials relating to the physical and/or biological sciences: The Academy of Natural Sciences of Philadelphia, American Philosophical Library, College of Physicians of Philadelphia, and The Library Company of Philadelphia. The holdings of most of these sixteen libraries can be found in the Union Catalog of Serials, which is usually found at the reference desk of any research grade university library reference desk. Note, because these libraries do not loan out their materials and due to the age of their holdings, they do not always appear on the various computer databases used by Interlibrary Loan Departments. For this reason it is imperative that one first check the Union Catalog of Serials when searching for old and/or obscure journals.

[357] A. Székely de Doba; Die Kontaktdetektoren [Point Contact Detectors]; Akademie der Wissenschaften in Wien Mathematisch-naturwissenschaftliche Klasse, Sitzungsberichte; Vol. 127; Pt. 2a; No. 6; 1918; pp. 719-792.

A. Székely; Beobachtungen an elektrolytischen Detektoren [Observations on electrolytic Detectors]; Akademie der Wissenschaften in Wien Mathematisch-naturwissenschaftliche Klasse, Sitzungsberichte; Vol. 128; Pt. 2a; 1919; pp. 1377-1400.

Idem; Über die Art des Elektrizitätsüberganges zwischen Metallen, die sich lose berühren [On the Types of Electrical Behavior between Metals in loose Contact]; Zeitschrift für Physik; Vol. 22; February-March 1924; pp. 51-69.

three papers were a very valuable and unique source of information on all the devices of interest in this thesis.

§5. SUMMARY. - In closing, I should like to point out that although one can find quite a few articles on the subject of ‘coherers’ by way of the logical linear search strategy outlined in this appendix, this method is only a starting point. Many of the most informative articles I found, relating coherers to STMs (Scanning Tunneling Microscopes) for example, were discovered through a very nonlinear search strategy (see APPENDIX E). Thus, there are no foolproof methods of finding information about a given topic, one simply has to try everything and assume nothing.

[Statistics: (1918) 74 p., 70 refs.; (1919) 24 p., 21 refs.; (1924) 19 p., 47 refs.]

APPENDIX D - BEILBY LAYER

"You need marginal contributors, scientists of good reputation generally whose obsessions don't strike fire with other members of their profession."
- novel, They Shall Have Stars, by James Blish

§1. INTRODUCTION. - The act of polishing a metal seems innocent enough to require no deep discourse or investigation, but this is not the case, especially with respect to how polishing influences the oxidation of a metal surface. When Sir George Thomas Beilby examined polished surfaces microscopically, he came to the conclusion that the act of polishing disrupted the surface on a molecular level, to be exact, he thought that this process transformed the first couple layers of atoms from their normally polycrystalline arrangement to an amorphous one. The polished layer is amorphous because, according to Beilby, the act of polishing caused the surface layer to melt and then freeze without recrystallization. [358] Beilby's hypothesis was, of course, attacked and rightly so since there was only indirect evidence, gathered via light microscope observations, to support such a radical suggestion. Then along came George Paget Thomson and C. G. Fraser with their high energy (>600 eV), low angle reflected (as opposed to transmitted) electron diffraction camera. [359]

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[358] C. Kajdas, S.S.K. Harvey, E. Wilusz; Encyclopedia of Tribology; Elsevier; 1990; p. 31.

[Sir] George Beilby; Aggregation and Flow of Solids; Macmillan; 1921. [Note, only one chapter in Beilby's book was devoted exclusively to the subject of polishing, but like all the other chapters it was lucidly written and a joy to read. The bibliography at the end of the book, which listed eighteen of Beilby's papers (1901-1915), did not appear to be an exhaustive accounting of his publications since, as was announced in its title, it only contained those papers referred to in the text.

The creation of Beilby's amorphous layers within worked metals, i.e., between the crystal grains of a polycrystalline sample, was posited as the mechanism behind work hardening. In a very real sense, Beilby's amorphous layer was the precursor of the now accepted concept of dislocations. See,

N.P. Allen; Fifty Years' Progress in the Understanding of Metals; Journal of the Birmingham Metallurgical Society; 1953 (Golden Jubilee No. [**Note**, it is important that you specify the 'Golden Jubilee No.' since there was more than one volume in 1953]); pp. 89-109.]

[359] G.P. Thomson, C.G. Fraser; A Camera for Electron Diffraction; Proceedings of the Royal Society (London); Vol. 128 (Series A); August 1930; pp. 641-648. [This apparatus appears to be the precursor of the RHEED (Reflective High Energy Electron Diffraction) equipment; the origin of just plain LEED (Low Energy Electron Diffraction) can be found in the apparatus developed at

Using this apparatus, Thomson was able to show that the act of polishing did indeed change the structure of the surface at an atomic or molecular level, [360] but as to exactly what the change was he could not say unequivocally, although he did eventually favor the amorphous layer scenario of Beilby. There were two competing theories for what was happening to a polished surface: 1) Beilby's hypothesis of a thin amorphous layer and 2) the hypothesis that the initially polycrystalline surface remained polycrystalline after polishing, only the size of the crystals were much smaller. Both these models led to diffuse reflected electron diffraction rings (a.k.a. halos). Quite a bit of effort was invested by many researchers in attempting to clarify what was actually happening to metal surfaces after polishing. [361]

The low angle of incidence electron diffraction camera of Thomson and Fraser produced, for flat metal surfaces, a series of concentric rings on the film or fluorescent screen used to see the reflected (diffracted) electrons; if the plane metal surface was polished, the corresponding diffraction rings became, instead, diffuse halos. [362] These ring and halo patterns are significantly different from

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Bell Labs by Clinton Davisson and Lester H. Germer with which they first proved the wave nature of the electron. See,

C. Davisson, L.H. Germer; Diffraction of Electrons by a Crystal of Nickel; Physical Review; Vol. 30; 1927; pp. 705-740.]

[360] G.P. Thomson; The Analysis of Surface Layers by Electron Diffraction; Proceedings of the Royal Society (London); Vol. 128 (Series A); August 1930; pp. 649-661.

[361] As an example of the kind of interest generated by this subject consider Vol. 31 (1935) of the *Transactions of the Faraday Society*. One issue of this volume contained 247 pages of text (pp. 1043-1290) by 44 authors plus 70 plates (at the end), each containing multiple figures, and all devoted to investigating the effect of polishing on metal surfaces. The end result of all these papers and discussions was that the 44 authors agreed that more work needed to be done.

[362] Almost everyone agreed that the electron diffraction pattern of rings became halos after polishing of the metal surfaces, except for one lone researcher. During the course of my literature search on the subject of the Beilby layer, I came across an article by a Japanese researcher, Mituwo Miwa, whose experimental results verified those obtained by G.P. Thomson,

M. Miwa; On the Nature of Polished Layer of Metals.; Tohoku University Science Reports; Vol. 24 [Report No. 343 of the Research Institute for Iron, Steel and Other Metals]; September 1935; pp. 222-239.

In the course his paper, Miwa mentioned that Lester H. Germer had also investigated the effect of polishing on electron diffraction patterns. Miwa noted that of all the researchers, Germer, alone, maintained that polished surfaces produced <u>no</u> electron diffraction patterns, diffused rings (halos) or otherwise. An examination of the cited paper revealed that Germer was, in fact, quite unequivocal about this result. See,

L.H. Germer; Diffraction of Electrons by Metal Surfaces; Physical Review; Vol. 43 (2nd Series); May 1, 1933; pp. 724-726.

Germer did <u>not</u> give any experimental details as to how he polished his metal samples or, in fact, what metals samples he employed; he did, however, quantify the wavelength (energy) of the electrons he used together with their grazing angle, but he provided <u>no</u> description of the electron diffraction camera. Eventually he did provide a description of his apparatus,

L.H. Germer; Electron Diffraction Camera; Review of Scientific Instruments; Vol. 6; May 1935; pp. 138-142.

In 1936, Germer wrote his last paper on the subject of the Beilby layer. In this paper, he made <u>no</u> mention of why his previous experimental results were at odds with everyone else's results. He the point images generated from the electron or x-ray diffraction of a fix single crystal, but they are characteristic of polycrystalline materials and are referred to as Hull-Debye-Scherrer or, in more recent literature, as Debye-Scherrer patterns.

Between 1915 and 1917, Albert W. Hull in America and Peter Debye and P. Scherrer in Europe were trying to obtain x-ray diffraction patterns of powdered polycrystalline materials, and in so doing observed the characteristic ring patterns. Hull, who worked for the General Electric Co., was interested in using x-ray diffraction to elucidate the crystal structure of metals.[363] Unfortunately, most metals cannot be induced to form single crystals large enough to be suitable for conventional x-ray diffraction crystallography. To circumvent this problem, Hull powdered his polycrstalline metal sample as fine as possible, put it into a long narrow glass tube, rotated the tube continuously along its long axis, and substituted this arrangement for the usual single crystal in a standard x-ray diffraction apparatus. He reasoned that if the bulk metal was polycrystalline, the powdered and rotated sample would allow every possible crystallite plane to have every conceivable orientation with respect to the x-ray beam, and hence produce a regular pattern on the film. The assumption of the polycrystalline nature of the bulk material was the crucial step, since without it the resulting pattern of concentric rings would be unintelligible. Proof of this assertion comes from the following fact. In 1913, W. Friedrich and H. B. Keene, while getting the x-ray diffraction pattern of certain waxes and thin sheets of metal, respectively, saw the characteristic powdered diffraction pattern of concentric rings. But since both researchers erroneously assumed that the bulk materials were amorphous, they were unable to capitalize on the information contained within the powdered diffraction patterns.[364] Besides enunciating the same conclusions as Hull, Debye and Scherrer's other major contribution to the powdered x-ray diffraction field was their camera arrangement, now called the Debye-Scherrer camera.

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did mention that the accepted experimental result, two diffuse diffraction rings whose radii were remarkably constant even between metals of very diverse atomic sizes, was hard to understand - it would not be until 1937, when S. Dobinski would try to solve this riddle. The important thing about this 1936 paper was that Germer appeared to have reconciled himself to the fact that two diffuse diffraction rings was the correct experimental result. It would be too much to call this paper a recantation, but he did appear to have conceded that his original experimental results were wrong. However, he still did not believe that Beilby's interpretation about the polished layer being amorphous was correct.

L.H. Germer; Diffuse Rings Produced by Electron Scattering; Physical Review; Vol. 49; January 15, 1936; pp. 163-166.

[363] A.W. Hull; The Crystal Structure of Iron; Physical review; Vol. 9 (2nd Series); No. 1; 1917; pp. 84-87.

Idem; The Crystal Structure of Aluminium [sic] and Silicon; Physical Review; Vol. 9 (2nd Series); No. 6; 1917; pp. 564-566.

Idem; A New Method of X-Ray Crystal Analysis; Physical Review; Vol. 10 (2nd Series); No. 6; 1917; pp. 661-696.

[364] Harold P. Klug, Leroy E. Alexander; X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials; John Wiley & Sons, Inc.; 1954; pp. 162-164.

§2. THE DOBINSKI COROLLARY AND PLESSING'S CRITICISM. - Now we come to part of this story which is highly relevant to our discussion of MOM 'diodes'. Among the myriad of questions troubling workers trying to understand metal polishing was why the diameter of the halos appeared, with few exceptions, not to depend on the size of the atoms making up the metal? A Polish scientist named Dobinski, working in G. P. Thomson's lab around 1937, came up with a very plausible answer. [365] He noticed that the standard procedure, when polishing samples before inserting them inside Thomson-Fraser camera, was to carry out the polishing in air. From this observation, he reasoned that if the polishing created a new surface on the metal either by abrading or plastically deforming the old surface, then exposure to the oxygen in air would result in extensive oxidation of the new layer. [366] Exactly why the oxidized portion of the Beilby layer would result in the observed homogeneity in halo sizes was not explained by Dobinski. There was also the question of why the polished surfaces appeared shiny if there was a layer of oxide present? The modern party line answer to this question is that the surface of a polished metal is a colloidal suspension of metal and it oxide, and that this composition gives the surface its luster.

To test his hypothesis, Dobinski performed his polishing operation under dry benzene, and then transferred the still wet, polished samples to the vacuum chamber of the Thomson-Fraser camera where they dried off during the course of evacuating the chamber. With this protocol, Dobinski was able to obtain diffraction halos whose size corresponded to the size of the metal atoms. It is this point, that polishing in air contributes to the oxidation of the metal, which is of interest to us with respect to MOM 'diodes', since the flat metal base used in

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[365] S. Dobinski; The Structure of Polished Metal Surfaces; Philosophical Magazine [and Journal of Science]; Vol. 23 (7th Series); 1937; pp. 397-408. [Dobinski's earliest paper was apparently an article he coauthored with C.F. Elam,

S. Dobinski, C.F. Elam; Surface of Copper formed by Solidification *in vacuo*; Nature; Vol. 138; October 17, 1936; p. 685.

The thrust of this article was that the chemical or mechanical (polishing, burnishing or lapping) treatments of metal surfaces prior to electron diffraction studies introduced undesired artifacts ("…distortions…") into the surface. Dobinski and Elam thought that by forming the metal surface via vacuum casting, they would be able to obtain an artifact-free surface. What they found to their surprise was that the vacuum cast surface of, say, copper was populated by crystals preferentially oriented with their Miller (111) and (100) planes parallel to the surface. That a polycrystalline metal sample, free from any chemical or mechanical treatments of its surface, should exhibit such nonrandom crystallographic orientations of the individual crystals making up its surface indicated, again, just how different the surface was with respect to the bulk.]

[366] Dobinski was also concerned about the use of rouge (Fe_2O_3) or other polishing compounds, such as alumina (Al_2O_3), with water. His reasoning here is, quite rightly, that depending on the oxidation potential of metal-metal ion couple in the polishing compound versus that of the metal-metal ion couple of the polished sample, the polished metal may be oxidized directly and more extensively by the polishing compound than by the oxygen in air. By doing the polishing under dry benzene, he hoped both to alleviate the influence of atmospheric oxygen and reduce any possible aqueously mediated redox (reduction-oxidation) reactions between the metal sample and the polishing compound.

these structures is many times made by polishing the end of a metal rod. We shall return to this point later on.

It would be nice if we could end the story on this happy note, but we can't. Perusal of the Science Abstracts, Series A for a couple of years after the date of Dobinski's work (1937) revealed that a researcher named Plessing disputed many of Dobinski's experimental findings. At this point I am not sure if this dispute between Dobinski and Plessing was ever resolved, since both researchers seemed to have disappeared during and after the Second World War. Briefly, Plessing claimed that with only a few exceptions, the act of polishing under benzene did <u>not</u> affect the diameter of the electron diffraction halos.[367] Later review papers and books on the Beilby layer or tribology, in general, sometimes mention Dobinski's work,[368] but none I have seen ever address Plessing's challenge to Dobinski's experimental results. Why? I still don't know.

Let me briefly describe exactly what the nature of the disagreement was between Dobinski and Plessing. In his 1938 paper, Plessing investigated five pairs of metal mirrors each made of a different metal: gold, silver, iron, nickel and copper. One mirror of each pair was created by polishing in air, while the second mirror was produced using Dobinski's method of polishing under benzene so as to exclude the influence of the air, specifically the chemical reactivity of oxygen. In addition, Plessing followed Dobinski's proscription on the use of any polishing agents such as rouge, and hence did all his polishing using only a rotating wheel covered in clean Gazelle leather ["…Gazellenleder…"]. The only mirror pairs which showed a difference in their electron diffraction patterns, due to polishing in air versus under benzene, were those made of gold and silver. The mirror pairs constructed of iron, nickel and copper exhibited the <u>same</u> electron

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[367] E. Plessing; Zur Struktur polierter Metallflächen [Structure of Polished Metal Surfaces]; Physikalische Zeitschrift; Vol. 39; August 15, 1938; pp. 618-620. [Or see Science Abstracts, Series A; Vol. 41A; 1938; Abstract No. 3980.]

S. Dobinski; Zur Struktur polierter Metallflächen, Bemerkung zur Arbiet von E. Plessing [Structure of Polished Metal Surfaces, Remarks on the Work of E. Plessing]; Physikalische Zeitschrift; Vol. 40; April 1, 1939; pp. 232-233. [Or see Science Abstracts, Series A; Vol. 42A; 1939; Abstract No. 2369. In this paper Dobinski maintains that his orginal work was correct in spite of Plessing's results.]

E. Plessing; Bemerkung zur vorstehenden Notiz von S. Dobinski [Remarks on the foregoing Note of S. Dobinski]; Physikalische Zeitschrift; Vol. 40; April 1, 1939; pp. 233-234.

E. Plessing; Untersuchung bearbeiteter Metalloberflächen mittels Elecktroneninterferenzen [Structure of Worked Metal Surfaces]; Zeitschrift fur Physik; Vol. 113; No. 1-2; 1939; pp. 36-55. [Or see Science Abstracts, Series A; Vol. 42A; 1939; Abstract No. 3161.]

[368] At a conference on surfaces held in September 1952, Sir George P. Thomson mentions the probable artifact due to oxidation when polishing a metal surface in air as opposed to performing the operation under, for example dry benzene. However, Thomson does not directly reference the work of either Dobinski or Plessing, nor does he give any indication of their whereabouts and/or research interests post-WWII. See,

George P. Thomson; The Study of Solid Surfaces; in Robert Gomer, Cyril Stanley Smith (Eds.); <u>Structure and Properties of Solid Surfaces</u>; The University of Chicago Press; 1953; pp. 185-202.

diffraction patterns regardless of whether they had been exposed to or protected from the air during their polishing. Given these results, Plessing hypothesized that polishing did not increase the rate of oxidation of the metal surface in the presence of air. In order to prove his hypothesis Plessing decided to show that iron, nickel and copper mirrors made in air did not contain any significant amounts of the corresponding metal oxides. To do this, he annealed these polished mirrors in vacuum until their surfaces recrystallized, and then he reexamined their electron diffraction patterns. After annealing he found that the electron diffraction pattern was the same as the powder diagram (Debye-Scherrer pattern) for the corresponding metal without any trace of the metal oxide. In other words, the amorphous metal surface, which resulted from polishing in air or under benzene, reverted, upon vacuum annealing, to the standard polycrystalline state whose electron diffraction pattern mimicked that of a powdered polycrystalline sample of the same metal. The absence of any hint of metal oxide in the vacuum annealed metal mirrors, which had been polished in air, was used by Plessing as proof that polishing in air did not cause any significant oxidation of the Beilby layer.

In his reply, Dobinski pointed out that the chemical reaction

$$Me_x + O_y <=> Me_xO_y \qquad (D1),$$

where Me was the metal and O was oxygen, was reversible. This meant that annealing the mirrors in a vacuum might simply have decomposed any metal oxide into the pure metal and oxygen, the latter being removed by the vacuum pump. Hence, the absence of any metal oxide in the electron diffraction pattern after vacuum annealing did not constitute a proof that no oxide was present on the mirror as a result of the polishing. To further buttress his argument, Dobinski reported on the following experiments. A piece of copper was heated in air so that its surface became oxidized and thus covered with a layer of red cuprous oxide (Cu_2O). When this same piece of oxidized copper was vacuum annealed, the surface of the copper reverted to its pure metallic form as evidenced by both visual inspection and electron diffraction examinations. Thus, the chemical reaction (D1) proceeded towards the left in this case. In a second experiment, Dobinski vacuum annealed a clean (unoxidized) iron sample, and showed that the resulting annealed surface exhibited metal oxide electron diffraction patterns. In this case, the thermodynamic data indicated that the chemical reaction (D1) proceeded to the right with the iron apparently combining with what little oxygen there was present in the vacuum chamber. In Plessing's reply to Dobinski's reply, he [Plessing] conceded that, at least, in the case of copper, Dobinski's argument probably held true. But Plessing maintained that in the case of nickel mirrors, the oxide was known to be resistant to thermal decomposition under the conditions employed by him during the vacuum annealing. Plessing closed his reply by revealing that he and Dobinski had exchanged detailed notes on the procedures they used for polishing and vacuum annealing, but they were still confused as to why they could not achieve concordant results.

Plessing's last and most detailed paper (~20 p.) on this subject appeared in 1939. Unfortunately, I was not able to finish translating it due to time constraints. However, I did translate enough of it so that I became aware of the fact that other researchers had been intrigued enough by Dobinski's work to test one of his basic tenets: that immersion under benzene protected the metal surface from oxidation during the course of polishing. In 1938, two workers, Campbell and Thomas at the Bell Telephone Laboratories, showed that copper polished with a emery cloth under benzene did, indeed, become oxidized. [369] They postulated that it was oxygen dissolved in the benzene which was responsible for the oxidation. The technique they employed to measure the thickness of the oxide on the copper sample was a refined version of the chronopotentiometric technique discussed in APPENDIX B - refined in the sense that the cathodic reduction was accomplished under an oxygen-free electrolyte, and so was sensitive enough to detect oxide layers only a few Ångströms thick. [370] Plessing used this result to backup his contention that his own electron diffraction results, which showed that the radii of the diffraction patterns were the same no matter whether the polishing was done in air or under benzene, were correct.

As a postscript it should be noted that some recent work, which studied via AES (Auger [pronounced, oh-jay] Electron Spectroscopy) machined surfaces versus machined surfaces after mechanical polishing, showed the presence of large amounts of oxygen in or on the surfaces which had been machined and then mechanically polished; the iron peaks of these mechanically polished stainless steel specimens were also accentuated. [371] The metal samples were pieces of 347 stainless steel in the shape of disks 10 mm in diameter and 1 mm thick. The machining gave one of the disk surfaces a 32 µinch finish (presumably root-mean-squared). Those surfaces, which were subsequently polished, were first polished with a slurry of silicon carbide 600 grit, then 5 µm grit and finally silica salts of 0.05 µm grit. It should be noted that an oxygen and iron Auger fingerprint, identical to that of the machined and then mechanically polished specimen, could also be obtained by taking a machined specimen and then electrochemically polishing it.

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[369] W.E. Campbell, U.B. Thomas; Films on Freshly Abraded Copper Surfaces; Nature; Vol. 142; No. 3588; August 6, 1938; pp. 253-254.

[370] W.E. Campbell, U.B. Thomas; Tarnish Studies. The Electrolyte Reduction Method for the Analysis of Films on Metal Surfaces.; Transactions of the Electrochemical Society; Vol. 76; 1939; pp. 303-328.

[371] D. Wu, R. Outlaw, R. Stevens, P. Hopson; An Auger Electron Spectroscopy Study of Surface Preparation Contaminants; US Government; NASA TP-2972; February 1990; 16 p. [I wish to thank Ronald Outlaw of the Langley Research Center, Hampton, Virginia for sending me a copy of this report.]

§3. THE PRESENT STATE OF THE BEILBY HYPOTHESIS. - Just to show that, "It ain't over, until it's over!" it should be noted that the controversy about what the Beilby layer is, still rages on even today. In 1950, Bowden and Tabor [372] pointed to the then recent work of Raether (1947), which suggested that rather than being amorphous, the Beilby layer was polycrystalline on a very small scale. G. P. Thomson suggested in 1952 that this alternative view of Raether's was not really all that different than Beilby's in the limit of small polycrystalline crystals. [373] Thomson also mentioned experimental research which indicated that it was the difference between the melting point of the polishing compound versus that of the material being polished which determined whether or not a Beilby layer formed. Melting and the subsequent reflow of the surface was most likely to happen when the polishing compound's melting point (m.p.) was higher than that of the material undergoing polishing, e.g., calcite (m.p. 1330°C), while not exhibiting melting and then reflow when rubbed with cuprous oxide (m.p. 1235°C), did show the required melting and reflow and so took on a polish under the action of zinc oxide (m.p. 1800°C). [374] In 1960, L. E. Samuels challenged Beilby's claim that polishing caused plastic flows; Samuels, as a result of his own work, found evidence that polishing was just micro-abrasion. [375] It should be noted, that Samuels' ideas about the nature of polishing were actually not new, Sir Isaac Newton also thought of polishing as micro-abrasion. Bowden and Tabor's 1964 retrospective, while agreeing with Samuels' findings, did not see the ideas of Samuels and Beilby as being mutually exclusive since they depended on the exact conditions of the polishing operation: for certain speeds and polishing compounds Samuels' mechanism would dominant, while under different conditions Beilby's would hold sway. [376] Rabinowicz's 1965 book on friction and wear took no prisoners, it squarely and

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[372] F.P. Bowden, D. Tabor; The Friction and Lubrication of Solids; Oxford University Press; 1950; pp. 58-60.

[373] George P. Thomson; The Study of Solid Surfaces; in Robert Gomer, Cyril Stanley Smith (Eds.); Structure and Properties of Solid Surfaces; The University of Chicago Press; 1953; pp. 185-202.

[374] This condition, that the melting point of the polishing compound be higher than that of the material undergoing the polishing, implied that a Beilby layer will be formed. But Beilby layers also appeared to form even when this condition was not met, e.g., later on in this appendix we will consider the activation of platinum (m.p. 1772°C), for use as a hydrogen electrode, by rubbing it with the rounded end of a glass (m.p. <1200°C) stirring rod.

[375] L.E. Samuels; Damaged Surface Layers: Metals; in Harry C. Gatos (Ed.); The Surface Chemistry of Metals and Semiconductors; John Wiley & Sons; 1960; pp. 82-84. [Samuels seems to be the selfappointed champion of the alternate view of the Beilby layer, i.e., that it is composed of a fine polycrystalline matrix. His work in supporting this point of view spans at least 25 years, see,

D.M. Turley, L.E. Samuels; Nature of Mechanically Polished Surfaces of Copper: Polishing with Fine Diamond Abrasives; Metallography; Vol. 18; No. 2; May 1985; pp. 149-160.]

[376] F.P. Bowden, D. Tabor; The Friction and Lubrication of Solids, Part II; Oxford University Press; 1964; pp. 362-363.

exclusively sided with Samuels. [377] The term Beilby layer, with all that it implied, was still employed in Moore's 1975 book on tribology. [378] A very detailed diagram of the strata (including the Beilby layer) composing the surface of a worked piece of metal can be found in the 1985 book by Nachtman and Kalpakjian; the Beilby layer being associated with a thin work hardened layer at the surface. [379] Nachtman and Kalpakjian pointed out that a worked metal surface had an outermost layer of contaminant, then a layer of adsorbed gas and water, then an oxide layer which transitioned into the Beilby layer, and then finally the bulk layer. Lastly and surprisingly, a very thorough recent treatise on the history of tribology excluded any mention of Beilby or his layer. [380] Why?

What exactly the Beilby layer is composed of and how polishing influences the rate and type of oxidation are questions still waiting to be answered. But it should be pointed out that some scientists have already utilized the Beilby layer without waiting for the fine points to be elucidated. For example, in 1954 two electrochemists named Feakins and French, discovered that a perfectly good hydrogen electrode could be fashioned from platinum without first coating it with platinum black (see APPENDIX B). [381] What they did was to 'activate' the surface of a piece of platinum foil by rubbing it with the rounded end of a glass stirring rod. They postulated that the reason why this procedure worked was because their polishing of the platinum foil was producing a Beilby layer which, as a result of its structure, had increased adsorptive power for gases, hydrogen in particular. These same workers also discovered that just dipping the platinum foil in aqua regia (1 part concentrated nitric acid + 3 parts concentrated hydrochloric acid [382]) had the same effect as polishing with the glass stirring rod. In practice, they first polished the foil with the glass rod and then they gave it a short dunk in aqua regia. Why the aqua regia worked by itself, they did not speculate on. However, I have a theory that might explain why just aqua regia also 'activated' the foil. The process of making platinum foil, which may involve rolling, probably polishes the surface of the platinum to some extent thus creating a Beilby layer. This inadvertently produced Beilby layer would have its outer

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[377] Ernest Rabinowicz; Friction and Wear of Materials; John Wiley & Sons; 1965; pp. 184-186.

[378] Desmond F. Moore; Principles and Applications of Tribology; Pergamon Press; 1975; pp. 49-50.

[379] Elliot S. Nachtman, Serope Kalpakjian; Lubricants and Lubrication in Metalworking Operations; Marcel Dekker, Inc.; 1985; pp. 39-48, chapter 4.

[380] D. Dowson; History of Tribology; Longman; 1979.

[381] D. Feakins, C.M. French; E.M.F. Measurements in 10% Solutions of Acetone in Water; Chemistry and Industry; September 4, 1954; pp. 1107-1108.

D. Feakins, C.M. French; E.m.f. Measurements in Acetone-Water Mixtures: the Cell H2(Pt)|HCl|AgCl-Ag.; Journal of the Chemical Society (London); Vol.56; 1956; pp. 3168-3172.

[382] Aqua regia is used to dissolve gold, platinum, palladium; the other platinum metals such as iridium, osmium, rhodium and ruthenium are attacked more slowly. The mode of action of this reagent is as follows. The nitric acid oxidizes the noble metal atoms to metal ions, while the chloride ions provided by the hydrochloric acid complexes the resulting free metal ions, thus driving the reaction to completion.

surface eventually saturated with oxygen from the surrounding air just from sitting around. If this outer oxygen saturated layer of amorphous platinum was removed, say by dipping in aqua regia, then the freshly exposed underlying amorphous layers could function as a hydrogen electrode. There is some recent evidence to back up my theory. In 1990, a group of British researchers using a pocket size STM (Scanning Tunneling Microscope) scanned some samples of commercially available platinum foil in air and found the surfaces to be indeed amorphous.[383]

§4. THE BEILBY HYPOTHESIS BEFORE BEILBY. - So far we have discussed the physical and chemical consequences of the Beilby layer, but this layer also directly affects the work function of the metal. Surprisingly, this effect was known ~25 years before Beilby wrote his classic and still controversial work on the subject. Lord Kelvin (a.k.a. Sir William Thomson), in a paper supporting Alessandro Volta's experimental findings on the presence of a contact potential between different metals, remarked that he was aware of some work being done by one J. Erskine-Murray, which demonstrated that burnishing a clean, i.e., freshly abraded, metal surface significantly changed the contact potential measured after this metal was brought in contact with a reference metal and then separated, i.e., it affected the contact or Volta potential.[384] The contact potential could be restored to its initial, i.e., preburnished, state by abrading the burnished surface with a sheet of clean glass paper (a form of sandpaper made by depositing crushed glass on an adhesive backed paper). Kelvin's reaction to these experimental results was best expressed in his own words. "This seems to me a most important result. It cannot be due to the removal of oxygen, or oxide, or of any other substance from the zinc [the burnished metal]. It demonstrates that change of arrangement of the molecules at the free surface, such as is produced by crushing them together, as it were, by the burnisher, affects the electric action between the outer surface of the zinc and the opposed gold plate [the reference metal]." What Kelvin intuited was that mechanical working of a surface, by itself, changed the inner potential of the bulk metal, and that this change was not the result of oxidation because the change in contact potential was determined immediately after burnishing ceased so that there was not enough time for a significant oxide layer to form; Kelvin was quite aware that an oxide layer also affected the contact potential, independent of any mechanical working of the surface.

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[383] C.J. Roberts, B. Hoffmann-Millack, W.S. Steer; Sequential imaging of an amorphous platinum surface down to atomic resolution by STM in air; Measurement Science and Technology; Vol.1; 1990; pp. 199-200. [The design details of their portable STM can be found in, Idem; A Versatile Scanning Tunnelling Microscope for Use in Air; Measurement Science and Technology; Vol. 1; 1990; pp. 881-886.]

[384] Sir William Thomson, Baron Kelvin; Mathematical and Physical Papers, Vol. VI; Cambridge University Press; 1911; Papers No. 250, Contact Electricity of Metals, pp. 110-145. [The papers by Lord Kelvin referred to here were published in the *Proceedings of the Royal Society (London)* and the *Philosophical Magazine* between 1897 and 1898.]

Because of the importance of J. Erskine-Murray's work to the whole subject of the Beilby layer, I will expend a little more effort detailing some of his experimental protocols having to do with the Beilby layer. [385] Erskine-Murray's paper is divided into ten sections; the section I will be concentrating on will be Section III, Effects of Different Methods of Cleansing the Metallic Surfaces. This section started out with a description of the rationale and methodology of obtaining a clean surface. Specifically, Erskine-Murray stated that the metal plate under investigation must be cleaned via abrasion with a much harder substance: a hardened steel file, emery cloth or glass paper so as to leave as small an amount of contamination on the metal plate as possible. Under no circumstances were liquids ever to be used, as for example in making a polishing compound slurry, since even when the metal plate appeared to be dry, one could usually smell the telltale presence of the liquid - especially if the liquid is very aromatic - and even this minuscule amount of liquid could and did affect the resulting contact potential. To achieve uniformity in the act of abrading, the emery cloth or glass paper was fixed to a wooden roller made to rotate at a circumferential velocity of 100 cm/sec. And, in addition, the scratches made by this device were kept parallel to one another by maintaining the metal plate at a fixed orientation during the act of abrading it; keeping the scratches parallel prevented abrasive particles from getting lodged in the metal plate at the intersection points of nonparallel scratches. As an addition precaution, the emery cloth or glass paper was used only once or twice, and never on different metal samples - thus avoiding cross contamination. The measured contact potential of the metal plates cleaned by the above procedure were taken to be 'true' value of this quantity, and everything else was compared to it. Of course, this 'true' value of the contact potential only held for the particular metal plate and would not necessarily be the same for another plate made of the same metal.

To make matters more concrete, assume that the metal plate being tested was made of zinc and that the reference plate was gold. The true contact potential for this zinc plate, after being cleaned with glass paper, was +0.70 V. After the zinc plate was burnished for a time with a hardened steel tool, the contact potential rose to +0.94 V; remeasured 2 hours later, it was +0.92 V. Additional burnishing to achieve an even finer polish yielded a contact potential of +1.00 V, with still further polishing increasing the result to +1.02 V. Scratching the zinc plate at this point with the glass paper brought its contact potential back down to its 'true' value, i.e., +0.70 V. In general, Erskine-Murray found that the smoother the finish, the more positive the resulting contact potential.

It should be noted that the contact potential for the steel-gold couple was more negative than that between zinc-gold, and so it was unlikely that the change in the zinc-gold contact potential, due to burnishing with the hardened steel tool, was the result of the contamination of the zinc surface with steel. Nevertheless, Erskine-Murray decided to double check this assertion by taking a

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[385] J. Erskine-Murray; On Contact Electricity of Metals; Proceedings of the Royal Society (London); Vol. 63; 1898; pp. 113-146.

cleaned, i.e., scratched, copper plate and burnishing it against another clean copper plate. What he found was that the contact potential increased, as it had in the case of the zinc plate, although not as much, due to the difficultly of polishing a soft material such as copper with itself. As another check on measurement artifacts, the zinc plate was scratched with the edge of the hardened steel tool instead of using the glass paper, its contact potential versus gold was then determined, it was then burnished with the same tool, and its contact potential reexamined. The results confirmed the original results using the glass paper, i.e., burnishing of the scratched plate increased, in an algebraic sense, the contact potential.

As I was engaged in finishing this thesis, I happened upon a very interesting paper by one Angelika Maria Josefa Székely (de Doba), which covered exactly the same subjects as are considered in this thesis. While Székely did not mention J. Erskine-Murray *per se*, she did reference a paper by two English scientists whose work had elements in common with the work done by Erskine-Murray fourteen years earlier.[386] Briefly, this paper by Anderson and Morrison showed that a zinc or copper plate that had been allowed to oxidize in air over the course of years had a more negative contact potential, when in contact with a reference plate, than after it had been cleaned. For example, the contact potential of the uncleaned zinc [copper] versus its reference plate was 0.466 V [0.000 V], while the same piece after it had been cleaned register 0.826 V [0.060 V]. From these results, Anderson and Morrison concluded the following. "It is perhaps not too much to assume that, whatever be the cause of contact difference, it has its seat in the surface and not in the interior of the metal." Note, these authors did not explain exactly <u>how</u> they cleaned the zinc and copper that they employed. Hence, it was not possible to tell if the cleaning process resulted in some degree polishing of the surface or simply abrasion.

In all the experiments that Erskine-Murray performed, the potential of the burnished or scratched disk invariably showed signs of a time effect, i.e., upon mechanical treatment, the potential of the treated metal did <u>not</u> immediately settle to a final value, but instead slowly relaxed to a stable final value in the course of 1-3 hours. Erskine-Murray hypothesized that <u>part</u> of the time effect was due to transient heating of the metal disk due to mechanical working of its surface. In my opinion, the balance of the time effect was probably due to exoelectron emission.

In exoelectron emission, a metal surface can give off low energy electrons after being mechanically worked, with the rate of emission falling off exponentially to zero in an hour or two. Exoelectron emission, due to mechanical working of a metal surface, was first unambiguously observed in 1936 by W. B.

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[386] A. Anderson, H.N. Morrison; On Contact Difference of Potential, and the Action of Ultra-Violet Light.; Philosophical Magazine [and Journal of Science]; Vol. 24 (6th Series); July-December 1912; pp. 302-307. [Note, <u>no</u> reference was made to the work of either J. Erskine-Murray or Lord Kelvin on the subject contact potentials.]

Lewis and W. E. Burcham in connection with spurious counts seen subsequent to the mechanical cleaning of the inside walls of a Geiger-Müller tube.[387] Lewis and Burcham were trying to verify the existence of artificial radioactivity induced in aluminum by bombarding it with high energy electrons. To this end, they employed a cylindrical Geiger-Müller tube constructed out of a brass tube; one end held an ebonite (hard rubber) plug with a wire electrode through its center, while the other end of the tube could be closed off by a removable aluminum plate. The aluminum end plate was exposed for a time to a beam of high energy electrons, the end plate was then mechanically cleaned to remove tarnish that formed during its irradiation, and finally it was mounted in the end of the Geiger-Müller tube. Lewis and Burcham noticed that the counter tube would always register transient activity, with a half life of 10-20 minutes, even with the negative control, where the negative control was an aluminum plate to which everything had been done except the irradiation. Upon examining this effect more closely, they ascertained that even so gentle a cleaning procedure as polishing with a cloth produced electron emission.

Erskine-Murray's work on the effect of surface preparation on the contact potential has direct relevance to Samuel I. Green and Paul D. Coleman's theory of why MOM structures function. The theory of Green and Coleman required the existence of a difference in work function between the two pieces of metal making up the MOM device. This difference in work functions is not too hard to come by when the two metals are of different elements, but their model becomes less tenable when the same metal is employed in both pieces of metal, e.g., their gold-on-gold MOM 'diode' which exhibited such a high sensitivity. From Erskine-Murray's work it is easy to see how the two pieces of gold could have the required difference in work function just from the difference in processing each piece of metal is subjected to: the whisker, made from a drawn piece of gold which was subsequently electrochemically etched, and the base, made by

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[387] W.B. Lewis, W.E. Burcham; An Attempt to Produce Artificial Radioactivity by an Electron Beam, with some Notes on the Behavior of Newly made Geiger-Muller Counters; Proceedings of the Cambridge Philosophical Society; Vol. 32; No. 3; 1936; pp. 503-505. [In passing, I should like to note that exoelectronic emission goes back even further than the paper by Lewis and Burcham. In 1902, J.C. McLennan investigated what he thought was a new kind of radioactivity - it was actually exoelectron emission - induced in salts exposed to cathode rays (electrons),

J.C. McLennan; On a kind of Radioactivity imparted to certain Salts by Cathode Rays.; Philosophical Magazine [and Journal of Science]; Vol. 3 (6th Series); January-June 1902; pp. 195-203.

McLennan's paper mentioned that in 1895, Eilhard Ernst Gustav Wiedemann discovered that certain substances, among them some salts, became luminous for a time upon being heated after they were first exposed to cathode rays or spark discharges. Today this phenomenon goes by the name, thermoluminescence, and is recognized to be a form of exoelectron emission. Salts that were strongly thermoluminescent included the so-called solid solutions of Jacobus Van't Hoff discovered in 1890, e.g., $CaSO_4$ + 2% $MnSO_4$. Such solid solutions are today used in the field of radiation dosimetry and are called TLDs (ThermoLuminescent Dosimeters).

Note, because Wiedemann showed that cathode rays and spark discharges excited thermoluminescent materials, it was probable that the materials were actually being excited by the x-rays produced by the cathode ray tubes and spark discharges. If Wiedemann had pursued this further he might have discovered x-rays at the same time as Röntgen in 1895.]

vacuum depositing gold using Joule evaporation. It would be truly amazing if these two pieces of gold had the same work function. This argument does not, of course, prove that their model is correct, it only provides a modicum of evidence supporting the feasibility of the mechanism if it is right.

An additional electrical effect arising from polishing and hence presumably from the presence of the Beilby layer was discovered by Josef Waszik in 1924.[388] During the course of some investigations on the coherer effect, Waszik noticed that if two metallic contact pieces were painstakingly polished and then carefully brought into contact by laying one on top of the other, the resulting contact junction exhibited extremely high resistance. This high resistance, on the order of 10^8 to 10^9 Ω, remained even when upwards to 200 V was applied across the junction. Waszik made no mention of the Beilby effect and I am not sure he even knew of the concept. He did suggest that the polished surfaces were covered with an unknown gaseous or fluid layer, which gave the surface its high resistance. This supposition with regards to the nature of the insulating layer bears some superficial resemblance to that proposed earlier by Beilby. Especially if one assumes that the fluid layer was composed of the metal of the contacts in an amorphous form. Note, slight damage to the finish of the contacts, either from poor polishing or too rough a laying on of the contact pieces, caused them to essentially cohere, thus destroying their high resistance property.

Besides the high resistance, this mechanical junction also exhibited a strong attractive force between the two contacts in response to an applied voltage. Waszik recognized this effect as a manifestation of the Johnsen-Rahbek effect from two articles he had read.[389] The canonical structure in the

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[388] J. Waszik; Beitrag zur Erklärung der elektrischen Anziehung, die als Johnsen-Rahbek-Phänomen bezeichnet wird [Contribution to the elucidation of the electrical attraction, which characterizes the Johnsen-Rahbek phenomenon].; Zeitschrift für Technische Physik; Vol. 3; No. 1; 1924; pp. 29-31.

[389] K. Rottgardt; Elektrische Anziehung nach Johnsen-Rahbek und ihre Anwendung [Electrostatic attraction according to the Johnsen-Rahbek effect and its application].; Zeitschrift für technische Physik; Vol. 2; No. 11; 1921; pp. 315-328.

L. Bergmann; Über einige Messungen am elektrostatischen Relais [Some measurements on electrostatic relays].; Zeitschrift für technische Physik; Vol. 4; No. 1; 1923; pp. 11-14. [Note, Ludwig Bergmann, in the course of his measurements, made the following rather interesting discovery. When he substituted glass for the polished stone portion of the standard Johnsen-Rahbek capacitor, he observed that only one of the glass samples he used produced an attractive force in response to the applied voltage. The only glass that exhibited the Johnsen-Rahbek effect was an alkali glass, V 47, with a matt (matte or mat) finish; the other glasses he tried included a borosilicate glass, a regular mirror glass and a red or ruby glass. The obvious question one would ask, was why only the alkali glass produced the Johnsen-Rahbek effect? Note, Johnsen and Rahbek stated that the stone plate worked because it was a semiconductor, i.e., it conducted electricity only slightly. Alkali glasses are and were known to be the most conductive of all the glasses, and this probably explained why this glass worked. However, Bergmann's own measurements of the leakage currents indicated that the red or ruby glasses conducted electricity weakly, yet they did not work - a surprising finding; the borosilicate and the mirror glasses both did not conduct any measurable currents up to the highest voltages used, and so the fact that they did not work was no surprise.]

Johnsen-Rahbek effect was - up until the time of Waszik's discovery - a capacitor formed of a polished piece of stone (e.g., agate) and a flat metal plate. When a voltage was applied across this structure, it was found that a strong attraction existed between the polished stone plate and the metal plate. Waszik showed that one could develop the same effect using two polished metal plates, whose polished surfaces were carefully brought into contact.

§5. PRESENT DAY APPLICATIONS OF THE BEILBY HYPOTHESIS. - Finally, it should be mentioned that the concept - fuzzy as it is - of a Beilby layer is not the exclusive domain of metallurgists, tribologists, mechanical engineers and persons of that ilk. Electrical engineers and semiconductor material scientists also use the concept of the Beilby layer, and in this age of heightened awareness of surface phenomenon other surface related concepts such as 'surface reconstruction' are employed equally by the semiconductor material scientists and tribologists.[390] Some recent examples of the invocation of the Beilby layer in non-metallurgical realms include,

> i) After the growth of a large silicon or gallium arsenide crystal by the Czochralski process, the crystal is sawed into thin wafers which are then polished, chemically etched and lapped to a specular finish, these wafers will eventually be the substrate on which will be tattooed, for example, VLSI (Very Large Scale Integrated) circuits. The sawing, polishing and lapping invariably induce subsurface damage to the wafer surface, i.e., create a Beilby layer. The purpose of the chemical etching after the sawing and polishing is to remove these damaged layers, but in the process of stripping off these degraded layers, the etching generates some surface unevenness, which in turn has to be lapped away leading to some more subsurface damage. A recent article calls attention to these facts, especially for gallium arsenide which is significantly softer than silicon, and this article offers a noncontact method of assessing the subsurface damage using photon backscattering.[391]

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[390] Charles Kittel; Introduction to Solid State Physics, 6th Ed.; Wiley; 1986; chapter 19, Surface and Interface Physics.

Donald H. Buckley; Importance and Definition of Materials in Tribology - Status of Understanding; in William R. Loomis (Ed.); New Directions in Lubrication, Materials, Wear, and Surface Interactions; Noyes Publications; 1985; pp. 18-31ff.

[391] R.M. Silva; Instruments Detect and Remove Subsurface Wafer Damage; Research & Development Magazine (New York); Vol. 27; No. 2; February 1985; p. 203, 206, 208.

ii) The reduced ability of a video tape record and/or playback head to induce or pickup high frequency magnetic signals has been linked to the Beilby layer created on the surface of the head during the precision grinding and/or lapping process used to give it the proper form. [392] In this case, the material whose surface gets Beilbyized was either HPF (Hot Pressed Ferrite) or SCF (Single Crystal Ferrite) used in the head core. The machining induced Beilby layer on these materials tended to have a lower magnetic permeability than the bulk, which explained why the magnetic signal to or from the head was attenuated.

iii) In this next example, the researchers do not explicitly mention the Beilby layer by name, but their work strongly suggests such an association. Around 1954, two researchers, D. G. Flom and R. H. Savage at General Electric, were called upon to investigate and, if possible, solve a real world problem having to do with switch contacts. Specifically, it was found from field experience that certain relay contacts, motor commutators, etc., which were utilized in low voltage applications, were not performing properly. And the substandard performance, many times, occurred in new units, i.e., units right off the assembly line. Flom and Savage, using a probe made of a loop of thin platinum wire driven by a differential micrometer screw, probed the surfaces of the contacts and commutators for areas of high resistance; the circular wire probe, when pressed against the surface of interest with a few milligrams of force, allowed them to sense the presence of high resistance films, which others methods would have missed either because of lack of sensitivity or destruction or penetration of the high resistance film during the act of probing.

One of the contacts they examined was a silver slip ring. This ring had been manufactured with two different surface finishes: 1) machined without a lubricant and not physically handled, and 2) buffed on a high speed wheel after being machined. The slip ring with the machined surface exhibited the desired low contact resistance, and any areas of high contact

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[392] L. Strawinski, Z.M. Wawrzyniak; Influence of the Head Core Machining Upon the Fringing Field; Applied Physics A, Solids and Surfaces; Vol. 40; 1986; pp. 247-251.

resistance could be removed via a mild cleaning with a solvent. The buffed slip rings, on the other hand, always had areas of high resistance, which were not amenable to any mild cleansing procedures. These buffed silver surfaces resemble, to my way of thinking, the Beilby layers found on polished surfaces. Their high contact resistance could be due to the formation of a resilient oxide layer of the type proposed by Dobinski.[393]

iv) Although vacuum technology has been around for at least 300 hundred years, starting as it did with the hand operated air pump of Otto von Guericke in the latter part of the 1600s, the process by which one cleans the inside of a vacuum chamber is still more of an art than a science. In 1991, Y. T. Sasaki wrote a survey article on the preferred methods used by companies and research organizations to clean their vacuum chambers.[394] In particular, Sasaki cited a NASA report by Wu *et al.* which examined the contamination found on freshly machined surfaces versus freshly machined surfaces which had been subsequently mechanically polished; the degree of contamination was quantified by AES (Auger Electron Spectroscopy). Wu *et al.* found that the machined and polished surfaces had lower amounts of carbon and sulfur contamination - due presumably to the machining oil - than the just machined surfaces.[395] They attributed this difference to the decreased surface area of the machined surfaces which had

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[393] R.H. Savage, D.G. Flom; Exploration of Metal Surfaces with Fine Wires; Annals of the New York Academy of Sciences; Vol. 58; 1954; pp. 946-950.

Idem; Insulating Films on Metal Contacts; General Electric Review; Vol. 58; March 1955; pp. 59-61. [Flom and Savage, while investigating a high resistance area of a contact, noticed that when a nearby electrically isolated 60 Hz transformer was switched on or off, the resistance of the contact they were examining dropped in an irreversible manner. They later confirmed that the drop in resistance was an electromagnetic effect by activating a small spark gap transmitter - a capacitor discharging into an inductor - nearby the contact, but electrically isolated from it. Obviously what they saw was the coherer effect, although, they did not recognize it as this - their only outside reference, and this was only cited in the next paper, was the book by Ragnar Holm.]

Idem; Contact Resistance Measurements at Low Loads; The Review of Scientific Instruments; Vol. 29: no. 11; November 1958; pp. 979-981. [In its most sophisticated form, their probe consisted of a quartz spring with either a loop of platinum wire or a gold ball at its end.]

[394] Y. Tito Sasaki; A survey of vacuum material cleaning procedures: A subcommittee report of the American Vacuum Society Recommended Practices Committee; Journal of Vacuum Science & Technology A; Vol. 9; No. 3; May-June 1991; pp. 2025-2035.

[395] D. Wu, R. Outlaw, R. Stevens, P. Hopson; An Auger Electron Spectroscopy Study of Surface Preparation Contaminants; US Government; NASA TP-2972; February 1990; 16 p.

been mechanically polished. They did not mention the idea of Beilby layers, but clearly the assumed reduction in the surface area was consistent with Beilby's idea that polishing produced a flowed layer of amorphous surface material which tended to fill in the surface irregularities. It was also noted that such machined and polished surfaces did not respond to cleaning by solvents, i.e., the amount of contamination showed little or no change after such cleanings. Again, this appeared to go along with Beilby's idea that his layer sealed the surface with a rather impervious pellicle. As I have stated, no one mentioned Beilby's name or his layer, but certainly his ideas are supported by these findings.

v) In this final example, I will posit the involvement of the Beilby layer in certain aspects of the photoelectric behavior. One of the more obstreperous problems in constructing photoelectric cells was how to introduce a clean alkali metal film inside the highly evacuated glass envelope without denigrating the vacuum and/or contaminating the newly introduced metal film. One solution, which provided relief for a number of years until better techniques evolved, was to generate, say, pure sodium by electrolysis through the glass of the photoelectric cell. Briefly, an evacuated glass envelope made of sodium glass and containing a filament was partially immersed in a molten (312ºC) bath of sodium nitrate ($NaNO_3$), the filament of the bulb is lit by connection across either an AC or DC voltage source, a copper electrode immersed in the molten sodium nitrate bath was connected through a milliampere meter to either the + lead of the DC powered filament or to either lead if the filament is AC powered. Sodium ions at the inside surface of the bulb were reduced, i.e., picked up an electron, to metallic sodium by the thermionically emitted electrons from the heated filament, the sodium ions lost by the glass were replenished by sodium ions from the $NaNO_3$ bath, the resulting unpaired negatively charged nitrate ion being oxidized to a gas at the copper electrode. This phenomenon of electrolysis of alkali metals through glass has a long and convoluted history starting with Emil G. Warburg.[396]

One of the interesting things noticed by researchers about photoelectric cells manufactured this way was how the sensitivity of the cell depended of how smooth the metal film was. By cooling the part of the glass envelope that was not immersed in the molten salt with a stream of air, the sodium could be made to preferentially deposit on this cooled surface. Depending on how robust the cooling, the resulting surface of the film facing the vacuum could have either a microscopically smooth (specular or mirror-like) silver finish or a finely granular dull gray finish; the surface of the film in contact with the glass always had a specular finish. Surprisingly, the highest photoelectric sensitivity was associated with the dull gray finish, while the specular surface exhibits negligible sensitivity.[397] Since, the specular metal film was obtained under conditions of robust cooling, its mirror-like finish was probably the result the film

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[396] E.[G.] Warburg; Ueber die Electrolyse des festen Glases [Electrolysis of hard glasses]; Annalen der Physik und Chemie; Vol. 21 (New Series, a.k.a. 3rd Series); 1884; pp. 622-646 + Plate 6. [Note, heated glass was know to conduct electricity as far back as the 1760s. In a letter to E. Kinnersley, dated February 20, 1762, Benjamin Franklin mentioned that Lord Charles Cavendish - Henry Cavendish's father - had performed an "…ingenious experiment…" which proved this fact. See,

Arthur J. Berry; Henry Cavendish, His Life and Scientific Work; Hutchinson of London; 1960; p. 13.]

Another paper by Warburg having to do with electrolysis through glass, in this case for the purpose of depositing clean sodium inside a vacuum tube in order to getter residual oxygen, was,

E.[G.] Warburg; Ueber eine Methode, Natriummetall in Geissler'sche Röhren einzuführen und über das Kathodengefälle bei der Glimmentladung [Procedure for supplying Na metal into a Geissler tube and on the cathode fall of glow discharges]; Annalen der Physik und Chemie; Vol. 40 (New Series, a.k.a. 3rd Series);1890; pp. 1-17. [An English language translation of this rather lengthy article can be obtained from the National Translation Center, Library of Congress, Washington DC 20541. The cost is $35.00, and the ID# of the translation is 77-22546. This is a reasonably good translation of the article.]

R.C. Burt; Sodium by Electrolysis Through Glass; Journal of the Optical Society of America; Vol. 11; 1925; pp. 87-91. [Burt's motivation for depositing sodium inside evacuated glass bulbs by electrolysis was for the purpose of building photoelectric cells. The electrolysis trick allowed him to deposit a fresh clean layer of sodium inside the glass bulb.]

V.[K.] Zworykin; Electrolytic Conduction of Potassium Through Glass; Physical Review (2nd Series); 1926; p. 813. [This reference was an abstract, not a complete paper. Note, Vladimir Kosma Zworykin was better known as the 'Father of television'. Zworykin's motivation was the same as R.C. Burt's, he was trying to construct photoelectric cells for use in the television and movie industry.]

[397] P. Selényi; The Manufacture, Properties, and Use of Sodium Photo-Electric Cells; in John S. Anderson (Ed.); Photo-Electric Cells & Their Applications; The Physical and Optical Societies; 1930; pp. 25-42.

not crystallizing properly, much in the same way as happens during the making of a glassy or amorphous metal, where a ribbon of molten metal is allowed to fall on a cooled rotating drum.

APPENDIX E - THE STM (Scanning Tunneling Microscope)

> "Nothing, of course, begins at the time you think it did."
> - Lillian Hellman

> "By the way, what I have just outlined is what I call a "physicist's history of physics," which is never correct. What I am telling you is a sort of conventionalized myth-story that the physicists tell to their students, and those students tell to their students, and is not necessarily related to the actual historical development, which I do not really know!"
> - book, QED… by Richard P. Feynman

§1. INTRODUCTION. - In its most basic realization, the STM consists of an atomically sharp metal tip 'flying' over the flat surface of an electrically conducting plane sample at a distance on the order of 5-10 Å; a low DC voltage on the order of a 1 V is applied between the tip and the conducting sample causing an electron tunnel current to flow between the available energy levels in the tip and plane sample; the tip's standoff distance (z-direction) from the sample is usually maintained via a servomechanism, whose reference signal is the desired magnitude of the tunnel current and whose control signal is applied to a z-direction piezoelectric crystal driver; and, lastly, the tip can also move parallel (x- & y-direction) to the surface of the sample via x-direction and y-direction piezoelectric crystal drivers.

In their August 1985 *Scientific American* article on the STM, [398] the inventors, Gerd Binnig and Heinrich Rohrer, who shared the 1986 Nobel Prize in Physics shared with Ernst Ruska for his work in the development of electron microscopy, [399] gave a very abbreviated and rather superficial history of the scientific developments which led up to the STM in its present form. The lack of historical rigor in this *Scientific American* article was most likely due to the fact that Binnig and Rohrer, like most practicing scientists, were less well acquainted with the history of their profession than they were probably aware of. Binnig and Rohrer's history of the STM started in 1927 with Clinton J. Davisson and Lester H. Germer's experimental verification of the wave nature of the electron, shown by the diffraction of electrons off the face of a single crystal of nickel; followed by the work, circa 1950, of Erwin W. Müller on the field-ion microscope (FIM), which allowed, for the first time, images to be made of individual atoms by inverse mapping of the intersected trajectories of field ionized helium ions scattered from a positively charged tungsten tip; and lastly, "…the first experimental verification of tunneling…", according to Binnig and Rohrer, by Ivar Giaever around 1960 - this last assertion was clearly erroneous as will become obvious later on in this appendix. A much more detailed and relevant discussion of the history of the STM can be found in Binnig and Rohrer's Nobel Prize lecture, but even here the history was not as complete as it should have been. [400] In particular, it did not address itself to the origins of the phenomenon of field emission which was first reproducibly observed with a device that presaged the modern STM in many ways.

I should like to propose a somewhat different history leading up to the invention of the STM. In this history, I shall show how the confluence of scientific insights coupled with technological advances conspired to make the discovery of the modern realization of the STM highly probable if not inevitable. The STM

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[398] G. Binnig, H. Rohrer; The Scanning Tunneling Microscope; Scientific American; Vol. 253; No. 2; August 1985; pp. 50-56.

[399] Note, a Nobel Prize may only be split a maximum of three (3) ways, and it is not awarded posthumously, except in the case where the winner(s) had been notified, accepted the award and then dies before they can travel to Stockholm to actually receive it.

[400] Gerd Binnig, Heinrich Rohrer; Scanning Tunneling Microscopy - From Birth to Adolescence; in W. Odelberg (Ed.); Les Prix Nobel, 1986; Almqvist & Wiksell International; 1987; pp. 91-111. [According to Rohrer, "… [he] had been involved for a short time with tunneling between very small metallic grains in bistable resistors…" This intriguing statement suggests coherer-like behavior. In order to find out more about this work, I have written to Dr. Rohrer requesting any references he might have on this subject. His address is: Dr. Heinrich Rohrer, IBM Zurich Research Laboratory, CH 8803 Rüschlikon, Switzerland. By way of reply, Rohrer sent me 16 reprints of articles on STMs! I have still not been able to determine which of these articles relates to the "…bistable resistors…" he spoke of in the Nobel Lecture. However, I was able to clear up something that had always confused me about Les Prix Nobel, 1986, namely why only Rohrer's biography appeared - Gerd Binnig's was nowhere to be found. One of the reprints sent me by Rohrer was of his and Binnig's contributions to Les Prix Nobel, 1986 and it contains, in addition to the their Noble Lecture, the separate biographies of both Rohrer and Binnig. The mystery is solved, the printer apparently simply forgot to include Gerd Binnig's biography in the finished volume.]

depends on three fundamental pieces of scientific or technological knowledge: 1) the existence of electron tunneling, 2) a stable and precise method for positioning the metal tip close to the plane conducting surface to be examined, and 3) a method of measuring steady currents in the picoampere (10^{-12} A) to nanoampere (10^{-9} A) range.

Our starting point will be the decade beginning with 1880. This decade produced Paschen's law of electrical conduction in gases, which then led directly to the initial discovery and then verification of electron tunneling between closely spaced metal electrodes within 20 years. In addition, the 1880s witnessed the invention of what was and still is the most sensitive method for measuring small distances, interferometry - specifically the Michelson interferometer and all its subsequent modifications and adaptations. And as if all this were not enough, the year 1880 also witnessed the discovery of the phenomenon of piezoelectricity by Jacques and Pierre Curie. These were all the basic ingredients needed to concoct the modern STM.

§2. PRELUDE: ELECTRICAL CONDUCTION IN GASES. - That air conducts electricity became obvious once one understood the electrical nature of lightning; the experiments to prove the electrical nature of lightning were first suggested by Benjamin Franklin in 1750. The actual experiments were first performed in France by d'Alibard - Franklin's famous kite experiments came later. [401]

Beside his experimental endeavors, Franklin also made a significant contribution to the theoretical understanding of electricity in the form of his one-fluid theory of electrical phenomena. Franklin's one-fluid theory of electricity was able to explain and, hence, organize the rather chaotic collection of observations of electrostatic phenomena then extant. The two-fluid ("vitreous [+]" & "resinous [-]") theory of Charles François Cisternay du Fay or Dufay, which was conceived somewhat before Franklin's one-fluid theory, was the other competing paradigm. The one-fluid theory of Franklin was able to account for electrostatic behavior in simpler manner, and it presaged, by more than a century, the discovery of the electron - the universal electric fluid.

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[401] There seemed to be some confusion about the actual name of this Frenchman. According to,

Martin A. Uman; All About Lightning; Dover Publications, Inc.; 1986; pp. 1-6.

his name was Thomas-François d'Alibard, but according to,

Albert Parry (Ed.); Peter Kapitsa on Life and Science; Macmillan Co.; 1968; pp. 38-39 & 245.

the man's name was Jean François Dalibard. What both books did agree on was that he [d'Alibard] did perform the experiments on the electrical discharge from clouds before Benjamin Franklin. In an effort to clarify the identity of d'Alibard, I checked the following reference,

Roman d'Amat; Dictionnaire de Biographie Française, Vol. 9; Librairie Letouzey et Ané; 1961; p. 1521.

which revealed that it was one Thomas-François d'Alibard (1709-1779) who translated into French Ben Franklin's book Experiments and Observations on Electricity. This still did not answer the question of where Peter Kapitsa [or more likely his editor, Albert Parry] obtained the attribution for the French translation to "Jean François Dalibard, 1703-99" found in endnote #2, p.245 of Peter Kapitsa on Life and Science . Endnote #2 referenced two books as the source of the information on the translation,

Leonard W. Labaree *et al.* (Eds); The Autobiography of Benjamin Franklin; Yale University Press; 1964; p. 331.

Alfred Owen Aldridge; Franklin and his French Contemporaries; New York University Press; 1957; p. 21 & 239.

Amazingly, these two books disagreed on d'Alibard surnames. Labaree's book correctly stated that Thomas-François Dalibard was the translator, while Aldridge's book touted Jean François Dalibard as the translator. Examination of the references in Aldridge's book revealed that he got his incorrect information on d'Alibard from,

I. Bernard Cohen; Benjamin Franklin's Experiments; Harvard University Press; 1941; p. 440.

In the Index of Cohen's book (p. 440), there was listed one "Jean François Dalibard (1703-1799)". The explanation for this appalling state of confusion probably originated in the fact that the French versions of Franklin's Experiments and Observations on Electricity are translated "par M. d'Alibard". This irritating affectation of dropping the surnames of French authors in this time period was quite common. The first and second editions of d'Alibard's translations can be found at The Library Co., 1314 Locust St., Phila. PA 19107, (215)546-2465; their hours are M-F 9:00 AM to 4:45 PM.

Conduction of electricity through other gases or mixtures thereof followed immediately, e.g., Alessandro Volta's eudiometric pistol, with which he discovered methane, and Sir William Watson's discovery of electrical conduction in rarefied air and the fact that the conduction increased as the pressure of the gas decreased. The quantification of this behavior attained its most succinct form - Paschen's law - as the result of the work of Louis Carl Heinrich Friedrich Paschen.[402] Paschen's doctoral thesis of 1888, suggested to him by his advisor, August Kundt, involved observing the sparking behavior of two spherical electrodes in a gas; with a fixed voltage applied to the electrodes, the sparking distance was noted for a given gas pressure. Note, the discharge voltages plotted by Paschen and the researchers who followed him were always the <u>minimum</u> voltages which produced a discharge under the conditions of the experiment. The results of these experiments by Paschen revealed that, for a fixed voltage, the spark length was inversely proportional to the gas pressure, i.e., gas pressure versus spark length yields a rectangular hyperbola, see Fig. E1. As was the case with most scientific laws, Paschen's law was subject to much testing to scope out the limits of its validity.

One of the most exhaustive attempts at verifying this law came as a result of the work of J. B. Peace in England.[403] Peace's work consisted of measuring the sparking voltage as a function of the gas pressure and plane electrode separation; the gas used in all his measurements was air. Peace's results confirmed Paschen's law in the portion of the rectangular hyperbola closest to the origin, i.e., the most curved part of the hyperbola; the agreement was less good for the two straight portions of the curve, i.e., the sections corresponding to low pressure or short spark lengths. Because Peace's gas pressures went below 2 cm. of Hg, his curves of gas pressure versus sparking voltage for fixed electrode separation exhibited a monotonic increase in the sparking voltage for pressures less than what has come to be called the 'critical' pressure; Paschen did not witness this behavior since his lowest pressures exceeded the critical pressure for the electrode separation he employed; in his spark voltage versus gas pressure curves at fixed electrode separation, the sparking voltage monotonically decreased with decreasing pressure.

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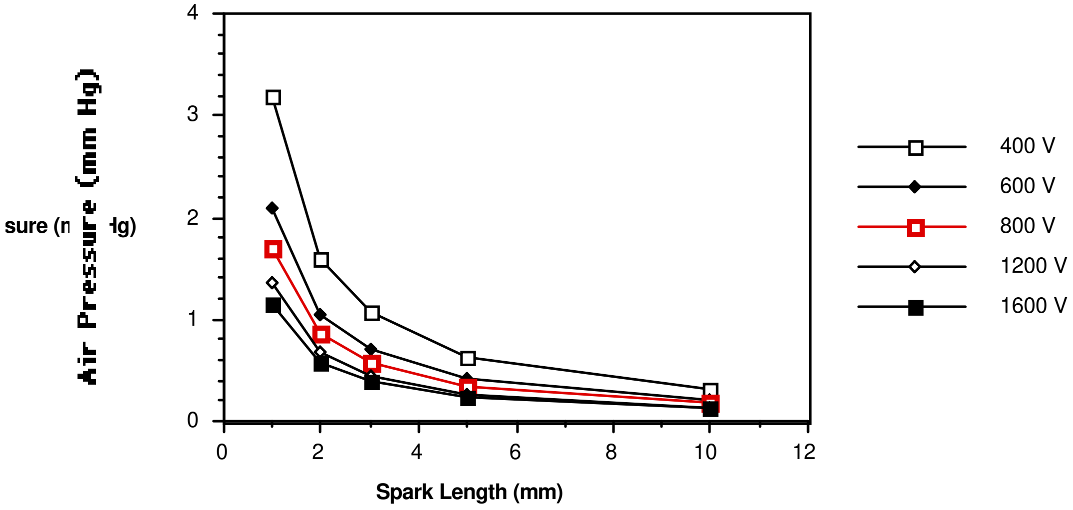
[402] [L.C.H.]F. Paschen; Ueber die zum Funkenübergang…erforderliche Potentialdifferenz [On the spark discharge…required potential difference]; Annalen der Physik und Chemie; Vol. 37; 1889; pp. 69-96.

[403] J.B. Peace; On the Potential Difference required to produce a Spark between two Parallel Plates in Air at Different Pressures.; Proceedings of the Royal Society (London); Vol. 52; 1892; pp. 99-114.

FIGURE E1 - Paschen Plot Using Data From W. R. Carr.



The nonconformance of some of Peace's data to Paschen's law stimulated a graduate student, W. R. Carr, at the University of Toronto to replicate the same experiments with better designed equipment. [404] From his reading of Peace's paper, Carr deduced that Peace's apparatus did not subject the gas to a uniform electric field due to the fringing fields present at the edge of the plates, which were exposed to the gas and, by Peace's own admission, were the site of corona discharges. Carr's apparatus also employed plane electrodes, but, unlike Peace's configuration, the edges of these electrodes were buried in ebonite (a hard rubber). Carr mentioned that when applying the voltage across the electrodes, starting at a low voltage and progressively increasing it until a discharge ensued, it was of utmost importance to wait more than fifteen minutes between each increase due to the time lag between application of an above

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[404] W.R. Carr; On the Laws governing Electric Discharges in Gases at Low Pressure.; Proceedings of the Royal Society (London); Vol. 71; February 11, 1903; pp. 374-376. [Note, this was only an abstract of the paper that appeared in the Philosophical Transactions of the Royal Society.]

Idem; On the Laws governing Electric Discharges in Gases at Low Pressure.; Philosophical Transactions of the Royal Society (London); Vol. 201 (Ser. A); 1903; pp. 403-433.

threshold voltage and the breakdown of the gas, an effect first alluded to by Warburg; the time lag is most pronounced near the critical pressure. [405] With this improved apparatus, Carr was able to show that Paschen's law held over all pressures, even those well below the 'critical' pressure. In addition, the family of plots of sparking voltage versus gas pressure for various electrode separations revealed the presence of a unique minimum spark voltage, this minimum voltage was, for a given electrode geometry, only dependent on the nature of the gas, changing the electrode material and/or spacing did not affect it, see Fig. E2. This result was very significant, since it meant that for a particular electrode geometry there was a definite ionization threshold for the gas in the interelectrode volume. The ability of STMs to work in air is explained by this fact as is the resistance of electrostatically driven micromachines to breakdown of the air gaps supporting these fields. [406]

The validity of Paschen's law was also extended by Carr to gases other than air: hydrogen, carbon dioxide, oxygen, hydrogen sulfide, nitrous oxide, sulfur dioxide and acetylene; all the gases tested by Carr were found to exhibit a unique minimum sparking voltage. [407]

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[405] E.G. Warburg; Ueber die Verzögerung bei der Funkenentladung [On the Time-Lag at the Spark Discharge]; Annalen der Physik und Chemie; Vol. 62 (3rd Series); No. 11; 1897; pp. 385-395.

[406] Re STMs, when asked why STMs are able to function in air without breaking down due to a gas discharge, a well worn explanation is that when the tip and base electrode are only 5-10 Å apart, no air can get between them to be ionized. The problem with this rationalization is that it ignores the breakdown path between the base electrode and the shank of the tip electrode, this distance is 1000s of Ångströms in length. What prevents the air from breaking down in this region? The answer is the existence of a minimum discharge voltage.

Re micromachines, "In fact, the breakdown electric field [emphasis added] increases in small gaps by a factor of over 10 times the macroscopic limit of 3 megavolts per meter, resulting in an even more favorable scaling for electrostatics." See,

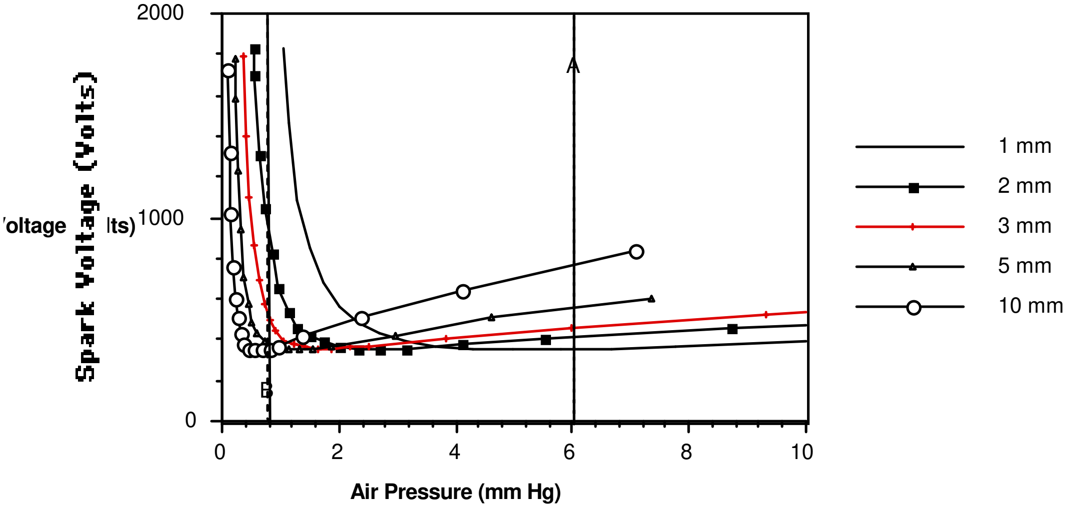
R.T. Howe, R.S. Muller, K.J. Gabriel, W.S.N. Trimmer; Silicon micromechanics: sensors and actuators on a chip; IEEE Spectrum; Vol. 27; No. 7; July 1990; pp. 29-35.

This quote implicitly pays homage to Paschen's law, since in air at STP (Standard Temperature & Pressure: 20°C & 760 mm Hg) smaller gaps require larger electric fields to initiate a discharge. Consider the following example taken from Fig. 8 of Carr's 1903 paper. The discharge electric field for a 250 µ gap @ STP was 1800 V/250X10^{-6} m = 7.6X10^{6} V/m, while for a 5 µ gap the required field was 380 V/5X10^{-6} m = 76.0X10^{6} V/m. I wish to thank Jennifer Coyle-Byrne for bringing this article by Howe *et al.* to my attention.

[407] Carr used R.J. Strutt's (the 4th Baron Rayleigh) values for the minimum spark voltage of nitrogen,

Hon. R.J. Strutt; On the Least Potential Difference Required to Produce Discharge through Various Gases.; Philosophical Transactions of the Royal Society; Vol. 193 (Ser. A); 1900; pp. 377-394.

FIGURE E2 - Critical Pressure Plots Using Data From W. R. Carr.



I should like to backtrack for a moment and set the record straight. W. R. Carr is rightly given the credit for having pointed out the deficiencies in J. B. Peace's apparatus and determining Paschen curves for a myriad of experimental conditions: different gases, pressures, and electrode spacings. But it must be pointed out that three years earlier, R. J. Strutt (son of J. W. Strutt, a.k.a. 3rd Baron Rayleigh or simply Lord Rayleigh) had taken similar precautions with his apparatus when he measured the minimum discharge voltage for a number gases, including the then very hard to come by gas, helium. [408] Strutt's

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[408] Hon. R.J. Strutt; On the Least Potential Difference Required to Produce Discharge through Various Gases.; Philosophical Transactions of the Royal Society; Vol. 193 (Ser. A); 1900; pp. 377-394. [Strutt obtained helium by either chemically digesting in sulfuric acid or roasting in a furnace a mineral called monazite, then chemically purifying the resulting gas given off by the treated mineral. The main impurity, nitrogen, was removed via the Cavendish method, i.e., pure oxygen was added to the gas mixture, an electrical spark was then passed through the mixture to cause the nitrogen and oxygen to react with one another forming compounds which could then be removed by chemical absorbents with the remaining unreacted gas being composed mostly of helium. Henry Cavendish originally used this technique with atmospheric air and showed that it was partially composed of an inert gas or gases; J.W. Strutt (a.k.a. 3rd Baron Rayleigh) and W. Ramsay redid Cavendish's work and were able to show that the inert gas was made up mostly of a new element, argon. They received the Noble Prize for this and other related work. Cavendish's other lesser known but significant contributions to science include his experimental proof of the inverse square law for electric charges, which he did before Charles Augustin de Coulomb, and his experimental proof of Ohm's law, which he did before Georg Simon Ohm. Cavendish did not receive credit for the aforementioned discoveries for a simple reason, he did not publish all of his results; many were found among his papers after his death.

Note, in 1906 Lord Kelvin used the fact that helium could be obtained from minerals such as clevite and monazite to argue against the then new theory of radioactive decay and its attendant transmutation of elements. Kelvin's reasoning was that just because a mineral contained helium, this did not prove transmutation - e.g., by alpha particle decay - since the helium could have simply been sequestered in the mineral from perhaps the atmosphere. Surprisingly, Kelvin was both wrong and right at the same time. He was wrong about the source of helium in clevite; clevite and monazite contained uranium and thorium, respectively, and so this accounted for the safeguards against measurement artifacts due to discharges from the edge or back of his plane electrodes consisted of setting the brass plates into recesses machined into the face of a pair of ebonite disks so that the electrode's front surface was flush with the surface of the insulator. Unlike Carr, Strutt did not employ electrochemical batteries, but used instead a motor driven Wimshurst electrostatic machine[409] connected in parallel with a large Leyden (Leiden) jar (capacitor) and a fluid resistor, this configuration formed a very stable adjustable power supply with the Leyden jar smoothing out the voltage ripple and the fluid resistor providing an adjustable load to the Wimshurst machine thus allowing the voltage to be varied; the discharge of the gas was sensed by the resulting sound in a telephone receiver in series with the brass electrodes. Strutt mentioned in passing that the first spark to pass through a gas could require as much a three times the voltage as the succeeding sparks. Consequently, his measurement protocol consisted of slowly increasing the applied voltage until the first spark occurred, ignoring this voltage reading and then decreasing the voltage; [410] the

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presence of helium - through transmutation. On the other hand, he was right that certain substances have a natural affinity for atmospheric helium, see APPENDIX B of this thesis where glass and certain metals are shown to be helium loving. For more details about Lord Kelvin's disagreement with the radioactive decay theory see,

Florian Cajori; A History of Physics…; The Macmillan Co.; 1935; pp. 298-302.

The theory of radioactive decay seems to have had a special place on Lord Kelvin's list of Ten Things I Hate the Most, since it was also responsible for shattering his estimation of the age of the Earth. The heat produced by radioactive decay was a significant source of heat generation inside the Earth, and so violated one of Kelvin's main assumptions. For more information see,

Joe D. Burchfield; Lord Kelvin and the Age of the Earth; The University of Chicago Press; 1990.]

[409] Until the advent of the Van de Graaff generator (circa 1933), the Wimshurst influence machine (a.k.a. Wimshurst machine) was the most reliable (i.e., no spontaneous polarity reversals), self-exciting, easy to use, high voltage generator around. James Wimshurst (1832-1903) produced the first Wimshurst influence machine in the early 1880s. It was of a radically different design than all the influence machines that had gone before it. In fact, Wimshurst himself took obvious delight in pointing out that his machine incorporated many of the same features specifically condemned as antithetical to 'good' influence machine design by the two reigning experts on such contrivances, Lord Kelvin (a.k.a. Sir William Thomson) and W.T.B. Holtz. For more information, see,

C.N. Brown; James Wimshurst, His Machine and its Antecedents; Papers Presented at the 10th IEE Weekend Meeting on the History of Electrical Engineering; Brighton, U.K.; July 2-4, 1982; 6 p. [**Note**, this paper was impossible to find in the U.S. I ordered the entire proceedings of the 1982 Brighton meeting through the London office of the IEE, P.O. Box 96, Stevenage, Herts. SG1 2SD, United Kingdom; these proceedings cannot be ordered through the IEE offices located in New Jersey, U.S. The price was £11.00.]

[410] Between 1946 and 1953 F. Llewellyn Jones investigated this effect, and determined first, that it was real and second, that it was most likely due to the layer of oxide on the surface of the electrodes. This oxide layer was thought to trap positive ions, which would then reduce the work function for electron emission thus reducing the required discharge voltage,

F. Llewellyn Jones; Electrical Properties of Tungsten Oxide Films; Nature; Vol. 157; March 23, 1946; pp. 371-372.

Idem; Electrode Ionization Processes and Spark Initiation; Proceedings of the Physical Society (London); Vol. 62 (Series B); 1949; pp. 366-376.

F. Llewellyn Jones, E.-T. De La Perrelle, C.G. Morgan; La rôle des électrodes dans le mécanisme d'amorçage de la décharge électrique dans les gaz. [The *rôle* of the electrodes in the subsequent cycles of cautiously increasing the voltage until the sound of the discharge was detected, were followed by recording of the discharge voltage and then decreasing the voltage, these cycles were usually repeated ten times.

At the conclusion of his paper, R. J. Strutt attempted to relate the minimum in the discharge voltage versus pressure curve to the corresponding value of the cathode fall for the same gas. [411] The cathode fall being the voltage drop of the glow discharge structures associated with the cathode, i.e., the various dark spaces (Faraday's, Crookes' & Aston's) and the corresponding intervening luminous areas, but excluding the positive column and those gas discharge structures associated with the anode. In fact, the cathode fall represented most of the voltage drop found in glow discharge. In this endeavor he was encouragingly successful, thus providing some physical insight into the physical nature of the discharge mechanism.

Once the validity and scope of Paschen's law had been confirmed, the next step was to develop a theory that would explain the observations. The person, whose theory most completely accounted for the observed facts, was the Irish physicist, John Sealy Edward Townsend. The crux of Townsend's theory was that the atoms or the molecules making up a gas could be ionized by single collisions with charged particles (electrons and/or positive ions) accelerated by the impressed electric field. [412] Since the resulting ion pair usually consisted of a

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initiation of electrical discharges in gases]; Comptes Rendus Hebdomadaries des Seances de l'Academie des Sciences (Paris); Vol. 232; 1951; pp. 716-718.

F. Llewellyn Jones, C.G. Morgan; Surface films and field emission of electrons; Proceedings of the Royal Society (London); Vol. 218 (Series A); 1953; pp. 88-103.

Note, Frank Llewellyn Jones also wrote a book on the subject of electric contacts. This is only the second book that I know of on this particular subject - the first, and by far the most famous, book addressing this topic was that penned by Ragnar and Else Holm. The citation for F. Llewellyn Jones' book is,

Frank Llewellyn Jones; The Physics of Electrical Contacts; Oxford University Press; 1957.

[411] The measurement of the cathode fall reached its most sophisticated form in the method first proposed by J.J. Thomson and then later realized by F.W. Aston,

F.W. Aston; The Distribution of Electric Force in the Crookes Dark Space; Proceedings on the Royal Society (London); Vol. 84 (Series A); 1911; pp. 526-535.

[412] Of the competing ionization-by-collision theories, the one by J.J. Thomson was the most interesting since it gave insight into his view of the atom. Thomson's idea was that an atom broke apart (ionized) as the result of repeated collisions with electrons or ions. He thought that these recurring collisions eventually destabilized the atom causing it to literally explode. This model was probably consistent with his "plum-cake" model of the atom (sometimes called the "plum pudding" model), wherein the electrons of the atom were distributed in a matrix of equal but opposite charge; the neutron had not been discovered, yet, and so was not part of the model. See,

Max Jammer; The Conceptual Development of Quantum Mechanics; McGraw-Hill Book Co.; 1966; p. 69.

According to this model, the electrons could be either stationary or moving. From Maxwell's work, it was realized that a single electron moving in a closed orbit would radiate away its energy. Thomson was, of course, aware of this, but pointed out that if the electrons were situated in a ring and rotated in such away as to maintain their relative positions to one another, the radiated energy was enormously reduced - in one simple example by as much as 10^{16}. The more electron and a positive ion, and because these charged particles, again under the influence of the impressed field, could produce further ionizations, the system could be said to possess a form of positive feedback. This self reinforcing behavior embedded in Townsend's model nicely explained the existence of self sustained discharges, e.g., glow discharges and arcs.

§3. VERIFICATION OF PASCHEN'S LAW AT SMALL DISTANCES AND THE RESULTING UNEXPECTED PHENOMENA (THE AMERICAN EFFORT). - The question of the nature of light and the medium which supported its vibration, the ether, began to assert itself in the 1800s. Even a brief history of this effort could take ten or twenty pages, and so I will not attempt it, here. [413] What I will discuss, briefly, was Albert Abraham Michelson's contributions to the study of the motion of the Earth through the ether.

In September 1880, Michelson arrived in Berlin to begin study for his PhD at the Humboldt University of Berlin. For his thesis, Michelson decided to attempt to detect the motion of the Earth through the ether. His thesis advisor, Hermann Ludwig Ferdinand von Helmholtz, could find no fault with the intended approach other than the difficulty in maintaining the temperature constant enough that it did not produce a measurement artifact. Using funds provided by Alexander Graham Bell, Michelson had the firm of Schmidt and Haensch construct his first "interferential refractor" or what has since been come to be known as a Michelson interferometer, and performed his first ether drift experiment in Potsdam in 1881. [414] In 1887, Michelson and E. W. Morley redid the Potsdam experiment at Case University in Cleveland with a much improved interferometer. [415] Despite the incontestable success of his ether drift

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electrons in the atom, the better its stability. For atoms with more and more electrons, one ring or shell would not do, but Thomson's model allowed for multiple rings or shells.

With this model it would be very difficult for a single collision to ionize the atom, since its electrons were effectively shielded, both physically and electrically, from the outside world by being embedded in the matrix of positive charge. For a description of Thomson's model of the atom, see,

J.J. Thomson; On the Structure of the Atom: an investigation of the stability and periods of oscillation…; Philosophical Magazine [and Journal of Science]; Vol. 7 (6th Series); March 1904; pp. 237-265.

It should be noted that this model was actually rather the favorite among the more classically disposed physicists. See,

Lord Kelvin; Aepinus Atomized; Philosophical Magazine [and Journal of Science]; Vol. 3 (6th Series); March 1902; pp. 257-283.

[413] J. Lovering; Michelson's Recent Researches on Light; Annual Report of the Board of Regents of the Smithsonian Institution; July 1889; pp. 449-468.

[414] A.A. Michelson; The Relative Motion of the Earth and the Luminiferous Ether.; American Journal of Science; Vol. 22 (3rd Series); 1881; pp. 120-129.

[415] A.A. Michelson, E.W. Morley; On the Relative Motion of the Earth and the Luminiferous Ether.; American Journal of Science; Vol. 34 (3rd Series); 1887; pp. 333-345. [Note, the mere possession of a Michelson interferometer did not guarantee that one could make the kinds of incredible measurements that Michelson was able to so regularly obtain. In fact, no one was to

experiments and the part played by his interferometer, Michelson never did patent it. As a result, by the 1890s, Michelson interferometers were being built commercially by a number of machine shops and began to appear in physics labs throughout the country. In 1892, Michelson was offered and accepted a post at the University of Chicago. It is to this University, specifically the Ryerson Laboratories, that we turn to next in our search for the origins of the STM.

Paschen's law had been subject to about 10 years worth of experimental verifications by many workers in the field, and it had held up well under this intense scrutiny. But around 1898, a PhD graduate student named Robert Francis Earhart decided, at the suggestion of Albert Abraham Michelson, to see if Paschen's law held at extremely small electrode separations, down to a wavelength of visible light. At first glance this would seem to be a foregone conclusion given the size of the law's demonstrated envelope of applicability. Earhart's apparatus consisted of a fixed ball electrode and a plane counterelectrode mounted on a movable carriage which also had a flat mirror that formed one arm of a Michelson interferometer. In its normal operation, the two electrodes were brought into contact, as sensed by the passage of current due to a very small test voltage, the plane electrode was then backed away from contact with the spherical one, the number of fringes was noted, where each fringe corresponded to half a wavelength of the monochromatic light being used with the interferometer. The whole apparatus was ensconced in an airtight box, which allowed measurements to be made at different gas pressures and with different carefully dried and filtered gases. [416] The experimental curves generated by Earhart were as follows: the x-axis was the electrode separation in wavelengths of sodium light, the y-axis was the value in volts of the sparking potential difference, and the resulting curves were measured at different pressures for the same gas, see Fig. E3. There were two regions of interest with respect to electrode separation: 1) ~3-5λ, and 2) <3-5λ, where λ was the wavelength of

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equal Michelson's finesse with his interferometer, until 1921 when Dayton C. Miller redid Michelson's ether drift experiment and found a slight positive result. These results stood for more than a quarter of century, until 1955 when R.S. Shankland *et al.* with the help of a digital computer were able to show that Dayton's positive result was most probably due to temperature changes,

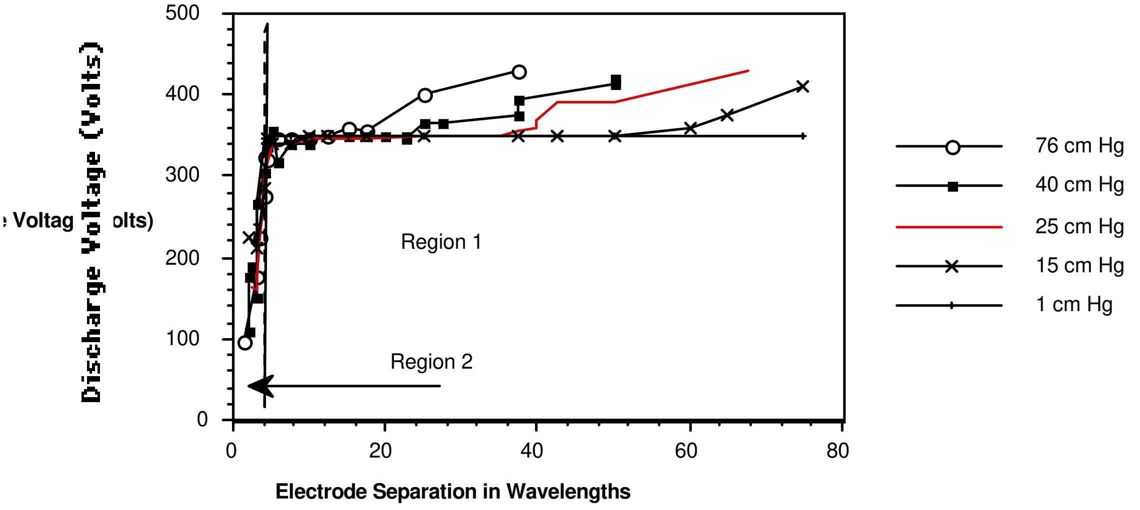
R.S. Shankland, S.W. McCuskey, F.C. Leone, C. Kuerti; New Analysis of the Interferometer Observations of Dayton C. Miller; Reviews of Modern Physics; Vol. 27; 1955; pp. 167-178.

The techniques used by Shankland *et al.* to detect the systematic variations in the fringe shift measurements are pretty much *de rigueur* today in the field of SPC (Statistical Process Control) and involved the use of the autocorrelation function to check the data for nonrandomness.]

[416] R.F. Earhart; The Sparking Distances between Plates for small Distances. ; Philosophical Magazine [and Journal of Science]; Vol. 1 (6th Series); 1901; pp. 147-159. [Note, because of my interest in learning more about Earhart's work, I tried to get a hold of his PhD thesis. To this end I consulted the Dissertation Abstracts Index (1861-1980) CD ROM at Temple University's Paley Library, and found that he had gotten his PhD in 1900 from the University of Chicago. Calling the Reference Desk at the John Crerar Library, (312)702-7874, I found out that Earhart's 1901 Philosophical Magazine articles was his PhD thesis. From the acknowledgement at the end of this paper, it was apparent that his thesis advisor was A.A. Michelson and also perhaps S.W. Stratton; Michelson was head of the Ryerson Laboratory of the University of Chicago at this time.]

sodium light. In Region 1 (~3-5λ), all the curves of sparking potential difference versus electrode separation started out with a high sparking voltage at large separations, with the sparking voltage decreasing with decreasing electrode separation in a roughly linear manner. The sparking voltage versus electrode separation curve maintained the same gentle downward slope at smaller and smaller separations until ~3-5λ of sodium light at which point the minimum sparking voltage began a precipitous but still linear decrease with decreasing separation, i.e., the slope increased dramatically, thus putting a 'knee' or 'elbow' in the curve. This rather unexpected behavior at small separations was ascribed, by Earhart, to the presence of an exceedingly thin air film tenaciously clinging to the surface of the electrodes. According to Earhart's view of the matter, in Region 1 (~3-5λ) the gas, which was being broken down, consisted mostly of the normal bulk gas. However, in Region 2 (<3-5λ), due to the closeness of the electrodes, the bulk gas was squeezed out of the interelectrode space, and only the condensed air film on the surface of the electrodes filled the space between the electrodes and was then subject to electrical breakdown. Because the gas making up this film was in a different state from the same species in the bulk, this was supposed to account for the unexpected electrical behavior that Earhart saw in Region 2. As we shall see later on in this appendix and, in more depth, in APPENDIX F where we will discuss the work of Lester H. Germer, Earhart was almost on the right track about the existence and importance of the gas and/or vapor films on the electrodes. In the 1950s and 60s, Germer would show experimentally that adsorbed gas films on the electrodes did indeed make it easier for field emission to initiate the so-called 'vacuum spark'.

FIGURE E3 - An Earhart Plot in Air Using Data From G. M. Hobbs.



The first person to confirm Earhart's findings was a British scientist, Philip E. Shaw. In 1904, Shaw used a Rube Goldbergish appearing arrangement of six mechanical levers in tandem to allow him to achieve the same range of small electrode separations as Earhart; Shaw called his apparatus an electric micrometer. [417] For reasons which were unclear to me, Shaw's work was not mentioned explicitly in Earhart's followup paper of 1908 or, for that matter, in any of the other papers written by other American researchers with the exceptions of Carl Kinsley, John E. Almy and, much later, James W. Broxon.

Before continuing, I should like to mention that while Earhart appeared to be the first person to try to verify Paschen's law at distances comparable to the wavelength of light, his work was in some ways anticipated about 60 years earlier. After the discovery of the Voltaic pile at the end of the eighteenth century, natural philosophers noticed that a tiny spark was formed on completing or breaking a Voltaic circuit. This result held true even in the case where the pile consisted of a single cell. Michael Faraday suggested that the spark was actually produced just before contact was made in closing the circuit. He was quickly challenged by one professional scientist, Dr. Jacobi, and also by a well-to-do amateur scientific sleuth named John Peter Gassiot. Jacobi in 1838 and Gassiot in 1840 had ordered constructed, according to their respective specifications, micrometer driven contrivances which allowed them to bring two electrodes to within extremely close approaches of one another. With these devices, they proceeded to lay waste to Faraday's claim of sparks being formed before a Voltaic circuit was completed. Their results were quite convincing: Jacobi showed a null result at a distance of closest approach of 1/20,000 inch, while Gassiot duplicated this null effect at 1/5,000 inch. Both researchers were able to demonstrate this negative result even with Voltaic piles consisting of hundreds of cells. [418] Today, of course, we know that Faraday was right but for

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[417] P.E. Shaw; The Sparking Distance between Electrically Charged Surfaces. - Preliminary Note.; Proceedings of the Royal Society (London); Vol. 73; 1904; pp. 337-342. [Besides replicating Earhart's work, Shaw had earlier used his electric micrometer to investigate the behavior of coherers,

P.E. Shaw; An Investigation of the Simple Coherer; Philosophical Magazine [and Journal of Science]; Vol. 1 (6th Series); No. 3; March 1901; pp. 265-296.

Around 1906, Shaw would again be linked to Earhart, this time because of simultaneous but independent work they were both doing with regards to the electrical breakdown of oils at small electrode separations - using again their respective contrivances, which served them so well during the course of their investigations into gas breakdown at small interelectrode distances,

P.E. Shaw; The Disruptive Voltage of Thin Liquid Films between Iridio-Platinum Electrodes; Philosophical Magazine [and Journal of Science]; Vol. 12 (6th Series); July-December 1906; pp. 317-329.]

[418] Jacobi; On the Galvanic Spark.; Philosophical Magazine and Journal of Science; Vol. 13 (3rd Series): No. 84; December 1838; pp. 401-405.

J.P. Gassiot; An account of Experiments made with the view of ascertaining the possibility of obtaining a Spark before the Circuit of the Voltaic Battery is completed.; Philosophical Transactions of the Royal Society; Vol. 130 (Parts 1 & 2); 1840; pp. 183-192. [According to Gassiot's biography,

Sir Leslie Stephen, Sir Sidney Lee (Eds.); Dictionary of National Biography, Vol. 7; Oxford University Press; 1937-38; pp. 935-936.

he was also 'famous' for demonstrating in 1844 "…by experimenting with delicate micrometer apparatus (*Philosophical Magazine* for October) that [Sir William Robert] Grove's arguments against the contact theory of electricity were correct." In doing this, Gassiot again convincingly the wrong reasons, while Jacobi and Gassiot were wrong for reasons which would not unequivocally show themselves for almost another hundred years.

Earhart's observations at small separations, in particular below the 'knee' (i.e., in Region 2, <3-5λ), were verified and extended to even smaller separations in 1904 by Professor Carl Kinsley, [419] who together with Albert A. Michelson, Robert A. Millikan, Henry G. Gale and Charles R. Mann formed the University of Chicago Physics Department and ran the Ryerson Laboratories. [420] Kinsley was able to restrict his measurements of the electrode separation to Region 2 (<3-5λ) by employing a modification of the Michelson's interferometer first suggested by Professor Clark W. Chamberlain of Dennison University, who was working at the Ryerson Laboratories on an unrelated project during the summer of 1903. [421] Kinsley began his paper with a review of the laws of electrical discharges in gases, Paschen' law, and then went on to talk about the work of Earhart and the still later work of Glenn M. Hobbs (who had not yet published his findings). In trying to explain the abrupt linear decrease in the sparking voltage characteristic of Region 2, Kinsley suggested that it was due to a change in the charge carrier. Specifically, he believeed that at extremely small electrode separations the charge carriers were no longer ionized gas molecules, but were instead metal ions from the electrodes, themselves. He based this hypothesis on the then well known behavior of coherers of forming metal bridges between the closely spaced metal particles or electrodes when cohered, and the fact that he had observed this same behavior in his modification of Earhart's basic apparatus if the discharge currents were large. Kinsley was himself quite familiar with the behavior of coherers, having done some work with them earlier in his career. [422] Another interesting fact uncovered by Kinsley was the change in the slope of the precipitous linear roll off as a function of the treatment of the electrode surfaces, e.g., due to buffing or polishing. Since we now know that the discharge in this

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'proved' the nonexistence of a phenomenon whose existence we take today for granted. A complete list of Gassiot's papers up to and including 1863 can be found in the following,

George E. Eyre, William Spottiswoode; Catalogue of Scientific Papers (1800-1863), Compiled and Published by the Royal Society of London, Vol. II; Her Majesty's Stationary Office; 1868; pp. 779-780.]

[419] C. Kinsley; Short Spark-Discharges; Philosophical Magazine [and Journal of Science]; Vol. 9 (6th Series); January-June 1905; pp. 692-708.

[420] J.L. Michel; The Chicago Connection: Michelson and Millikan, 1994-1921; in Stanley Goldberg, Roger H. Stuewer (Eds.); The Michelson Era in American Science 1870-1930; American Institute of Physics; 1988; pp. 152-176.

[421] C.W. Chamberlain; Note on the Compound Interferometer; Physical Review; Vol. 23; July-December 1906; pp. 187-188.

Idem; The Radius of Molecular Attraction; Physical Review; Vol. 31; July-December 1910; pp. 170-182. [**Caution**, the unit of distance measurement used in this and other papers of this era was the $\mu\mu$. Do not - as I did - assume that $\mu\mu = 10^{-12}$ m; a $\mu\mu$ was a millimicron, i.e., $\mu\mu = 10^{-9}$ m = nm (nanometer), see, for example p. 693 of Carl Kinsley's 1905, *Philosophical Magazine* article. Why physicists of this time period did not deign to designate a millimicron as the logically consistent symbol 'mμ', I do not know.]

[422] C. Kinsley; Coherers Suitable for Wireless Telegraphy; Physical Review; Vol. 12; January-June 1901; pp. 177- 183.

region was due to electron tunneling, and that the ability of surface treatment to affect the work function of the metal was shown conclusively by J. Erskine-Murray in 1898 (see APPENDIX D), [423] it should be obvious why the slope changed.

Kinsley appended an appendix to his paper where he discussed the results of his experiments on the properties of the presumably metallic bridge(s) that formed when the electrodes in his contrivance cohered. Specifically, he examined how the resistance of the metallic bridges, formed by cohering the electrodes, changed as they were stretched by slowly pulling apart the electrodes. From this data he attempted to estimate the diameter of the bridge. The answer he got was $4.4X10^{-5}$ cm, which was significantly less than the wavelength of the mercury light he was using, meaning that the bridge would not be visible with a light microscope. Kinsley admited that he did not understand the process behind the formation of the bridge.

In order to transfer a significant amount of material across the interelectrode space much higher currents than one could reasonably expect from field emission would be needed. The mechanism I wish to postulate as providing the needed current is something called a ‘vacuum spark, arc or discharge’, see APPENDIX F. The vacuum spark, besides furnishing essentially unlimited current, satisfies Occam’s razor by providing us with a simple way of achieving the required mass transport of electrode material, i.e., thermal vaporization - electron tunneling and/or field emission, in contrast, do not involve any significant thermal effects. [424] But before we digress to the subject of ‘vacuum sparks’, I

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[423] J. Erskine-Murray; On Contact Electricity of Metals; Proceedings of the Royal Society (London); Vol. 63; 1898; pp.113-146.

[424] The only postulated thermal effect related to electron tunneling that I am aware of was the so-called Nottingham effect,

W.B. Nottingham; Remarks on Energy Losses Attending Thermionic Emission of Electrons from Metals.; Physical Review; Vol. 59 (2nd Series); 1941; pp. 906-907.

Fortunately for my hypothesis, this effect has not been unequivocally observed experimentally even though people have assiduously searched for it. See,

G.M. Fleming, J.E. Henderson; The Energy Losses Attending Field Current and Thermionic Emission of Electrons from Metals.; Physical Review; Vol. 58 (2nd Series); November 15, 1940; pp. 887-894.

Idem; On the Energy Losses Attending Thermionic and Field Emission; Physical Review; Vol. 59 (2nd Series); 1941; pp. 907-908.

R.H. Good Jr., E.W. Müller; Field Emission.; in S. Flügge (Ed.); Handbuch Der Physik; Springer-Verlag; 1956; pp. 196-231, in particular, see p. 199.

Additional evidence against thermal effects in electron tunneling and field emission was provided in 1965 by Bert Halpern and Robert Gomer when they showed that field emission persisted even at liquid helium temperatures (~4°K),

B. Halpern, R. Gomer; Field Emission in Liquids; Journal of Chemical Physics; Vol. 43; No. 3; August 1965; pp. 1069-1070.

The only positive results were obtained in the mid 1960s by a group at the Field Emission Corporation, McMinnville, Oregon. However, these results were highly questionable due to the complexity of the experimental arrangement and the large number of assumptions embedded in their methodology. See, should like to continue for awhile with the work inspired by Earhart's original experiment.

During the period 1902 to 1905, Glenn Moody Hobbs also investigated gas discharges between closely spaced electrodes at Ryerson Labs.[425] Hobbs' apparatus employed a standard Michelson interferometer, but with a more finely cut main lead screw to allow control down to a tenth of a fringe and other mechanical enhancements to reduce backlash. Able to capitalize on the experiences of Earhart and Kinsley, who worked in the same laboratory as himself, Hobbs essentially redid all the work of the two previous investigators, and was able to obtain data which was less influenced by the various measurement artifacts that made Earhart doubt his own data in the neighborhood of the knee. The main problem with Earhart's earlier curves was the uncertainty about whether or not there was a plateau (asymptote) in Region 1 just before the knee separating the two regions. Hobbs, by performing Earhart's experiments at a number of different gas pressures, was able to prove conclusively that there was indeed a plateau in Region 1 just before the knee; the plateau was most easily discerned at air pressures less than normal atmospheric pressure, and the length of the plateau decreased as the air pressure increased to atmospheric, see Fig. E3. Hobbs' verification of the existence of a plateau was very important, since Paschen's law predicted such behavior in the case of non-planar (e.g., ball & plane or point & plane) electrodes.

W. R. Carr was actually the first to point out that a plateau was required of Earhart's data. His argument to this effect can most easily be understood by consideration of Fig. E2 and goes as follows. For large electrode separations, one is above the critical pressure, e.g., the dotted vertical line labeled 'A' in Fig. E2. In this case, as the electrode separation is decreased at constant pressure it is obvious that the voltage required to cause a discharge also decreases (see Fig. E3). But Fig. E2 indicates that the critical pressure increases as the electrode separation decreases and eventually when the separation approaches ~10λ the critical pressure becomes greater than normal atmospheric pressure. At this point, we would use the dotted line labeled 'B' in Fig. E2 to predict the behavior of the discharge voltage with decreasing electrode separation. Here, as the electrode separation is decreased at constant pressure, the discharge voltage should increase, and not plateau out as it was actually shown to do by both Earhart and Hobbs. The reason why the discharge voltage plateaus, according to Carr, is that both Earhart and Hobbs used an electrode configuration consisting of a plane and spherical electrode. As the plane and

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F.M. Charbonnier, R.W. Strayer, L.W. Swanson, E.F. Martin; Nottingham Effect in Field and T-F Emission: Heating and Cooling Domains, and Inversion Temperature; Physical Review Letters; Vol. 13; No. 13; September 28, 1964; pp. 397-401.

L.W. Swanson, L.C. Crouser, F.M. Charbonnier; Energy Exchanges Attending Field Electron Emission; Physical Review; Vol. 151; No. 1; November 4, 1966; pp. 327-340.

[425] G.M. Hobbs; The Relation between P.D. and Spark-length for Small Values of the later.; Philosophical Magazine [and Journal of Science]; Vol. 10 (6th Series); December 1905; pp. 617-631+Plate XIII.

sphere approach one another, the discharge instead of taking place at the point of closest approach, which requires larger and larger voltages as this distance shrinks, actually starts to occur at points on the sphere removed from the point of closest approach, and so the discharge voltage does not need to increase and it remains constant, i.e., plateaus. The same behavior would be found in the case of a plane electrode and a needle electrode as, for example in the case of an STM. In fact, this is the real reason behind why the STM can function in air: the plateau voltage represents the minimum voltage necessary to cause a discharge to occur through the air and this minimum is quite high, ~300 V, which is larger than the voltages usually used with STMs. Note, the gas discharges I am speaking about are classed as self-sustaining discharges, which include both glow discharges and arcs; the glow discharges, in particular, are the ones which have the minimum voltage requirement. It is true that gas discharges can occur at voltages below the minimum voltage, but these Townsend type discharges usually result from the passage of cosmic rays or other ionizing radiations. These nonselfsustaining discharges are used by nuclear physicists in various particle detectors, such as ion chambers, proportional counters and Geiger-Müller tubes.

Hobbs showed that for a given type of electrode material, the slope of Region 2 was independent of both the type of gas and its pressure. On the other hand, the slope in Region 2 did depend on which metal or metals were employed in the electrodes. **Another way of looking at this was that the threshold voltage at a fixed distance within Region 2 was a function of only the electrode material and any surface treatments it might have undergone.** These two previous results supported Kinsley's idea that the reason for the change in slope in going from Region 1 to Region 2 was due to a change in the nature of the charge carrier taking part in the discharge. Since we now know that electron field emission was actually the mechanism which initiated conduction in Region 2, another result of Hobbs' makes sense: in Region 1 the onset of the discharge took a sensible amount of time, [426] while in Region 2 there was not a noticeable time lag. Hobbs also verified Kinsley's observation that coherence took place in Region 2 with sufficiently large discharge currents.

Around 1906, Earhart revisited his original work and extended it. [427] This time around, he utilized a pointed electrode and a plane counterelectrode; the pointed electrode consisted of No. 10 Sharp needles winnowed for their close adherence to the figure of a 'master' needle. With this electrode configuration, Earhart's apparatus had many of the characteristics of an STM save the ability to

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[426] This time lag was apparently first discovered by Warburg,

E.G. Warburg; Ueber die Verzögerung bei der Funkenentladung [On the Time-Lag at the Spark Discharge]; Annalen der Physik und Chemie; Vol. 62 (3rd Series); No. 11; 1897; pp. 385-395.

[427] R.F. Earhart; Discharge from an Electrified Point and the Nature of the Discharge occurring through very small Distances.; Philosophical Magazine [and Journal of Science]; Vol. 16 (6th Series); 1908; pp. 48-59 + Plate I.

scan in the x-y plane and the ability to directly measure the currents, this last shortcoming would be rectified ten years later by Franz Rother. Using this electrode arrangement, Earhart was able to verify the well known fact that gas discharges took place more readily between a point and a plane electrode when the point was negatively charged with respect to the plane electrode. This behavior was mentioned in the main part of this thesis in the section entitled THE RESURRECTIONS, when we were discussing Arthur Schuster's discovery of nonohmic conduction and Lord Kelvin's comments on the use of his quadrant electrometer. Physically this was so because when the point electrode was negative, the intense electric field gradient caused positive ions to intensely bombard the surface of the point, releasing copious amounts of secondary electrons and thus contributing to ionization of the gas. Earhart's data indicated that this polarity effect existed only in Region 1, once Region 2 was entered the discharge voltage versus electrode separation curves coincided.

Thus, by the time Earhart publishes, in 1908, what will be his last paper on the subject of spark discharges between closely spaced electrodes, his discoveries will have been verified and/or extended by Shaw, Kinsley and Hobbs. But 1908 was also to usher in the first papers to present empirical evidence contradicting some of his findings. While many who were to subsequently redo his experiment, from 1908 onward, would confirm the results he got for Region 1 (~3-5λ), a few people would present opposing data for Region 2 (<3-5λ).

Near the end of 1908, John E. Almy of the Brace Laboratory, Lincoln, Nebraska redid Earhart's experiment, substituting a Fabry-Perot interferometer in place of the Michelson interferometer, using two tiny platinum balls for the electrodes [later still, two needles], and observing the discharge directly with a 500X microscope instead of intuiting its existence electrically by measuring the resulting voltage drop across the electrodes. [428] Almy's experimental protocol was to set the electrodes at a known distance apart and then slowly increase the applied voltage until he saw a steady glow discharge appear about the electrodes. As was the case with Earhart, Shaw, Kinsley and Hobbs, Almy recorded that the minimum voltage necessary to produce a glow discharge was about 360 V. However, unlike Earhart and company, Almy claimed that this minimum voltage held even in Region 2 (<3-5λ). This was a very significant point. Earhart's results indicated that the minimum discharge voltage in Region 2, rather than remaining constant, decreased linearly. Almy, on the other hand, said that in Region 2, the minimum discharge voltage was the same as in the flat part of Region 1. In Region 2, if Almy decreased the applied voltage from say

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[428] J.E. Almy; Minimum Spark Potentials; Philosophical Magazine [and Journal of Science]; Vol. 16 (6th Series); July-December 1908; pp. 456-462. [Almy produced his spherical platinum electrodes by melting the ends of 0.057 mm diameter platinum wires in an oxygen-hydrogen flame. Years later, in 1978, Edgar Clayton Teague would use a similar strategy to study electron tunneling, except he would employ spherical gold electrodes made by melting the ends of 1.25 mm gold wires under UHV (Ultra High Vacuum) using an electron beam instead of the oxygen-hydrogen torch employed by Almy.]

360 V to 350 V, he observed that the glow discharge went out. From this result, he stated that Paschen's Law held even at the extremely small separations characteristic of Region 2, and further that no discharges were possible below this minimum of ~360 V. In contrast, Earhart never said that you could not get a glow discharge in Region 2 at 360 V, what he did assert was that there was some sort of discharge occurring in Region 2 which had a linearly decreasing threshold with decreasing electrode separation.

When John E. Almy examined his closely spaced electrodes with his microscope, his criterion for a 'discharge' was the presence of a steady light indicating a glow discharge. Almy showed that even in Region 2, one could get a glow discharge provided that the voltage was slightly above the minimum discharge voltage of Carr. But what about the sub-minimal voltage discharges, measured by Earhart *et al.* , in Region 2? Why did Almy not observe any light from any transient discharges in Region 2? The simple answer, that even though these transient discharges can and do produce light but that their transitory nature makes them difficult to see even in the case of Almy with his microscope, is hard to believe. The reason I doubt this scenario is that these discharges, although very short lived, are nevertheless extremely bright and should have been easy to spot, especially by someone who expects them *a priori*. My explanation of why Almy failed to observe a light flashes in Region 2 is that, as would be demonstrated in the 1950s by Lester H. Germer (see APPENDIX F), smooth clean noble metal contacts do not easily form 'vacuum sparks'.

Almy also revealed that when he employed needles for the electrodes, the glow discharge, for the flat portion of Region 1 and all of Region 2, extended well back along one of the needles, just as one would expect from W. R. Carr's explanation of the plateauing of the minimum glow discharge voltage. Carr stated that below the critical pressure the minimum glow discharge voltage should increase with decreasing electrode separation in the case of plane electrodes. If one or both of the electrodes was not planar, the glow discharge would tend to creep back along the nonplanar electrode so that the discharge would not take place across the distance of closest approach, and hence the minimum discharge voltage would remain constant rather than increasing with decreasing interelectrode distance.

The next person to cast doubts on Earhart's results was a researcher at the University of Illinois, Elmer H. Williams. In 1910, Williams revisited Earhart's work with an apparatus very similar in design to that utilized by Earhart in 1901: a ball and plane electrode configuration, the electrode separation measured with a Michelson interferometer, lead screw actuated motion, and the occurrence of a discharge sensed by the drop in voltage across the electrodes. [429] Williams' results match those found by Almy in that his data indicated that the flat portion

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[429] E.H. Williams; The Nature of Spark Discharge at very small Distances; Physical Review; Vol. 31 (1st Series); No. 3; July-December 1910; pp. 585-590.

of the voltage versus distance curve continued unchanged into Region 2. There was no ‘elbow’ or ‘knee’ at 3-5λ followed by a linear decrease in minimum discharge voltage with decreasing distance. The minimum discharge voltage measured by Williams was ~360 V, and this minimum did not appear to depend on the electrode material. Williams tried the following combinations: aluminum-aluminum, brass-aluminum, platinum-platinum, aluminum-silver, platinum-silver and brass-platinum. Additionally, photomicrographs of the plane cathodes revealed that the pitting of its surface - due to bombardment by positive gas ions with the attendant lose of material, i.e., cathodic sputtering - was arranged in a circle with its diameter increasing as the interelectrode separation decreased. This behavior was, of course, another confirmation of W. R. Carr’s theory that below the critical pressure the discharge in the case of nonplanar electrodes did not take place at the distance of closest approach.

Besides replicating Earhart’s earlier work, Williams also examined the effect of ultraviolet (UV) light on this arrangement. What he found was that, at small electrode separations (1.5-5λ), irradiation by UV light caused the minimum voltage for discharge to decrease with decreasing distance. The effect of UV light, according to Williams, was to enhance ionization of the gas between the electrodes, and by doing so to affect a reduction in the value of the minimum discharge voltage. Because Williams’ results were so different in Region 2 from those uncovered by the workers at Ryerson Labs, it was not surprising that a year later (1911) he authored another paper on the same basic topic, in an obvious effort to buttress the conclusions stemming from his previous paper. [430] In this 1911 paper, Williams investigated the influence of different gases (hydrogen and carbon dioxide), the influence of pressure on the discharge of air, and he returned to the effects of UV light on the system. Of the three things just mentioned, it was what he found with respect to the illumination of the system with UV which was the most interesting. In the second paper, Williams stated that he had concerns about the fact that his original UV source, two aluminum electrodes in a quartz tube, required such a high operating voltage that significant amounts of radio frequency (RF) energy were also being generated, and so might be confounding the results. Because of his concerns, Williams decided to redo the experiment employing a low voltage UV source which worked by drawing an arc between an iron and a mercury electrode (i.e., a mercury vapor lamp), andwhich operated at only 14 V. With this new source, the data indicated that there was <u>no</u> effect on the breakdown voltage, i.e., the minimum breakdown voltage in Region 2 (<3-5λ) was still ~360 V for air. This negative result was very interesting, since it unequivocally showed that RF energy could cause a substantial decrease in the minimum discharge voltage in the range 1.5-5λ - remembering, of course, that Williams maintained that his data, in the absence of any illumination, exhibits no ‘elbow’ or ‘knee’ at 3-5λ. It seems obvious to me that the decrease in the minimum discharge voltage

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[430] Idem; Spark Discharge at very small Distances; Physical Review; Vol. 32 (1st Series); No. 6; January-June 1911; pp. 585-590.

experienced by Williams, due to the RF energy coming from his high voltage UV source, was a manifestation of self-restoring coherer behavior. While he did agree that the effect was due to the presence of RF energy, Williams did not mention coherers at all, which was very strange given their commercial success and relative prominence just a few years earlier. That coherence could happen even when the distance between metal electrodes was on the order of 10,000-25,000 Å was probably due, in this case, to the large DC bias voltage 100-350 V and the proximity of an extremely strong RF source. **This result suggests that RF energy can induce a substantive increase in the field emission current at a constant bias voltage.** Why RF energy appears to be able to do this is not clear.

The last American, that I know of, to reinvestigate Earhart's work was Edna Carter in 1914. [431] Carter, like Kinsley, measured her distances with a Chamberlain compound interferometer, but, unlike the others, her the experiments were performed at the highest vacuum at her disposal, ~10^{-4} torr (1 torr = 1 mm Hg). Due to time constraints, I was unable to pursue this further.

As was mentioned in APPENDIX B, Robert Williams Wood published his theory of 'electron atmospheres' in 1912. The details of his theory were shown to be wrong. In particular, his idea that these 'electron atmospheres' extended for tens of thousands of Ångströms from the metal's surface, which he believed were responsible for the low voltage conduction he observed between metallic edges of scribe marks on mirrors, was shown not to be in accordance with the facts. Between approximately 1912 and 1922, there arose a cottage industry among physicists who were deluging the physics community with experimental result refuting Wood's theory. It was among some these experiments that I found instances of people redoing or doing variants of Earhart's basic experiment. An example of this would be the work of Englund. In 1914, Carl R. Englund published an account of his repetition of Earhart's experiment. [432] According to Englund this was done at the suggestion of Robert A. Millikan, while he [Englund] was at the Ryerson Laboratory of the University of Chicago during the spring of 1911. Sensitive to the criticism that Earhart's observed conduction in Region 2 was probably due to the electrodes being pulled into contact by the large electrostatic forces present at these minute distances, Englund provided both the movable and fixed electrode with a mirror thus producing a double fringe system. The end result of all his work was that he verified Hobbs' work and by extension Earhart's work, while at the same time refuting Wood's theory.

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[431] E. Carter; Discharge Potentials across very short Distances; Physical Review; Vol. 3 (2nd Series); No. 6; January-June 1914; pp. 453-456. [Carter apparently did this work in Europe at the University of Würzburg under the guidance and with the technical help of one Professor Wien. The apparatus she employed to allow her to bring the iridium electrodes to subwavelength distances in a vacuum closely resembles what Franz Rother would ultimately use in his 1926 paper on tunneling and field emission.]

[432] C.R. Englund; Note on the Electron Atmosphere (?) of Metals.; Philosophical Magazine [and Journal of Science]; Vol. 27 (6th Series); January-June 1914; pp. 457-458.

§4. WHAT EARHART *et al.* ACTUALLY SAW: 'VACUUM SPARKS'. - I have characterized the electrical discharges seen by Earhart in Region 2 as being due to 'vacuum sparks', but I have not clarified what I mean by this term. It is time to do so. The first point that needs clarification is the term 'discharge'. Earhart, Kinsley and Hobbs slowly increased the voltage across the closely spaced electrodes - thus avoiding any artifacts from the time lag effect - until the needle on their respective Weston voltmeters started to dance about, indicating a transient current flow; Shaw employed a telephone receiver shunted by a low value resistor as his detector.

In Region 1 (~3-5λ), this transient current flow represented the onset of a glow discharge, where - its name not withstanding - a glow discharge was a <u>steady</u> ionization of the gas between the electrodes accompanied by a <u>steady</u> muted light. The onset of the glow discharge marked the border between a Townsend discharge and a glow discharge; in a Townsend discharge, the applied electric field was less than what was needed to produce a self-sustained discharge in the gas, but was enough to support transient discharges caused by external sources of ionization, such as cosmic ray, natural radioactivity, etc.

In Region 2 (<3-5λ), the discharges Earhart *et al.* observed were recognized to be of a different character than the gas discharges observed in Region 1. In fact, what they had actually observed were 'vacuum sparks' in which field emission, a low current phenomenon, transitioned into a transient high current discharge similar to an electric arc. As we shall see later on, it was not until the work of Franz Rother that this became clear.

At this point I need to digress and provide some substantive discussion of 'vacuum sparks' and their characteristics. The linearly decreasing discharge voltage observed by Earhart *et al.* in Region 2 appears to be a threshold phenomenon, i.e., a transient burst of current flows only when the applied voltage attains a certain value, which depends on the electrode separation in a linear manner. This burst of current must be both large in intensity and reasonably long lived in duration to register on a Weston moving coil voltmeter or a telephone receiver. Also, these discharges, as we shall see shortly, do generate a blue-white flash of light rich in ultraviolet (UV) radiation. The first recorded observations of the 'vacuum spark' phenomenon were associated with various investigations into the production of x-rays.

The discovery of x-rays in 1895 by Wilhelm Conrad Röntgen understandably electrified the scientific and medical communities, and caused scientists all over the world to drop what they were doing and try their hand at this new phenomenon.[433] It should be noted that not everyone partook of the

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[433] Note, the phenomena of tunneling and field emission did <u>not</u> show themselves in the operation of the standard cold cathode x-ray tubes (a.k.a. Hittorf-Crookes tubes). The operation

religion of Röntgen rays - Lord Kelvin, for example declared that, "X-rays will prove to be a hoax". [434] In America, Henry Augustus Rowland was experimenting with various Crookes tubes in an effort to gain firsthand knowledge of these new rays. In particular, he was interested in localizing the source of these rays in terms of the electrodes and envelope of the tube. As a result of this work, he and some other researchers published a series of short papers on their findings. The most significant paper, from our present perspective, was a one page note in the journal, *Electrical World (New York)*. In this April 25, 1896 note, Rowland *et al.* mention that when the metal electrodes of their x-ray tube were situated about 1 mm apart, the Ruhmkorff discharge was conducted across the vacuum separating the two electrodes in the form of "…a faint spark or arc…"; they also mentioned that it was their impression that copious amounts of x-rays were produced in concert with these 'vacuum arcs or sparks'. [435] In what was another remarkable coincidence of scientific discovery,

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of these types of tubes were neatly accounted for in terms of gas discharges, only. At atmospheric pressure, the air in the tube acted like an insulator. As the air pressure in the tube was lowered, the gas began to conduct and exhibited the luminous manifestation of this conduction known as the glow discharge; the glow discharge being composed of many luminous and dark areas. Conduction was predominantly due to cathode rays (electrons) due to their high mobility compared to that of the heavier, and hence less mobile canal rays (positive ions). The discovery that cathode rays were actually particles was usually credited to Cromwell Fleetwood Varley in 1870, even though he appeared to have reached his conclusion with far less than unequivocal proof. In 1886, E. Goldstein discovered the existence of canal rays ["…Kanalstrahlen…"] when he put a hole in the cathode, and noticed a luminous glow on the far side of the cathode, i.e., the side facing away from the anode, radiating through the hole.

It was the collision of the cathode rays with the anode or, in fact, any other material body, including the glass envelope and the residual gas, in the Hittorf-Crookes tube which produced the x-rays. As the air pressure was reduced even more, a particular region of the glow discharge adjacent to the cathode and known as the Crookes dark space appeared and with still lower pressures, this dark space occupied more and more of the volume of the tube. When the Crookes dark space filled the whole tube, one had the optimum conditions for the production of x-rays.

That these types of tubes required the presence of some gas to operate properly was supported by the following operational observations. The quality, i.e., penetration power or hardness, of the x-rays increased the longer the tube was operated. This undesirable side effect was due to the cleanup of the residue gas by the electrodes and glass envelope. As more and more of the residual gas disappeared, higher and higher voltages were necessary to achieve significant conduction. At around $4X10^{-7}$ atmospheres, it was no longer possible to pass discharges through the residual gas with normally available voltages, and so x-rays ceased to be produced. These early so-called 'gas' x-ray tubes - to distinguish them from the Coolidge or electron x-ray tubes with their 'hard' vacuums - usually had provisions for <u>in</u>creasing the gas pressure via slow leaks or arc decomposition of volatile compounds, in order to maintain the gas pressure in the optimum range over the life of the tube.

[434] M. Nicholls; The Perils of Prediction; New Scientist; December 21-28, 1991; pp. 63-64.

[435] H.A. Rowland, N.R. Carmichael, L.J. Briggs; Notes on Röntgen Rays; Electrical World (New York); Vol. 27; No. 17; April 25, 1896; p. 452.

All the above papers can also be found in,

Henry Augustus Rowland; <u>The Physical Papers</u>; The Johns Hopkins Press; 1902; pp. 571-575. [Rowland pointed out the sometimes unappreciated fact that when energizing an x-ray tube with a Ruhmkorff coil, one was using a source of AC voltage, specifically a damped sinusoid. For x-ray tubes of low resistance, the AC current resulted in weak x-rays due to the anode and one Dr. Sydney D. Rowland of 38 Wimpole St., W. London, England, was reported to have done the following,

> Professor Rowland obtained excellent [Röntgen rays] with a perfect vacuum tube, in which the electrons were placed within one millimetre from each other. The starting point of the rays is then less than the one-thousandth part of an inch in diameter, and gave a shadow of remarkable sharpness. [436]

Although, S. D. Rowland does not explicitly mention anything about vacuum sparks, it was nevertheless clear that his apparatus must have generated them because: 1) in a tube of "high vacuum", no gas discharge would be able to occur, and 2) the extremely small diameter ("less than the one thousandth part of an inch") of the source of x-rays - as measured by the apparently insignificant penumbra cast by the x-ray shadow of an opaque object - was consistent with x-ray generation via vacuum sparks. [437] Slightly more than a year later in July 1897, Robert Williams Wood, in an article in the the *Physical Review*, described the same effect in almost the same words as the two Rowlands. [438] Wood's epiphany came about as a direct result of his trying to build a point source x-ray tube. The doyens of modern field emission, Erwin W. Müller and R.H. Good Jr., indicated in their treatise on the subject, that R. W. Woods was the first to publish his observations of 'vacuum sparks', but from what has been stated earlier this assertion is clearly incorrect. [439]

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cathode flipping back-and-forth between the two electrodes. In the case of an x-ray tube of high resistance, the Ruhmkorff coil output was so heavily damped that the current was predominantly only in one direction.]

[436] Anon.; Untitled; The British Journal of Photography; Vol. 43; No. 1883; June 5, 1896; p. 356.

[437] The book in which I found the reference to S.D. Rowland's work,

Otto Glasser, Margret Boveri; Wilhelm Conrad Röntgen, and the Early History of the Roentgen Rays; Charles C. Thomas; 1934; p. 322.

concurred in the assessment that S.D. Rowland's tube was a forerunner of later 'auto-electronic' (i.e., field emission) tubes made by, for example J.E. Lilienfeld.

[438] R.W. Wood; A New Form of Cathode Discharge and the Production of X-rays, together with some Notes on Diffraction; The Physical Review; Vol. 5 (1st Series); No. 1; July 1897; pp. 1-10.

[439] R.H. Good, Jr., E.W. Müller; Field Emission; in S. Flügge (Ed.); Handbuch Der Physik, Vol. 21; Springer-Verlag; 1956; pp. 176-231, in particular, see p. 176. [Note, so great was, and still is, the influence of Erwin W. Müller, that subsequent articles, concerned with various facets of field emission, have also cited R.W. Wood as the discoverer of field emission and/or the 'vacuum spark'. See, for example,

W.P. Dyke, J.K. Trolan; Field Emission: Large Current Densities, Space Charge, and the Vacuum Arc; Physical review; Vol. 89; No. 4; February 15, 1953; pp. 799-808.

W.P. Dyke; Progress in Electron Emission at High Fields; Proceedings of the I.R.E.; Vol. 43; 1955; pp. 162-167.

W.P. Dyke; Advances in Field Emission; Scientific America; Vol. 210; No. 1; January 1964; pp. 108-116, 118. [**Warning**, p. 108 of this article referred to, "The German physicist Werner Schottky…", when it apparently meant Walter Schottky.]

Note, a complete accounting of the exact mechanisms involved in the operation of the standard Hittorf-Crookes tube as a source of x-rays has not ever been made to my knowledge. While it was understood early on that cathode rays (electrons) produced in the gas discharge generated x-rays when they collided with the glass walls of the tube or, better still, with the metal anode, questions still remained about x-rays created by the electrons colliding with the gas itself and the exact nature of the residual gas clean up during the operation of the tube. The main reason for these unanswered questions, and others, was that the Coolidge x-ray tube replaced the Hittorf-Crookes version in very short order. X-rays were discovered, using the Hittorf-Crookes tube in 1895, but by 1913, William D. Coolidge's hot filament cathode x-ray tube with its 'hard' vacuum had appeared and almost immediately replaced the 'older' Hittorf-Crookes version of x-ray tube. [440] In this respect, the Hittorf-Crookes x-ray tube shared the same fate as befell the coherer: too short a commercial lifetime to evince enough scientific interest in the details of its inner workings. [441]

Note, after having determined that R.W. Wood was <u>not</u> the first person to observe 'vacuum arcs' I <u>almost</u> reversed myself. The popular biography of Wood,

William [B.] Seabrook; <u>Doctor Wood, Modern Wizard of the Laboratory</u>; Harcourt, Brace and Co.; 1941.

contained an exhaustive bibliography of Wood's scientific papers and books - 263 of them all together. The first page of the bibliography contained the following citation,

"16. The X-ray Arc. *Electrician*, 38 (1896), 289, 371"

which led me to jump to the conclusion that Wood had discovered 'vacuum sparks' the same year as Henry A. Rowland and Sydney D. Rowland. However, upon examining the article called out in the aforementioned citation, two things became clear: first, the citation was incorrect and should have read,

R.W. Wood; Experimental Determination of the Temperature inside Vacuum Tubes [Parts I & II]; The Electrician(London); Vol. 38; pp. 289-290, 322-324.

and second, the article was concerned with the measurement of temperatures inside the various regions of the glow discharge, not the 'vacuum spark'.

Warning, Seabrook's rather breathless biography of the adventures of Robert Williams Wood made for easy reading, but sometimes at the expense of the facts. Take, for example the famous incident where Wood exposed N rays as a fake (see the chapter entitled Debunker of Frauds). This episode, as related in the biography, took a number of liberties with the facts. See,

R.T. Lagemann; New light on old rays: N rays; American Journal of Physics; Vol. 45; No. 3; March 1977; pp. 281-284.]

[440] W.D. Coolidge; A Powerful Röntgen Ray Tube with a Pure Electron Discharge; Physical Review; Vol. 2 (2nd Series); No. 6; December 1913; pp. 409-430. [The technology, which made the Coolidge x-ray tube possible, was the ability to fabricate tungsten into filaments. This process was developed initially for use in electric light bulbs by Coolidge, himself. A fascinating discussion of the battle waged by Coolidge to domesticate tungsten can be found in,

John W. Howell, Henry Schroeder; <u>History of the Incandescent Lamp</u>; The Maqua Co.; 1927; pp. 75-122.]

[441] The ability of the Hittorf-Crookes tube to clean up the residual gas during operation had a parallel in the operation of the tungsten filament light bulb. It was known for some time that modern light bulbs in operation reduced the amount of residual gas present in the glass envelope, but no one knew where the gases went. This problem came under the scrutiny of Irving Langmuir, who elucidated much about this process including the location of the occluded gases. Perhaps his explanations can also account for the clean up that was observed in the Hittorf-Crookes x-ray tubes. See,

While it is not clear to me whether or not Rowland, Rowland and Wood's point source x-ray tube ever found commercial success, 'vacuum sparks' became an essential tool in the science of spectroscopy. In 1905, R. E. Loving published his findings on the nature of the 'vacuum spark'. [442] Besides confirming the observations of Rowland, Rowland and Wood on the location and appearance of the 'vacuum spark and the erosion of the anode with the concomitant buildup of material on the cathode - the opposite of sputtering, [443] Loving was able to empirically prove that the light emitted by the 'vacuum spark' was characteristic of the material making up the anode. To accomplish this in an unequivocal manner, Loving built a vacuum spark gap with the anode and cathode composed of different metals. The vacuum chamber had a quartz window to allow light from the violet end of the spectrum to leave, and the

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Irving Langmuir; Phenomena, Atoms and Molecules; Philosophical Library; 1950.

Besides the question of precisely what happened to the residual gas upon extended operation of the Hittorf-Crookes tube in the x-ray mode, there was also the uncertainty about the source of the x-rays. It was discovered early on that the glass walls produced x-rays when bombarded by the cathode rays (electrons), and that more efficient generation of x-ray could be achieved by having the cathode rays impinge on the metal anticathode (anode). But as late as the mid-1920s, researchers were still collecting experimental data on the radiations given off by the gas in the tube,

J.J. Thomson; On the Electric Discharge through Gases at very low Pressures; Philosophical Magazine [and Journal of Science]; Vol. 48 (6th Series); July-December 1924; pp. 1-33.

Idem; Radiation given out by Gases through which Electric Discharges are passing; Philosophical Magazine [and Journal of Science]; Vol. 49 (6th Series); January-June 1925; pp. 761-786.

A. Dauvillier; Researches on the Electric Discharge in Gases and the accompanying Radiations; Philosophical Magazine [and Journal of Science]; Vol. 2 (7th Series); July-December 1926; pp. 1046-1052.

J.J. Thomson's work originated in some observations made by E. Wiedemann in 1895; Dauvillier's investigation was inspired in turn by Thomson's papers. What Thomson and Dauvillier found was that the gas in the Hittorf-Crookes tube also acted as an anticathode (anode), and so produced x-rays and Schumann-Lyman radiation (ultraviolet and/or soft x-rays). Most of radiations from the gas originated in the negative glow and the positive column.

[442] R.E. Loving; The Arc in High Vacua; Astrophysical Journal; Vol. 22; No. 5; December 1905; pp. 285-304. [Both R.E. Loving and, in a later paper, Edna Carter, gave Henry A. Rowland priority for the discovery of the 'vacuum spark'. See,

E. Carter; The Vacuum-Spark Spectra of the Metals; Astrophysical Journal; Vol. 55; January-June 1922; pp. 162-164 + 2 plates.]

[443] In sputtering, the material of the cathode is eroded by the bombardment of positive gas ions; the positive gas ions arise due to the ionization of the gas between the electrodes, i.e., the voltage difference across the electrodes has got to be greater than the minimum discharge voltage for that particular gas. The difference in the way in which the electrodes are eroded allows one to distinguish between a 'vacuum spark' and a gas discharge.

According to J.J. Thomson's book, Conduction of Electricity through Gases, sputtering was first observed by Julius Plücker around 1858. In parallel with the sputtering, Plücker also witnessed the gradual clean up of the gas. However, as the reader has already come to expect, the history of who discovered what when is a slippery subject. A recent treatise on the subject of sputtering claims with good justification that William Robert Grove was the first researcher to report the phenomenon of sputtering around 1853, followed by John Peter Gassiot in 1858. See,

Peter Sigmund; Sputtering by Ion Bombardment: Theoretical Concepts; in R. Behrisch (Ed.); Sputtering by Particle Bombardment I; Springer-Verlag; 1981; pp. 9-71.

resulting light passed into a grating spectrometer - all Loving's work was done with a high voltage DC power supply, and so the electrodes, which were his anode and cathode, were fixed and well-defined. In one experiment, when the anode was made of magnesium and the cathode of platinum, no platinum lines appeared on the photographed spectrum; reversing the electrodes so that the anode was platinum and the cathode magnesium, produced a spectrum devoid of magnesium lines. It should be noted that Loving was not the first person to determine that the 'vacuum spark' spectrum was characteristic of the anode material. In a paper published in 1862, George G. Stokes made the same observation, and indicated further that William Allen Miller had also done some work along these same lines. [444] Stokes' interest in the spectra of 'vacuum sparks' was an offshoot of his work on fluorescence, a phenomenon which was well known even before his time, for which he provided the first correct interpretation. Since the fluorescent substances employed by Stokes were best excited by ultraviolet light, he later went on to study artificial sources of this light and, hence, found that metal vapor arcs were copious producers of these highly refrangible rays. While Loving employed the light from the 'vacuum spark' only to investigate the source of the light, Robert A. Millikan and his student Ralph A. Sawyer coopted Loving's apparatus for the purpose of measuring the spectra of metals and other refractory materials.

While the emission spectrum of hydrogen had been completely characterized up to its highest possible frequency in the UV by Theodore Lyman, [445] it was expected that heavier elements, all of which were metals, would have emission spectra extending into the far UV and even into the x-ray frequencies. The problem with verifying these expectations was the lack of a suitable source to thermally excite the elements into producing light. [446] That was until, Millikan

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[444] Sir George Gabriel Stokes; Mathematical and Physical Papers, Vol. IV; Johnson Reprint Corporation; 1966; pp. 203-233. [pp. 203-233 contains the abstract, first published in the *Proceedings of the Royal Society (London)*, of the full paper contained in the 1862 volume of the *Philosophical Transactions of the Royal Society*.]

[445] The light spectrum of hydrogen consists of lines extending from the infrared (IR) to the ultraviolet (UV). The line are group in four series named after their discoverers: Brackett (IR), Ritz-Paschen, Balmer, and Lyman (UV) series.

[446] The use of spectroscopy for the identification of elements - initially just the alkali metals - was the result of a collaboration between Robert Wilhelm Bunsen and Gustave-Robert Kirchhoff. An immediate result of this work was the discovery of two new elements, cesium and rubidium. The so-called 'Bunsen burner' was pivotal to Bunsen and Kirchhoff's spectroscopic research since it provided them with a convenient source for thermally exciting the various alkali metals they were investigating. Described in 1857 by Bunsen and Sir Henry Roscoe, the Bunsen burner utilized the premixing of ~3 parts air with 1 part coal gas (made by carbonization - coking - of coal, i.e., heating up coal in the absence of air to drive off the volatile fractions) to produce a flame that was both hot and nonluminous. The nonluminousity of the flame guaranteed that the only light it produced would come from the externally supplied salts that were used to 'seed' the flame. This light was then passed through a spectrograph, and the resulting emission lines photographed. Today this type of spectroscopy is still in use for the detection of alkalis and it is called flame photometry. Cesium was discovered by flame photometry of mineral water by the process of elimination: the spectral line were assigned to all the known alkalis, and any lines

and Sawyer resurrected Loving's 'vacuum spark' light source and ensconced it inside a vacuum chamber together with a Henry A. Rowland concave grating, thus forming a far UV vacuum spectrometer. [447] Although the 'vacuum spark' was normally tiny, it could be significantly enhanced in intensity by paralleling the spark gap with large value capacitors, which increased the amount of current carried by the spark. The fact that this ploy does yield a more robust spark, substantiates my contention that this was the phenomenon detected by Earhart *et al.* in Region 2, since it means that the currents resulting from these types of sparks carry enough current that the resulting voltage drop across the gap can be easily detected by the kind of moving coil meters used by, for example Earhart. With this device firmly in hand, Sawyer proceeded to obtain the far UV spectra of every metal he seemed to be able to lay his hands on, and in the process made a name for himself in the field. [448]

Any doubt that the 'vacuum sparks' are hot - thermally speaking - should be dispelled by the following fact, mentioned by Sawyer in his book. In 1936,

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remaining were judged to be due to a hitherto unknown alkali. Bunsen was then able to isolate about 17 grams of cesium chloride from ~40 tons of mineral water. See,

Sir. H. Roscoe; Bunsen Memorial Lecture; Journal of the Chemical Society, Transactions (London); Vol. 77; 1900; pp. 513-554.

It should, of course, comes as no surprise to the more discriminating reader to learn that Bunsen did not actually invent his burner. The credit for this device is usually given to either Peter Desdga and/or Michael Faraday.

Note, while the Bunsen burner was a good beginning for a thermal source it had a very real shortcoming: it was only hot enough (~2000ºK) to excite alkali metals, i.e., elements with small ionization potentials. Since the emission spectra arose from the transition of excited electrons falling back to lower energy states, e.g., the ground state, higher temperatures were necessary to excite the bound electrons of most metals, other than the alkalis. For elements of higher ionization potential, the electric arc and the high energy spark were used because of their higher temperatures ("…4000 to 8000ºK or more…"), see,

I.M. Kolthoff, E.B. Sandell, E.J. Meehan, Stanley Bruckenstein; Quantitative Chemical Analysis, 4th Ed.; The Macmillan Co.; 1969; pp. 997-999.

By the term "high energy spark", Kolthoff *et al.* were actually referring to the phenomenon known to physicists and electrical engineers as 'vacuum arcs, sparks or discharges'.

[447] R.A. Millikan, R.A. Sawyer; Extreme Ultra-Violet Spectra of Hot Sparks in High Vacua; The Physical Review; Vol. 12 (2nd Series); No. 2; September 1918; pp. 167-170.

Idem; Three Fourths of an Octave Farther in the Ultra-Violet; Science; Vol. 50; No. 1284; August 8, 1919; pp. 138-139.

R.A. Sawyer; A New One Meter Vacuum Spectrograph Design; Journal of the Optical Society of America & Review of Scientific Instruments; Vol. 15; July-December 1927; pp. 305-308. [Note, the idea of using the light from the 'vacuum arc' in far UV spectroscopy was rediscovered in 1930 by F. Rother and W.M. Cohn. These two researchers, during the course of working with a field emission x-ray tube of J.E. Lilienfeld's design, decided to investigate the nature of the "Brennfleckstralung [incandescent spots]" produced on the anticathode (anode). Preliminary results revealed that the spectrum of these spots extended into the far UV, and this led Rother and Cohn to suggest utilizing this radiation in spectroscopy.]

[448] Ralph A. Sawyer; Experimental Spectroscopy; Prentice-Hall, Inc.;1944.

Bengt Edlén, using a 'vacuum spark', captured the spectrum of Cu (XIX).[449] To appreciate this feat one must remember that neutral, i.e., un-ionized, copper (Cu) has 29 electrons, and each time an electron is lost due to the atom being ionized (or oxidized, in chemistry lingo), the positive charge of the resulting ion increases by one - Cu (XIX) has lost approximately 1/3 of its normal compliment of electrons. Note, the orbital structure of copper is assumed to be the following in order of energy: 1s (2e-), 2s (2e-), 2p (6e-), 3s (2e-), 3p (6e-), 4s (1e-), 3d (10e-), with orbitals 3s (2e-), 3p (6e-), 4s (1e-), 3d (10e-) comprising the valence band and containing nineteen electrons (19e-). Thus, it appeared that Edlén was able to strip all the valence electrons from the copper atom. The shortest wavelength of UV light produced by a electron reattaching itself to the Cu (XIX) ion was ~47 Å. Calling electromagnetic radiation of this short a wavelength far UV or even far far UV is definitely stretching the bounds of reasonableness, wavelengths of this order are best characterized as soft x-rays or - stretching, again - soft soft x-rays. In fact, the use of the 'vacuum arc' by Millikan *et al.* effectively allowed them to bridge the gap between the part of the spectrum we call light and the portion known as x-rays.[450] In this it mirrored the efforts of E. F. Nichols and J. D. Tear in 1923 to bridge the gap between radio waves and light waves by utilizing a tiny Righi oscillator.

Returning to the observations of Earhart *et al.*, one could reasonably ask the following question. Can 'vacuum sparks' be formed at atmospheric or near atmospheric pressures? The case for 'vacuum sparks' in the presence of significant amount of gas is buttressed by the fact that Rowland, Rowland and Wood observed 'vacuum sparks' in tubes evacuated by mechanical pumps, which could produce at best a vacuum of only 10^{-6} atmospheres (~1 mtorr, 1 torr = 1 mm Hg). The advent of so-called 'hard' vacuums ($<10^{-3}$ mtorr, $<10^{-6}$ torr) had to await the invention of the mercury diffusion pump, circa 1915, by Wolfgang Gaede and its independent reinvention and improvement by Irving Langmuir a few years later. However, this is still begging the question because I have still not presented experimental evidence showing that this phenomenon was observed in air. The best evidence for the occurrence of 'vacuum sparks' in air at atmospheric pressure comes from the work of Lester H. Germer, circa 1950, which is treated in some detail in APPENDIX F.

Having introduced ourselves to the phenomenon of 'vacuum sparks', it is time for a reality check. To wit, what are 'vacuum sparks' and what causes them? Unfortunately, these are not questions which can be answered completely, confidently and truthfully, even today. Due to the transient nature of

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[449] B. Edlén; Na I-ähnliche Spektren der Elemente Kalium bis Kuper, K IX - Cu XIX. [Na I like Spectra of the Elements Calcium through Copper, Ca IX - Cu XIX.]; Zeitschrift für Physik; Vol. 100; 1936; pp. 621-635.

[450] This idea, that Millikan *et al.* bridged the gap between light and x-rays with the 'vacuum arc', was brought to my attention by the following book,

Herman Goodman; Story of Electricity, and a Chronology of Electricity and Electrotherapeutics; Medical Life Press; 1928; p. 62.

these types of discharges they were and are difficult to study. However, one thing that was eventually determined was that ‘vacuum sparks’ were initiated by field emission. Of course, almost thirty years had to pass between the time of Earhart’s first paper in 1901 and general acceptance by the physics community of the existence of field emission. Starting around the late 1920s, researchers began to find empirical data showing that ‘vacuum sparks’ were preceded by field emission. This fact was ascertained by the work of at least three groups: Hull & Burger, Snoddy, and Beams. [451] All three groups observed the behavior of high potentials across metal electrodes in a vacuum. What they saw was that the breakdown started as a high voltage, pure electron discharge (field emission), which then evolved into a low voltage, high current discharge (‘vacuum spark’). One way to follow this metamorphosis in real time was to use an old but still reliable technique, the rotating mirror or streak camera. Using this technique, one could observe the anode lighting up as a result of its bombardment by field emission electrons, followed by the gradually movement of the luminosity to the cathode during the formation of the ‘vacuum spark’; the time duration between the field emission stage and the ‘vacuum spark’ stage of the discharge was on the order of 1-2X10^{-7} sec.

Note, J. W. Beams had earlier shown that a discharge in air followed a similar course, except that it started with a Paschen (glow) discharge and then changed into metal vapor arc (‘vacuum spark’). [452] In this case, Beams employed two different methods to follow the various stages of the discharge: 1) the Kerr cell method, whose arrangement mimics the methodology utilized by Erich Marx to measure the speed of x-rays; and 2) the rotating mirror method, which was discussed in the previous paragraph. With either method, the light from the discharge was passed through a spectrometer. During the Paschen stage of the discharge, the spectrograph revealed the presence of the so-called air lines (N_2 emission lines), while the metal vapor arc (‘vacuum spark or arc’) stage was characterized by the presence of metal lines (metal emission lines).

In 1935, H. W. Anderson did what can best be described as a <u>macroscopic</u> version of Earhart’s landmark 1901 & 1906 experiment. [453] The

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[451] A.W. Hull, E.E. Burger; Some characteristics of the discharge between cold electrodes in vacuum.; Physical Review; Vol. 21 (2nd Series); 1928; p. 1121. [This was only an abstract of talk.]

L.B. Snoddy; Vacuum spark discharge.; Physical Review; Vol. 37 (2nd Series); 1931; p. 1678. [This was only an abstract of talk.]

J.W. Beams; Field Electron Emission from Liquid Mercury; Physical Review; Vol. 44 (2nd Series); November 15, 1933; pp. 803-807.

[452] J.W. Beams; Spectral Phenomena in Spark Discharges; Physical Review; Vol. 35 (2nd Series); January 1, 1930; pp. 24-33.

[453] H.W. Anderson; Effect of Total Voltage on Breakdown in Vacuum; Electrical Engineering (New York); Vol. 54; December 1935; pp. 1315-1320. [For a complete description of the apparatus, see,

Idem; Apparatus for the Measurement of Breakdown Voltage Between Metal Electrodes in Vacuum; Review of Scientific Instruments; Vol. 6; October 1935; pp. 309-314.]

ball and plane electrodes employed by Anderson were placed inside a vacuum chamber; the separation between the electrodes was on the order of millimeters and the voltages impressed across them went up as high as 500,000 VDC. For a fixed separation of the electrodes, Anderson determined the threshold voltage for breakdown. In Earhart's experiment, the electrode separations for measurements in Region 2 were on the order of ~1000 Å and the voltages were usually <100 VDC. Because the applied voltages, in Earhart's case, were below ~300 VDC his electrodes did not need to be in a vacuum for reasons we have already discussed.

One of Anderson's first results was that the breakdown voltage depended on the electrode material and/or surface finish, the same result Earhart, Kinsley and Hobbs had also found for Region 2. Anderson went on, however, to demonstrate an even more important result, namely that the breakdown voltage saturated at increased electrode separations. This result was counterintuitive since it implied that the electric field at the cathode - the site of electron field emission - decreased with increased electrode separation instead of remaining constant. Anderson was aware that that it was the electric field which was responsible for electron field emission. This indicated that while the breakdown was initiated by electron field emission, it was brought to its conclusion by another mechanism. Anderson determined that the breakdown was actually the result of the emission of positive metal ions - perhaps by field desorption - from the anode in response to the initial burst of field emission electrons from the cathode. These positive metal ions, which moved from the anode to the cathode as a result of the applied voltage, increased the field emission by three means: 1) by reducing the electron space charge between the electrodes; 2) by lowering work function of the cathode, because of their positive charge, as they approached the cathode surface; and 3) by producing secondary electrons when they impacted the cathode surface. Due to their low mobility, compared to electrons, a single positive metal ion could provide for increased electron field emission for thousands of electrons, at the least; by measuring the temperature rise in a thermally insulated electrode, when it was alternately the cathode and then anode, Anderson showed that the temperature rise was greatest when the electrode was the anode, implying that most of the current was, in fact, carried by electrons. The newly released electrons would, in turn, release even more positive metal ions, which would, in turn, generate more field emitted electrons, and so forth and so on.

The culmination of all this positive feedback was the production of a 'vacuum arc or spark', which resulted in the electrical breakdown of the gap. The saturation of the breakdown voltage could then be explained as follows. The electron field emission necessary to initiate the breakdown was always present since, even though the electric field decreased with increased electrode separation, the field was always above the minimum needed to cause field emission. The energy with which the positive metals ions approached and then impacted the cathode increased with increased electrode separation, since the total voltage always increased, though, only slowly; the energy picked up by the positive metal ions in crossing the interelectrode space was, of course, proportional to the total applied voltage and not the electric field. This paper provided a beautiful and elegant experimental confirmation of what was happening, albeit on a smaller scale, in the apparatus utilized by Earhart *et al.*

§5. FIELD EMISSION UNDERNEATH THE 'VACUUM SPARKS' (THE EUROPEAN CONNECTION). - Although Earhart can rightly be said to have provided the first quantitative data on the phenomenon of 'vacuum sparks' via his 1901 and 1908 papers and the papers that were inspired by these papers, his later research seemed to concern itself mainly with experiments whose results were clearly explainable by the normal laws of discharges in gases, i.e., Paschen's law and the like. This was not surprising given that the explanation for the effects he uncovered at very short distances was not convincingly accounted for theoretically until the late 1920s, only a few years before he retired. In fact, a complete explanation of 'vacuum sparks and arcs' is wanting, even today. Glenn Moody Hobbs and Carl Kinsley seemed to have also lost interest in these electrical discharge experiments at small separations even faster than Earhart did, because neither of them published any papers on any subjects after 1908. To be exact, the Science Abstract, Series A showed no citations for either of these gentlemen between 1909 (Vol. 12A) and 1925 (Vol. 28A). Experimental interest in electrical conduction at small distances between electrodes appeared to have pull up stakes and adjourned to Europe, starting about 1910.

On the Continent, Gerhard Hoffmann was the first to verify Earhart's work, which he did in 1910. [454] Hoffmann's work was important in three respects: 1) because he used a hydraulic actuator using mercury as the working fluid and later on a magnetic field actuator, see Fig. E4, to control the spacing between the two electrodes instead of the more traditional lead screw; [455] 2) because like all

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[454] G. Hoffmann; Elektrizitätsüberung durch sehr kurze Trennungastrecken. [Passage of Electricity across very Minute Air-gaps]; Physikalische Zeitschrift; Vol. 11; 1910; pp. 961-967. Or see Science Abstracts, Series A; Vol. 14A; 1911; Abstract No. 122. [Hoffmann's dedication and love for his instrumentation were no better illustrated than on p. 965 of this article, where he referred to the electrometer used to measure the discharge voltages as "…einen guten Kameraden […a good friend…]".]

[455] In what was an interesting example of what biologists call 'parallel evolution', researchers at the University of Pennsylvania investigating point contact diodes during the Second World War also built separate hydraulic actuators (again employing mercury) and magnetic actuators to study the effect of mechanical tapping on these diodes. It had been observed during the course of manufacturing point contact diodes that their characteristics could be improved by tapping the diode case with a mallet before filling the structure with a nonhardening wax. The actuators were used to control the pressure with which the sharpened metal whisker was pressed on the semiconductor slab in a test fixture in the hope of simulating, in the laboratory, the effects of tapping by substituting for it mechanical pressure. See,

A.W. Lawson, P.H. Miller, L.I. Schiff, W.E. Stephens; Effect of Tapping on Barrier Capacity; NDRC 14-???; University of Pennsylvania; September 1, 1943. [Note, this report was originally the previous investigators, he measured the nullpoint (a.k.a. zeropoint, the datum representing the two electrodes in mechanical contact) before the discharge, but unlike them he redetermined the nullpoint after the discharge; and 3) because in the discussion that followed his first paper on this subject, he was asked by Erich Marx why he had not measured the current through the gap directly? Let us examine each of these points in some detail.

Hoffmann's use of a hydraulic and later a magnetic actuator showed that extremely small movements, free of backlash, could be effected by mechanisms other than the lead screw. Hoffmann also credited these actuators with allowing him to be able to revisit the nullpoint. By measuring the change in the nullpoint, Hoffmann was able to show unequivocally that the discharge eroded the surface of the electrodes, the amount of erosion of his plane-point electrode pair depended on the polarity of the applied voltage. This was just what one would expect of a 'vacuum spark' process, where the positive electrode experienced the greater loss of material. In the case of a plane-point electrode pair, one would expect that the polarity dependent erosion would be greatest when the pointed electrode was the anode. Hoffmann's data did, in fact, show a distinct asymmetry in electrode wear. Erich Marx's prescient question about measuring the discharge voltage and current was answered by Hoffmann in the following way. Hoffmann indicated that the currents, besides being transient, also appeared to vary with each discharge even under ostensibly the same conditions which made them not only difficult to measure, but also of questionable value.

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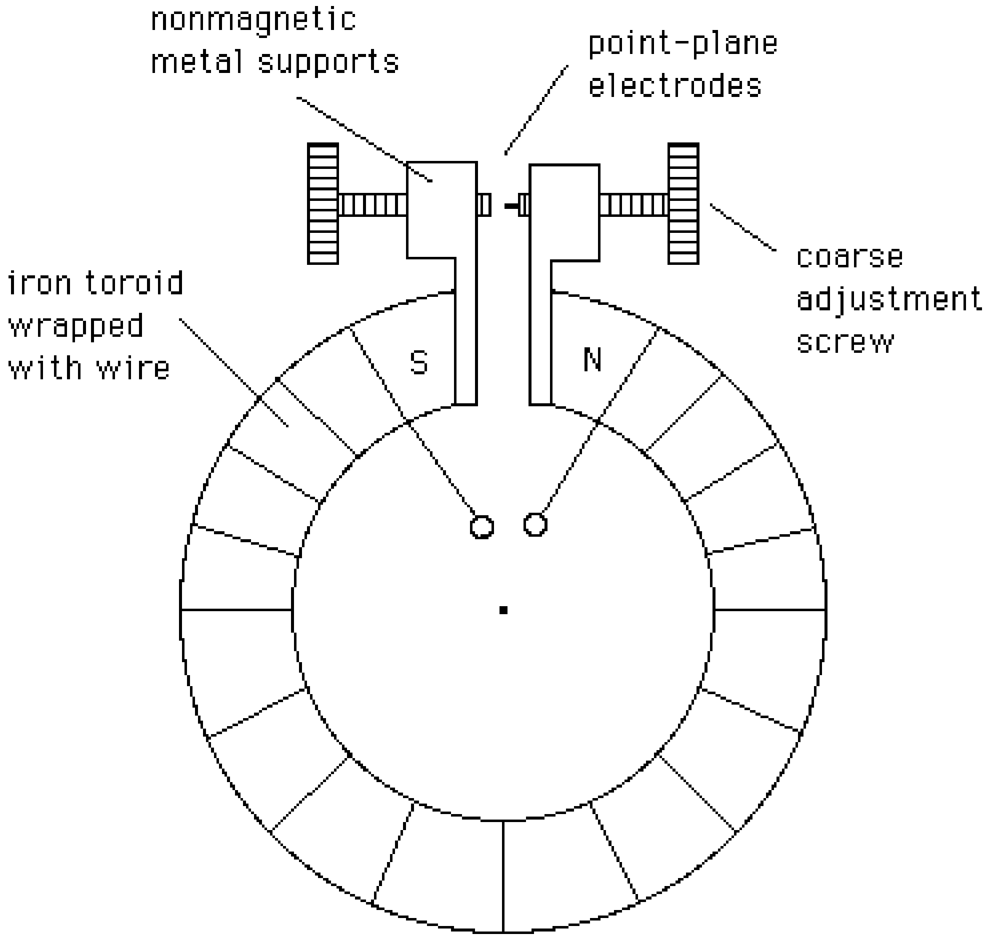
classified SECRET, but was declassified by authority of the Secretary of Defense in a memo written August 2, 1960. The particular copy I have of this report was found in The University of Pennsylvania Archives, North Arcade, Franklin Field, Philadelphia, PA 19104-6320, (215)898-7024. I wish to thank Gail Pietrzyk for her help in locating all the NDRC (National Defense Research Council) reports held in the U. of P. archives.]

FIGURE E4 - Hoffmann's Magnetic Apparatus for Bringing Electrodes Close Together



Perhaps Hoffmann’s most lasting legacy was his verification of Earhart’s results - results which were very controversial, even though they had been duplicated by a number of independent investigators. Hoffmann enumerated at the start of his 1910 paper all the pertinent objections voiced against Earhart’s methodology, and then proceeded to construct his apparatus so as to obviate each one of them. The list of objections presented by Hoffmann was as follows:

i) Vibration.
ii) Destruction of the electrode surfaces at the point of contact used to establish the nullpoint by the discharge.

iii) Impossibility of re-examining the nullpoint after the discharge due to the severity of the destruction.
iv) Inability of the Earhart configuration to allow for the measurement of displacement of the fixed electrode due to electrostatic attraction between the electrodes.

Hoffmann's contributions did not stop with his 1910 paper. In 1921, after a hiatus of more than a decade during which he designed and built a more sensitive vacuum electrometer, he returned one last time to verify, again, Earhart's measurements. This obsessive checking and rechecking was a hallmark of the really good workers in this particular field: Earhart obtained his first results in 1901 and then verified and extended them in 1908; Hoffmann, as I just indicated, verified Earhart's results in 1910 and then again with some extensions in 1921; and, as we shall see later on, Franz Rother, who would be the first to observe pure field emission - as opposed to 'vacuum arcing' - using the Earhart apparatus, obtained his first results in 1911, verified them in 1914 and then rereverified them under even more stringent conditions in 1926.

The next person on the Continent to reexamine Earhart's work was a German graduate student named Franz Rother. Using basically the same apparatus to control the electrode spacing as Earhart, Rother in 1911 did what no one had yet been able to do, he measured the current flowing between the two closely spaced electrodes. Rother understood that the transient nature of the 'vacuum sparks' made it difficult to accurately divine their currents. In addition, he also realized that the 'vacuum sparks' changed the electrode surfaces, and in so doing probably resulted in the arc current varying at each occurrence. His stroke of genius was twofold: 1) he lowered the DC voltage applied across the electrodes to the point where the arcs did not occur, and 2) he apparently assumed that a current would flow even in the absence of any 'arcing'. Rother's assumption, that there would be current flowing across the gap without 'arcing ["…Lichtbogenbildung…"]', appeared to be quite daring given that the concepts of electron tunneling and field emission, in their modern incarnations, had not yet even been stated. However, as we shall see later on, the first clear notions about what we today call field emission were only first enunciated in 1903 by J. J. Thomson, but in strictly classical terms. Note, Rother averred, at the start of his paper, that the idea for his research originated with his thesis advisor Dr. Otto Wiener in 1907, but a perusal of the Science Abstracts, Series A did not reveal any papers by Wiener addressing this phenomenon, at least directly. Rother's first paper, which contained all the basic experimental methodologies and techniques albeit in a very terse form, 3 pages, was published in 1911 while he was still a graduate student.[456] Three years later, when he finally earned his doctorate, he published a fairly detailed account of the

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[456] F. Rother; Der Elektrizitätsübergang bei sehr kleinen Kontaktabständen [Electrical Conduction at very small Electrode Separations].; Physikalische Zeitschrift; Vol. 12; 1911; pp. 671-674.

experimental work, 35 pages compared to the paltry 3 pages in the 1911 article. [457]

Although I will not be able to delve into exactly how Rother made the measurements of these exceedingly small currents due to time constraints, it is important to, at least, touch on the current measurement abilities of that era.

§6. CURRENT MEASUREMENT CAPABILITIES CIRCA 1900. - The currents measured by Earhart, Shaw, Kinsley, Hobbs, etc. were relatively speaking very large since they were due to either glow discharge or a 'vacuum spark' discharge. Rother made use of two methods for measuring very small currents: 1) the platform galvanometer, which he employed in his later papers; and 2) the quadrant electrometer method, which he used in his first paper in 1911.

The platform galvanometer (also known as the d'Arsonval movement) was first presented in a paper in 1882 by Marcel Deprez and Jacques-Arséne d'Arsonval. [458] This instrument was devised, according to its creators, for the

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[457] F. Rother; Der Elektrizitätsübergang bei sehr kleinen Kontaktabständen und die Elektronenatmosphären der Metalle [Electrical Conduction at very small Electrode Separations and the Electron Atmosphere of Metals].; Annalen der Physik und Chemie; Vol. 44 (4th Series); 1914; pp. 1238-1272.

[458] [M.] Deprez, [J.] d'Arsonval; Galvanomètre apériodique de MM. Deprez et d'Arsonval [Transient galvanometer of Deprez and d'Arsonval]; Comptes Rendus Hebdomadaries des Seances de l'Academie des Sciences (Paris); Vol. 94; 1882; pp. 1347-1350. [As the reader has, no doubt, come to expect, Deprez and d'Arsonval were not the first persons to invent the galvanometer. The progenitor of all galvanometers was discovered around 1819 by Hans Christian Oersted when he accidentally brought a wire carrying DC current near a magnetic compass and observed the resulting deflection of the compass needle. All sources agree on the significance and priority of Oersted's work, it is on the question of who took the next step that disagreement appears. According to one source, two months after Oersted announced his findings, the instrument we now call the galvanometer was invented by Johann Salomo Christoph Schweigger. See,

Herman Goodman; Story of Electricity and a Chronology of Electricity and Electrotherapeutics; Medical Life Press; 1928; pp. 27 & 60.

Schweigger's galvanometer consisted of a magnetized needle suspended somehow and placed inside a fixed coil of wire. According to a different source,

Forest Klaire Harris; Electrical Measurements; John Wiley & Sons, Inc.; 1952; pp. 44-45.

the galvanometer, consisting of the pivoted magnetized needle arranged inside a fixed coil, was first described by Claude Servais Matthias Pouillet in 1837; this type of galvanometer was usually called a tangent galvanometer. An improved version of the tangent galvanometer, called the moving-magnet galvanometer, was invented by William [?] Thomson in 1858. This version suspended the magnet from a delicate torsion fiber and surrounded the galvanometer with, for example an iron cylinder to shield it from the perturbing effects of the Earth's magnetic field. According to Forest K. Harris, the moving coil galvanometer was first described by William Sturgeon in 1836, who apparently began his professional life as a shoemaker; it was improved in 1867 by Thomson when he added a fixed iron core (armature) to the coil; and finally achieved its modern day form with the addition of pole pieces for the fixed magnet by Deprez and d'Arsonval in 1882.

purpose of detecting small transient currents. Its amazing sensitivity owed much to its use of a light beam as its pointer or indicator, the torsion fiber suspension system, and the small gap between the rotating coil and the stationary magnet due to the shaped pole pieces of the latter. Specifically, this moving coil galvanometer used a mirror a fixed to the coil to reflect a beam of light from a stationary light source to a distant, movable scale. As originally conceived by Deprez and d'Arsonval, the torsion fiber supporting the rotating coil was made of very fine silver wire ["…à deux fils d'argent…"]. Silver was used undoubtedly because of its enormous ductility, which allowed it to be drawn down into extremely fine wires; the silver torsion wires, supporting the rotating coil from above and below, also served as the electrical connections to the coil. Unfortunately, silver torsion wires were far from ideal. Modern versions of the Deprez-d'Arsonval platform galvanometer employed torsion fibers made by rolling gold (14K or 24K), copper or phosphor-bronze into fine ribbons. Note, while the use of metal torsion fibers was the rule for engineering instruments, the highest sensitivity could only be obtained using drawn quartz fibers whose superior mechanical properties were second to none. [459] The drawn quartz torsion fibers were usually silver plated to allow the electrical connections to be made to the rotating coil.

When Rother wrote his *magnum opus* on field emission in 1926, he employed a commercially built, high sensitivity, platform galvanometer manufactured by Hartmann & Braun [460] with a 1 mm deflection equaling $2.6X10^{-11}$ A (26 pA) on a scale located 2 m away. It was obvious that these commercial instruments were certainly sensitivity enough to be able to detect field emission currents which were nominally around 10^{-8} - 10^{-7} A (10-100 nA). In fact, this same type of galvanometer <u>would</u> have been able to detect the smaller, by an order of magnitude, tunneling currents, if it had been so desired. The proof of this last assertion can be found in a 1904 paper by F. Harms, in which he stated that he was using a Deprez-d'Arsonval type platform galvanometer manufactured by Hartmann & Braun with a sensitivity of $9.04X10^{-}$

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[459] C.V. Boys; Quartz Fibers; Nature; Vol. 42; October 16, 1890; pp. 604-608. [Boys drew his quartz fibers by the crossbow method, i.e., he heated two piece of quartz until they were soft, one piece fixed to a lab bench the other on the end of an arrow, and then he touched them together and fired the arrow which drew out the fiber.]

[460] The Braun of Hartmann & Braun - today called Hartmann & Braun AG - was Wunibald Braun, the eldest brother of Karl Ferdinand Braun. Hartmann & Braun AG started out as a small instrument making company owned by Eugen Hartmann in the town of Nürtingen. Ferdinand Braun, who besides being a world class scientist was also a good businessman and recognized a 'comer' of a business when he saw it, put his brother in touch Hartmann, and Wunibald became initially a silent partner in the renamed firm, E. Hartmann & Co. Ferdinand Braun would himself become involved with the Hartmann & Braun as an idea man. Being a small company, Hartmann & Braun did not have the capital to invest in research and development of new produces, and so Ferdinand Braun struck a deal with them to take over some of the R&D work on a consulting basis. More details can be found in,

Friedrich Kurylo, Charles Susskind; <u>Ferdinand Braun</u>; The MIT Press; 1981; pp. 46-47, 57-58, 191.

^{10} A.[461] Platform galvanometers continued to be used to measure small currents up until about the early 1960s.

The current sensitivity of a galvanometer, regardless of its type (pointer type meters, portable reflecting meters, wall galvanometers, platform galvanometers, or high sensitivity galvanometers), was given by a number of different figures-of-merit. For example, Forest K. Harris defined the current sensitivity as the response/stimulus, where the response was the number of millimeters (mm) of deflection for a given current expressed in microamperes (µA). He also used a figure-of-merit called a scale factor, which was the inverse of the current sensitivity, i.e., it had units of µA/mm and was the number one multiplied the deflection by to obtain the actual current reading. Note, the movable scale to galvanometer distance was assumed to have been set to 1 m. Most authors discussing galvanometers used one of these two figures-of-merit.[462] Harris' book, which was published in 1952, listed the then current sensitivity and scale factor for a number of commercially available galvanometers. The surprising thing about this tabulation was that the best scale factor in 1952 was 0.00001 µA/mm, i.e., 10^{-11} A per mm @ 1 m scale distance, which was only slightly better than that of the galvanometer used by Rother in his 1926 paper. Thus, it appeared that the ultimate sensitivity of galvanometers was reached early on, probably before 1926. The limit to the ultimate sensitivity was shown by Gustav Ising in 1926 to be due to Brownian motion of the rotating coil about its equilibrium position.[463]

Although I will not have the time or space to delve into the subject, I should like to just mention that the sensitivity of the platform galvanometer could also be increased by the use of an ultra-high stability, vacuum tube (FP-54 Pliotron), DC amplifier. Using such an arrangement, in 1939, F. R. Abbott and Joseph E. Henderson were able to make continuous measurements of field emission currents over the current range, 10^{-17} - 10^{-5} A.[464]

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[461] F. Harms; Über eine Vorrichtung zur exakten Eichung von Elektrometern für Elektrizitätsmengen und ihre Anwendung auf die absolute Messung äusserst geringer Stromstärken [On an apparatus for the exact calibration of electrometers for electrical quantities and their application to the absolute measurement of extremely small current strength].; Physikalische Zeitschrift; Vol. 5; No. 2; 1904; pp. 47-50.

[462] Walter C. Michels; Electrical Measurements and Their Applications, 7th Ed.; D. Van Nostrand Co., Inc.; May 1968; pp.20-23 & 32-36. [**Caution**, even though this is the 7th edition of this book, it nevertheless contains a significant number of errors and inconsistencies.]

[463] G. Ising; Natural limit for the Sensibility of Galvanometers; Philosophical Magazine [and Journal of Science]; Vol. 1 (7th Series); 1926; pp. 827-834. [Also see,

R.B. Barnes, S. Silverman; Brownian Movement as a Natural Limit to All Measuring Processes; Reviews of Modern Physics; Vol. 6; No. 3; July 1934; pp. 162-192.]

[464] F.R. Abbott, J.E. Henderson; The Range and Validity of the Field Current Equation; Physical Review; Vol. 56; July 1, 1939; pp. 113-118. [Consult the following articles for detailed descriptions of ultra-high stability, vacuum tube, DC amplifiers:

L.A. DuBridge; The Amplification of Small Direct Currents; Physical Review; Vol. 37; February 15, 1931; pp. 392-400.

While the moving coil galvanometer eventually became the instrument of choice for Rother, it was not the way in which he measured his first field emission currents in 1911. Rother's first technique for measuring field emission currents involved using a quadrant electrometer. The quadrant electrometer, also known as the Thomson quadrant electrometer, had a long and distinguished lineage going all the way back to the gold leaf electrometer (a.k.a. electroscope).

The gold leaf electroscope was invented around 1786 by Abraham Bennet. As the materials technology of insulators evolved during the 19th century, the electroscope became a more and more sensitive indicator of electrical charge. The goal of instrument makers and scientists - many times the same person - was to insulate the metal leaves so well that one could detect a single electric charge. However, it was soon discovered that no matter how well one constructed the electroscope, its charge leakage rate could not be brought to zero; even with the best insulators (amber) and filling the electroscope with dry filtered air, the charged up leaves invariably lost charge. The first hint as to what was causing this leakage was provided by a 1879 paper by William Crookes.[465] Crookes built a blown glass electroscope where the metal leaves were completely isolated from the outside, i.e., they hung on a glass hook which, in turn, was attached to the inside of the glass envelope. He then evacuated and sealed off the glass bulb, and finally charged up the leaves by a very clever process - a process so clever I am still at a loss to explain it. What he found was that if he immersed the charged electroscope in a water bath that was grounded, so as to keep excess charge from inadvertently accumulating on the outside of the bulb, the leaves held their initial charge for more than a year. Taking a hint from Crookes' work, other researchers soon discovered that something was ionizing the air inside their electroscopes and that was why the charge was leaking off. The 'something' turned out to be a combination of natural radioactivity and cosmic rays. The fascinating story behind this discovery is, however, beyond the scope of this thesis.[466]

As was the case with the galvanometer, the electrometer underwent a dizzying array of modifications on its way to becoming a truly reliable, useful and commonplace laboratory instrument. I'd like to explain how Rother adapted a quadrant electrometer to the task of measuring currents on the order of 10^{-14} A, but I have run out of time.

A.W. Hull; Electronic Devices as Aids to Research; Physics; Vol. 2; No. 6; June 1932; pp. 409-431.

L.R. Hafstad; The Application of the FP-54 Pliotron to Atomic Disintegration-Studies; Physical Review; Vol. 44; August 1, 1933; pp. 201-213.

D.B. Penick; Direct-Current Amplifier Circuits for Use with the Electrometer Tube; Review of Scientific Instruments; Vol. 6; April 1935; pp. 115-120.]

[465] W. Crookes; On Electrical Insulation in High Vacua; Proceedings of the Royal Society (London); Vol. 28; 1878-79; pp. 347-352.

[466] C.T.R. Wilson; On the Ionization of Atmospheric Air; Proceedings of the Royal Society (London); Vol. 68; 1901; pp. 151-161.

§7. SCANNING, THE MISSING ELEMENT? - In all of the discussions so far about the work of Earhart and Rother there has been no mention of the idea of scanning. This was the one element that would have made their apparatuses functionally identical with modern versions of the STM. It turns out, though, that the idea of using piezoelectric actuators to create a raster scanned image of a microscopically sized area was thought of as early as 1932, if not earlier, in a slightly different context. This need for scanning arose as a logical consequence of the near-field microscope, which was proposed as a way to 'beat' the Abbe limit.

The first analytical foray into the question of the resolution of a microscope was the work of one Ernst Abbe.[467] In a paper published in 1873, Abbe first expounded his optical resolution model.[468] I have not yet obtained and translated this paper, but a clear and succinct description of Abbe's ideas can be found in an English language paper published in 1906 by Albert B. Porter.[469] Porter's description was so lucid that I could not improve upon it, so it shall be presented here verbatim,

> If a lens is to produce a truthful image of an illuminated object, it must have an aperture sufficient to transmit the whole of the diffraction pattern produced by the object; if but part of this

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[467] Ernst Abbe (pronounced "ah-buh") was a professor of mathematical physics at the University of Jena, Germany. An alternative criterion for calculating optical resolution was the Rayleigh criteria, which though derived from different assumptions, yielded the same result. Rayleigh was, of course, John William Strutt, a.k.a. the 3rd Earl of Rayleigh, a.k.a. Lord Rayleigh.

It must be mentioned that Abbe displayed a sense of social responsibility far ahead of his time and perhaps of ours. Together with a university mechanic named Carl Zeiss, Abbe in 1866 helped the firm, Carl Zeiss, become world famous for optics. In 1884, Abbe joined Otto Schott and made the firm, Schott Glass, equally famous. All the while not losing sight of his responsibilities to the workers in both companies. Besides having secure positions, the workers shared in the profits, there were pension plans which also covered their families, and in 1900 Schott Glass became one of the first companies to institute an 8 hour work day. Abbe's position was best summed up in his own words, "I do not intend to die a millionaire." And he didn't, he willed all his money to the Carl Zeiss Foundation - a charitable foundation. See,

Heinz G. Pfaender, Hubert Schroeder; Schott Guide to Glass; 1983; pp. 11-13.

Friedrich K. Möllring; Microscopy from the very beginning; Carl Zeiss; 1979; p. 63.

[468] E. Abbe; Ueber einen neun Beleuchtungsapparat am Mikroscop [On a new illumination apparatus for the microscope]; Archiv für mikroskopische Anatomie; Vol. 9; 1873; pp. 469-480.

[469] A.B. Porter; On the Diffraction Theory of Microscopic Vision.; Philosophical Magazine [and Journal of Science]; Vol. 11 (6th Series); January-June 1906; pp. 154-166. [**Warning**, Porter's citation of Abbe's paper in the journal, *Archiv für mikroskopische Anatomie*, incorrectly gives the paper's date as 1837 instead of 1873 - probably a typo.

Porter pointed out that even 32 years after Abbe first proposed his ideas on resolution, they were still considered controversial by microscopists and were not well known even to physicists. He also revealed that diffraction can affect even macroscopic seeing depending on the illumination and the size of the object which was viewed. To this end he demonstrated a very simple experiment where the human eye replaced the microscope and in which the diffraction effects could be quite easily shown using a spatial low pass filter.]

> diffraction pattern is transmitted, the image will not truthfully represent the object, but will correspond to another (virtual) object whose whole diffraction pattern is identical with that portion which passes through the lens; if the structure of the object is so fine, or if the aperture of the lens is so narrow, that no part of the diffraction pattern due to the structure is transmitted by the lens, then the structure will be invisible no matter what magnification is used. [470]

As Porter went on to explain, in order to see an object, the object must diffract the light and then the microscope must have a large enough aperture to collect the higher order diffraction spectra. If the object was significantly smaller than the wavelength of the light (~1/2 λ) used to illuminate it, it would not produce a diffraction pattern and so would be invisible no matter what size the microscope aperture and magnification. This last point appeared to throw up an insurmountable barrier to viewing very small objects, at least using light. However, the insurmountability of this barrier turned out to be illusionary. By using a clever trick one could significantly extend the resolution of a visible light microscope.

In an article published in 1928, Edward Hutchinson Synge showed that it was theoretically possible to image below the Abbe limit by using the following ploy. He suggested stationing a 10^{-6} cm [100 Å] diameter pinhole made in an opaque screen beneath a thin perfectly parallel embedded and sectioned specimen at a distance that was a fraction of the hole's diameter. The pinhole was to be illuminated from underneath by an intense source of light; any light which came through the specimen was to be passed through a microscope and detected by a phototube. The image of the complete specimen was to be formed by moving the specimen back and forth in a raster scan manner with each increment of movement being 10^{-6} cm. [471]

This configuration is called a near-field microscope, and it works as follows. The pinhole should not allow any light to pass through due to its diameter being only a small fraction of a wavelength of the incident visible light.

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[470] Ibid.; p. 154.

[471] E.H. Synge; A Suggested Method for extending Microscopic Resolution into the Ultra-Microscopic Region; Philosophical Magazine [and Journal of Science]; Vol. 6 (7th. Series); 1928; pp. 356-362

Due to technological limitations Synge's ideas were not realized during his lifetime and his original work faded into obscurity. Many years later, his idea was independently rediscovered by a number of different researchers and the realization of these ideas created the discipline of near field optics. Synge's earlier contribution was made known to the microscopy community via a 1990 article by Dennis McMullan,

D. McMullan; The Prehistory of Scanned Image Microscopy, Part 1: Scanned Optical Microscopes; Proceedings of the Royal Microscopical Society; Vol. 25; No. 2; March 1990; pp. 127-131.

Idem; The Prehistory of Scanned Image Microscopy, Part 2: The Scanning Electron Microscope; Proceedings of the Royal Microscopical Society; Vol. 25; No. 3; May 1990; pp. 189-194.

But due to strictly classical considerations, an evanescent wave does emerge from the far side of the pinhole. The specimen is located so close to the far side of the pinhole, that the diameter of the evanescent wave going through the specimen is approximately that of the pinhole; the specimen is in the near-field of the pinhole. Upon exiting the specimen, the evanescent wave, attenuated by the optical density of the specimen, begins to spread out. The microscope objective, which is located at a macroscopic distance from the specimen (far-field), captures the zeroth order (central) fringe of the resulting diffraction pattern. This central fringe contains the information about the average brightness of the illuminated spot which is then transmitted to the photoelectric cell located at the eyepiece. Thus by scanning the sample, a gray scale picture of the scanned area can be built up.

Initially, Synge proposed using differential screws to move the sample in its own plane and thus generate the scanned image. But in 1932, he suggested that a far better method would be to use piezoelectric actuators to do the scanning. [472] Synge said that he got the idea while reading a book by P. Vigoureux. Whatever his inspiration, the idea was ahead of its time. As I said earlier, I do not know if Synge was the first person to suggest the use of piezoelectric actuators for doing raster scanning of microscopic areas. However, it would be amazing if he was the first given that piezoelectricity had been around since its discovery in 1880 of the brothers Curie.

§8. FIELD EMISSION & ELECTRON TUNNELING THEORY, THE J. J. THOMSON CONNECTION. - Surprisingly, the nascent idea of emission of electrons from cold metals was already out and about in a theory proposed by Joseph John Thomson. I first became aware of this in a 1910 paper by Elmer H. Williams. [473] On pages 218 & 219 of this paper, Williams stated that J. J.

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[472] E.H. Synge; An Application of Piezo-electricity to Microscopy; Philosophical Magazine [and Journal of Science]; Vol. 13 (7th Series); No. 83; February 1932; pp. 297-300.

[473] E.H. Williams; The Nature of Spark Discharge at very small Distances; Physical Review; Vol. 31 (1st Series); July-December 1910; pp. 216-240. [Williams indicated that he had read these ideas in the following book by Thomson, Conduction of Electricity through Gases; p. 456. Unfortunately, Williams did not indicate which edition of the book he was referring to. This was and still is a very famous book and went through three editions - four if you include the prequel,

J.J. Thomson; The Discharge of Electricity Through Gases; Charles Scribner's Sons; 1898.

It turned out, that the passage quoted by Elmer H. Williams came from the 2nd edition (1906) of J.J. Thomson's book, and was found in the section detailing the work of Earhart, Kinsley & Hobbs. This same passage could also be found in the 1st edition (1903) on p. 386 and in Vol. II of the 3rd edition (1933) on pp. 493-494. In the 1st edition of Conduction of Electricity through Gases, the only work on discharges between closely spaced electrodes discussed by J.J. Thomson was the first paper by Robert Francis Earhart. At the end of his description of Earhart's work, Thomson presciently stated that this work of Earhart was very important and he hoped it would be pursued.

Thomson had proposed a "…possible explanation…" for conduction between very closely spaced electrodes. The model proposed by J. J. Thomson included many of the ideas that we associate with the modern theory of electron tunneling and field emission: 1) some electrons inside the metal were free to move about in the same way as gas molecules inside a container, 2) these free electrons could not normally escape from the metal due to the image force, [474] and 3) the image force could be counteracted by a strong electric field impressed across the electrodes. The discharge, arc, spark etc. resulting from this model would be, according to Thomson, "…entirely carried by the corpuscles [electrons] and no part of it by the positive ions." In other words, this type of discharge would be very different from, for example a glow discharge in which the current was carried by positive gas ions, electrons and sometimes negative gas ions. J. J. Thomson was well aware of the minimum potential difference needed to ionize a gas, and at the same time he was also cognizant of the experiments of Earhart *et al.* which, in Region 2, could not be explained away as a gas discharge. It is very possible that Rother had read or heard of these ideas of J. J. Thomson's, and had subscribed to them. Note, these same essentially classical ideas, by which J. J. Thomson attempted to explain the emission of electrons from cold metals, were resurrected in 1923 by Walter Schottky in his bid to rationalize the conduction behavior of closely spaced conductors.

In 1923, Walter H. Schottky suggested that the various phenomena associated with conduction across closely spaced electrodes might be due to the emission of electrons from cold metals. [475] Schottky's scenario for emission of electrons from cold metals was in its essence a semi-classical theory with the purely classical portion having already been espoused some twenty years earlier by J. J. Thomson in his book, Conduction of Electricity Through Gases. Note, the second footnote at the bottom of p. 67 of Schottky's 1923 article referenced one of his earlier articles entitled: Über den Einfluß von Strukturwirkungen, besonders der Thomsonschen Bildkraft, auf die Elektronenemission der Metalle.

After finding Williams' paper, I also happened upon an earlier article by K.E. Guthe which made mention of J.J. Thomson's theory of electron emission from cold metals. Guthe was trying to enlist Thomson's ideas on cold emission in support of coherer action, which Guthe was actively interested in. See,

K.E. Guthe; Coherer Action; The Electrician (London); Vol. 54; November 4, 1904; pp. 92-94.]

[474] The method of images as used in the study of electricity and magnetism originated, according to Maxwell,

James Clerk Maxwell; A Treatise on Electricity and Magnetism, Vol. 1; Oxford at the Clarendon Press; 1892 (3rd Ed.); p. 245.

with Sir William Thomson (a.k.a. 1st Baron Kelvin of Largs, Lord Kelvin) and first appeared in the Cambridge and Dublin Mathematical Journal in 1848. Note, William Thomson was knighted in 1866 for, among other things, his work on the Atlantic submarine telegraph cable; he became a peer of the realm - a Lord - in 1892.

[475] W. Schottky; Über kalte und warme Elektronenentladungen [On cold and warm Electron Emission]; Zeitschrift für Physik; Vol. 14; 1923; pp. 63-106. [An English language translation of this rather lengthy article can be obtained from the National Translation Center, Library of Congress, Washington DC 20541. The cost is $35.00, and the ID# of the translation is TT-123-82. **Warning**, this was not a very good translation!]

The term Thomson Image Force [Thomsonschen Bildkraft] in this title referred to Sir William Thomson's (a.k.a. Lord Kelvin's) concept of image forces and not, at least directly, to the explanation for emission of electrons from cold metals postulated by J. J. Thomson in Conduction of Electricity through Gases. The semi-classical part of Schottky's theory came from his use of what we call today 'quantum levels' to describe the energy levels of the conduction electrons in the metal contacts, a concept he borrowed from Niels Bohr. The actual full blown quantum mechanical description of the processes considered by Schottky would have to wait until the 1928 paper by R. H. Fowler and L. Nordheim; the Fowler-Nordheim paper was itself only possible after the 1926 *début* of Erwin Schrödinger's series of papers on wave mechanics published in *Annalen der Physik*. 1928 was, in fact, a bellwether year for tunneling theory, since no less than four papers appeared postulating tunneling as an explanation for such diverse phenomena as the ionization of hydrogen by an externally applied electric field (J. Robert Oppenheimer), electron emission from cold metals (R. H. Fowler and L. Nordheim), and radioactive decay by alpha particle emission (Ronald W. Gurney and Edward U. Condon, and George [Georgii] Gamow). [476] Note, it is not generally appreciated that Gamow's paper had certain fundamental errors in it, which were pointed out and corrected in a later paper by Max von Laue. [477]

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[476] J.R. Oppenheimer; Three Notes on the Quantum Theory of Aperiodic Effects; Physical Review; Vol. 31; 1928; pp. 66-81.

R.H. Fowler, L. Nordheim; Electron Emission in Intense Electric Fields; Proceedings of the Royal Society (London); Vol. 119 (Series A); 1928; pp. 173-181.

G. Gamow; Zur Quantentheorie des Atomkernes [On the Quantum Theory of Atomic Nucleus]; Zeitschrift für Physik; Vol. 51; 1928; pp. 204-212. [Gamow acknowledged that his ideas did not come from a vacuum by referencing both the Oppenheimer and Fowler-Nordheim papers. **Note**, a few day before Gamow submitted his paper, two American scientists, Ronald W. Gurney and Edward U. Condon, delivered a preliminary paper to the journal, *Nature*, which covered the same topic (α decay) and postulated the same conclusion (that it was due to tunneling) as Gamow. See,

R.W. Gurney, E.U. Condon; Wave Mechanics and Radioactive Decay; Nature; Vol. 122; September 22, 1928; p. 439. [This preliminary paper was followed shortly by a more detailed and quantitative paper,

R.W. Gurney, E.U. Condon; Quantum Mechanics and Radioactive Disintegration; Physical Review; Vol. 33 (2nd Series); No. 2; February 1929; pp. 127-140.]

In a talk given in 1969, Condon indicated that Gurney was the 'idea man' of the Gurney-Condon team. See,

E.U. Condon; Tunneling - how it all started; American Journal of Physics; Vol. 46; No. 4; April 1978; pp. 319-323.

Many books and papers failed to mention that the tunneling theory of alpha decay should rightfully be referred to as the Gurney, Condon and Gamow theory, and not simply the Gamow theory. To add insult to injury, some citations, which did reference all three people, nevertheless managed to somehow introduce an error or two into their citing of the Gurney & Condon paper. For example, Max Jammer referred to them as "…R.W. Gurner [sic] and E.U. Condon…", see,

Max Jammer; The Conceptual Development of Quantum Mechanics; McGraw-Hill Book Co.; 1966; p. 247, footnote 191.]

[477] M. von Laue; Notiz zur Quantentheorie des Atomkerns [Note on the quantum theory of the atomic nucleus]; Zeitschrift für Physik; Vol. 52; December 31, 1928; pp. 726-734.

§9. TUNNELING IN SOLIDS: COHERERS AND SUPERCONDUCTIVITY. - Franz Rother extended the work of Earhart *et al.* to very high vacuums in 1926 using essentially the same apparatus. [478] Starting slightly after the mid 1920s and following an entirely different line of reasoning having to do with the the elucidation of the mechanism behind the demodulation (detection) of AM radio signals by galena point contact diodes, H. Pélabon in France, and later Bruno Benedetto Rossi together with G. Todesco in Italy, built lead screw driven contrivances for bringing metal electrodes - usually a ball and a plane - to close approaches on the order of the distances attained by Earhart, but without the benefit of a Michelson interferometer to double check the distance (for more details see the main section entitled WHAT IS KNOWN (PRE-1970)). Coincident with all this other work, the 1920s also witnessed the first realization of electron tunneling by squeezing a MOM (Metal-Oxide-Metal) junction, which grew out of an observation during the course of work at low temperatures.

Heike Kamerlingh Onnes' pursuit of ever lower temperatures produced the unexpected phenomenon of superconductivity in 1911, when he discovered that mercury lost all measurable electrical resistance at ~4.2ºK. [479] Superconductivity was unexpected in that some of then current theories actually predicted a parabolic relationship between resistance and temperature. For example, according to the theory of Lord Kelvin, the resistance would initially drop as the temperature decreased due to the decreased scattering of the free electrons as a result of the attenuated thermal motions of the ion cores; eventually, though, the falling temperatures would cause the free electrons to reattach themselves to their respective ion core, i.e., freeze out, thus causing the resistance to begin to increase. The superconductivity of mercury, of course, demolished this theory. Extending his investigation to other metals, Kamerlingh Onnes showed that they too became superconducting at different temperatures close to absolute zero. In 1914, he showed that it was possible to build a superconducting switch using two pieces of lead lightly pressed together; when

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[478] F. Rother; Über den Austritt von Elektronen aus kalten Metallen [On the Efflux of Electrons from cold Metals]; Annalen der Physik; Vol. 81; No. 20; 1926; pp. 317-372, + Plates 2-4.

[479] Heike Kamerlingh Onnes won the 1913 Nobel Prize in Physics for his pioneering working in low temperature physics, specifically for his success in liquefying helium in 1908 and discovering superconductivity in 1911. It should be noted that while liquefying helium was certainly a great triumph, just the logistics of obtaining enough gaseous helium to liquefy required an equally heroic effort. Initially, he petitioned his friend and rival, James Dewar, for a supply of helium from the natural gas wells at Bath [England?]. Dewar turned him down, saying that, "It is a mistake to suppose the Bath supply is so great. I have not been able so far to accumulate sufficient [helium] for **my** [Emphasis added.] liquefaction experiments." Eventually, Kamerlingh Onnes was able to extract a sufficient quantity of helium from monazite sands found in North Carolina, USA. See,

Kostas Gavroglu, Yorgos Goudaroulis (Eds.); Through Measurement to Knowledge, The Selected Papers of Heike Kamerlingh Onnes 1853-1926 (Vol. 124, Boston Studies in the Philosophy of Science); Kluwer Academic Publishers; 1991; p. lv.

this lead-lead sandwich was exposed to temperatures below the point where lead becomes superconducting, the switch closes, i.e., becomes superconducting. [480] In all his earlier electrical experiments at low temperatures, the ends of the lead (Pb) wire forming the superconducting coil were joined by simply melting together the ends of the lead (Pb) wire; the superconducting current was started by magnetic induction, after the lead (Pb) coil was immersed and thermally equilibrated in liquid helium. When it was first suggested to him that he should try a lead-lead switch in his experiments, Kamerlingh Onnes was doubtful it would work given that his own measurements had shown that, at room temperature, the transition or crossing resistance (due to a foreign film at the surface of the lead contacts) of such a switch was relatively large. However, it turned out that at liquid helium temperatures the switch became superconducting, its room temperature behavior notwithstanding. Kamerlingh Onnes did not pursue an investigation into why this switch should exhibit such counterintuitive behavior. These questions and others were investigated in the late 1920s and early 30s by Holm and Meissner.

Employing two crossed metal rods pressed against one another, Ragnar Holm and Karl Wilheim Meissner [481] attempted to measure whether or not a transition or crossing resistance ["…Übergangswiderstand…"] existed at the area of contact between two metal contacts of the same or different metals, this was their original purpose, not proving the existence of electron tunneling in this structure. In the crossed rod experiment, the total resistance was the sum of the spreading or constriction resistance ["…Ausbreitungswiderstand…"] due to the fanning out or crowding in of the current as it flows between the crossed rods through the minuscule circular area of contact, and the transition or crossing resistance, which was postulated to originate at the surface of each metal contact due to the inevitable presence of oxides, adsorbed or condensed gases or any other foreign layer ["…Fremdschicht…"]. Because the sought after transition or crossing resistance was deduced to be of the same order of magnitude as the

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[480] H. Kamerlingh Onnes; Further experiments with liquid helium. L. The persistence of currents without electromotive force in supra-conducting circuits. (Continuation of J).; Communications from the Physical Laboratory at the University of Leiden [sometimes referred to as the 'Leiden Communications']; Vol. 141b; 1914; pp. 15-21. [Note, this journal is not easily found at most university libraries. However, this particular paper can be found in the following book, which enjoys a more widespread distribution,

Kostas Gavroglu, Yorgos Goudaroulis (Eds.); Through Measurement to Knowledge, The Selected Papers of Heike Kamerlingh Onnes 1853-1926 (Vol. 124, Boston Studies in the Philosophy of Science); Kluwer Academic Publishers; 1991; pp. 356-362.]

[481] Karl Wilheim Meissner was best known for his experimental work in 1933, together with R. Ochsenfeld, which led to the discovery of magnetic flux exclusion from the interior of a superconductor (a.k.a. perfect diamagnetism), the so-called Meissner effect,

W. Meissner, R. Ochsenfeld; Ein neuer Effekt bei Eintritt der Supraleitfähigkeit [A New Effect at the Onset of Superconductivity]; Die Naturwissenschaften; Vol. 21; No. 44; November 3, 1933; pp. 787-788.

It was this work which laid the foundation for the microscopic theory of superconductivity as enunciated by J. Bardeen, L. Cooper, J. Schreiffer and N. Bogoliubov in 1957, the so-called BCS theory.

spreading or constriction resistance, the rods were cooled with liquid helium, thus greatly, and in some cases completely, reducing the spreading or constriction resistance by reducing the bulk resistivity; measurements were also performed at room temperature for comparison sake. The measured transition or crossing resistances were orders of magnitude smaller than one would calculate based on ohmic conduction of the current through the assumed thickness of oxide. In addition, the transition resistivity was very <u>in</u>sensitive to temperature - they differed only slightly between liquid helium temperatures and room temperature, not a result consistent with normal ohmic conduction which was <u>not</u> independent of temperature, depending as it did on the temperature coefficient of the resistivity of the conducting material. In some cases, the total resistance of the contact junction vanished [482]

In 1973, the Nobel Prize in physics was awarded to Leo Esaki, Ivar Giaever and Brian David Josephson "…for the discoveries on the phenomena of tunneling in solids,…" ["…pour les découvertes sur des phénomènes de tunneling dans des solides,…"]. In his Nobel Prize lecture, Esaki said the following about the work of Holm and Meissner. "These measurements probably constitute the first correctly interpreted observations of tunneling currents in solids,…". [483] This statement implied that Holm and Meissner had the obvious advantage, over earlier workers such as Earhart, in that at the time they did their work (circa 1930) quantum theory was firmly established as was the theoretical basis of tunneling; in other words, Holm and Meissner had a theoretical framework on which to hang their results - Earhart (circa 1901-1908) did not. However, it should be noted that the two papers by Holm and Meissner ("Holm, R. and Meissner, W., Z. Physik 74, 715 (1932), 86, 787 (1933)") cited by Esaki did <u>not</u> specifically refer in their respective texts to tunneling. As a matter of fact, it was Ragnar Holm, alone, who "…first correctly interpreted…" their observations as examples of tunneling, and he did it in a 1931 article in the journal, *Zeitschrift für technische Physik*. [484]

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[482] R. Holm, [K.]W. Meissner; Messungen mit Hilfe von flüssigem Helium. XIII. Kontaktwiderstand zwischen Supraleitern und Nichtsupraleitern [Measurements with the help of liquid helium. XIII. Contact resistance between superconductors and normal conductors].; Zeitschrift für Physik; Vol. 74; January-March 1932; pp. 715-735.

Idem; Einige Messungen über den Fließdruck von Metallen in tiefen Temperaturen [Some measurements on the deformation of metal at low temperatures].; Zeitschrift für Physik; Vol. 74; January-March 1932; pp. 736-739.

Idem; Einige Kontaktwiderstandsmessungen bei tiefen Temperaturen [Some contact resistance measurements at low temperatures].; Zeitschrift für Physik; Vol. 86; October-December 1933; pp. 787-791.

[483] L. Esaki; Long Journey into Tunneling; in W. Odelberg (Ed.); <u>Les Prix Nobel</u>; Almqvist & Wiksell International; 1974; pp. 66-83.

[484] R. Holm; Vorläufige Mitteilung über Metallkontakte mit sehr dünner Fremdschicht [Preliminary communication on metal contacts with very thin foreign layers].; Zeitschrift für technische Physik; Vol. 12; 1931; pp. 663-665.

Holm started out his article with a description of the crossed rod contact junction. The contact junctions were formed in a 'hard' vacuum. When the two rods were of the same material and were both clean, they stuck to one another after being pressed together in the crossed configuration. In fact, the adhesion between them was so great that an audible "crack" could be heard as they were pulled apart. Upon the exposure of the two separated rods to air for a fixed amount of time and after reformation of the contact junction, it was found during subsequent separations that the adhesion had disappeared. It was thus surmised that a foreign layer, presumably an oxide, had formed on the surface of the two rods. For most metals, the thickness of the foreign layer increased with the length of exposure to the air. The electrical behavior of the crossed rods depended greatly on the thickness of this foreign layer. Crossed rods with thick foreign layers exhibited the expected electrical conduction behavior based on the contact junction resistance being the sum of the spreading or contraction resistance and the transition or crossing resistance - the foreign layer invariably possessed a finite resistivity. On the other hand, contact junctions formed with a thin foreign layer present (perhaps composed of a monolayer of adsorbed gas), exhibited an anomalously low resistance, all other things being the same; the resistivity of the foreign layer, which had been determined beforehand on a thicker foreign layer, was assumed to be constant. The resistance of the thin foreign layers was an astounding eight orders of magnitude less than was expected. Not only that, but for certain metals, e.g., tin, the resistance of the contact junction vanished, i.e., became immeasurably small, at slightly below the critical or transition temperature, T_c, at which the metal - but not the oxide or gas layer - became superconducting. Since the MOM junction was superconducting for temperatures ~T_c, a finite current was observed to flow through the junction without incurring any voltage drop. Today this current is known as a 'supercurrent', and its existence would be predicted in 1962 by Brian David Josephson - many years after it was unknowingly observed.

The fact that the transition or crossing resistance was, to all intents and purposes, independent of temperature over an ~300ºK range, and the occurrence of a DC supercurrent in the case of the tin-tin contact junction for temperatures below 3.6ºK (N.B., for tin T_c = 3.729ºK) led Holm to speculate that he and Meissner were seeing a new phenomenon. Holm pointed out that the temperature independence of the transition or crossing resistance was a feature of electron tunneling and that it had been predicted in a recent paper by J. Frenkel.[485] His tunneling theory not withstanding, Holm did leave open the

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[485] J. Frenkel; On the electrical resistance of contacts between solid conductors.; Physical Review; Vol. 36 (2nd Series); December 1, 1930; pp. 1604-1618. [Frenkel was concerned with electrical conduction in granular structures such as conducting powders and thin metallic films made by cathodic sputtering. It was a well known fact that the resistivity of a sufficiently thin metallic film was measurably larger than the normal bulk value. By sufficiently thin was usually meant that the thickness of the film was on the order of the mean free path of the free electrons, this thickness was called the critical distance, d. One explanation, proposed by J.J. Thomson, was that the free electrons in the thin film sensed the presence of the nearby surface and, in fact, were scattered by it; in a normal size object the majority of the free electrons at any one time

possibility that conduction could be due to something less dramatic such as a mechanical rupture of the foreign layer during the pressing together of the cross rods followed by metallic contact via one of the resulting pores. We will return a little later to this possible artifact as it affected Holm & Meissner and subsequent workers. Note, while Holm & Meissner were able to explain the electrical conduction of the MOM junctions for temperatures $>T_c$ in terms of electron tunneling, they were still at a loss as to why the whole junction became superconducting for temperatures $\sim T_c$? It appeared as if, when the metals on either side of the oxide or adsorbed gas layer became superconducting, they caused the insulating layer, in turn, to also become superconducting.

This article by Holm was the first paper, I am aware of, which used the expression tunnel effect ["…Tunneleffekt…"] to describe the ability of a microscopic material particle to penetrate into a potential energy region in which it could not normally exist according to classical mechanics. Holm implied that the expression 'tunnel effect' was out and about at the time he wrote this paper: "…und die Leitungselektronendie Haut infolge des sogenannten Tunneleffektes durchqueren […and the conduction electrons traverse the (foreign) layer as a result of the so-called Tunneleffekt]." If Holm was not the first person to use the term 'Tunneleffekt' in the open literature as he implied, then I am not sure who was. Note, the word 'Tunnel' is an Austrian word meaning tunnel, i.e., 'Tunneleffekt' is <u>not</u> a Germanized version of the corresponding English expression. [486] Although, Ragnar Holm was Swedish - born in Skara and educated in Uppsala, both in Sweden - he spent many years working in Germany for the Siemens company, and so was quite familiar with the German language.

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were never close enough to any of the surfaces to be influenced (scattered) by them. Frenkel, however, pointed out that if Thomson's explanation were true, then the critical distance, d, would have to have the same temperature dependence as the mean free path, i.e., it would have to vary as 1/T where T was the temperature. Frenkel then made the observation that the critical distance was found experimentally to be independent of temperature. From this Frenkel surmised that sufficiently thin metallic films were probably granular with each separate grain communicating with its nearest neighbors via electron tunneling. For a somewhat more contemporary discussion, see,

R.M. Hill; <u>Electrical Conduction in Ultra Thin Metal Films. (Report No. 5232)</u>; The Electrical Research Association; 1967; 56 p.

Note, Hill, who discussed sputtered thin films and screened thick films, mentioned that they exhibited a <u>negative</u> temperature coefficient of resistance ($1/R\ \partial R/\partial T < 0$) - in the corresponding bulk metals it was positive. This assertion probably meant that the temperature coefficient of resistance could be effectively 'tuned' by varying the thickness of the films. Going from positive with very thick films to negative with very thin films and undoubtedly passing through zero for a film of intermediate thickness.

This idea of Frenkel's recalled the 'electron atmosphere' idea of Robert Williams Wood, see APPENDIX B.] In 1959, Ragnar Holm resurrected Wood's idea of an electron atmosphere, but referred to it as an electron cloud,

R. Holm; Electron cloud outside a metal surface; Journal of Applied Physics; Vol. 30; No. 5; May 1959; pp. 792-793.

[486] Harold T. Betteridge; <u>Cassell's German-English English-German Dictionary</u>; Macmillan Publishing Co.; 1978; p. 621.

This makes it highly probable that he knew of the Austrian word ‘Tunnel’, and may have come up with the expression ‘Tunneleffekt’, himself.

It should not go unmentioned that at the time (circa 1930) that Ragnar Holm was making these landmark and, for their time, radical discoveries, he was at the chronological age (50 years old; born on May 6, 1879) where most scientists are out to pasture - intellectually speaking, that is. In addition, his unmatched book on electric contacts first appeared in 1941 when he was 61 years old, and over the years it underwent may revisions and eventually translation into English with still further revisions. The last edition of this book, that I am aware of, was published in 1967 by Springer-Verlag; Holm would have been then 87 years old. Also, his output of technical papers continued unabated up to the early 1960s. After coming to America in 1947, he and his wife, Else, worked as consulting physicists for the Stackpole Carbon Co., St. Marys, Pennsylvania until their simultaneous retirement in 1964, at which time Ragnar Holm would have been 84 years old. I do not know exactly when Holm died, but the biographical entries for both he and his wife, which appeared in the 1966 edition of American Men of Science (11th Ed.), were absent from the 1972 edition (12th Ed.). [487]

As was mentioned previously, Holm and Meissner employed crossed metal wires pressed together in their work. What was left out of most, if not all, summaries of their research was their familiarity with a use of coherer behavior. Holm and Meissner were well aware that their experimental arrangement constituted a single contact coherer. In preparation for some of their experiments, they would deliberately cohere [“…gefrittert…”] the contact junction by applying a voltage greater than the ‘critical voltage’ of the particular junction materials; to prevent excessive currents from flowing, the greater than ‘critical voltage’ voltage was applied using a capacitor. The reason why they deliberately induced some of their contact junctions to cohere was - as near as I can figure out - so that they would have a control against which they could compare their uncohered contact junctions. This illustrates the caution with which they viewed the currents crossing the contact junction. They could not dismiss the possibility that the currents were crossing the contact junction via one or more inadvertent metallic bridges. The best way to eliminate this prosaic explanation was to examine two contact junction pairs which were identical in every way except that one had been deliberately cohered. If these two contact junctions behaved the same, this would strongly imply that the conduction was not some new phenomenon, but simply metallic conduction across a bridge. But to understand how the contact junctions were supposed to behave, and under what conditions, one needs to make the acquaintance of the Silsbee hypothesis.

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[487] The Jaques Cattell Press (Ed.); American Men of Science, Vol. H-K; R.R. Bowker Co.; 1966; p. 2363.

Idem; American Men and Women of Science, Vol. 3, H-K; R.R. Bowker Co.; 1972; p. 2788.

Kamerlingh Onnes knew that a closed coil of, say, mercury [488] became superconducting at the critical temperature, in this case ~4.2ºK, provided that the test current was very small. He also knew that the critical temperature increased in the presence of an externally applied magnetic field. It was also known that with zero external magnetic field, the critical temperature would rise for sufficiently large test currents. These two phenomena were thought to be independent, and no one had an idea why the magnetic effect occurred. The current effect, however, was thought to be due to ohmic heating. It might appear obvious to us today that these two effects were related, but it should be remembered that early workers in the field of superconductivity only knew that the superconducting resistance was very small - not identically zero. With a finite but very small value of superconducting resistance, ohmic heating effects could have still been possible and plausible, hence the separation of the magnetic from the current effects. In 1918, a physicist at the NBS named Francis B. Silsbee made the bold assertion that the magnetic effect <u>and</u> the current effect were really one effect due solely to the presence of a magnetic field, in the one case externally generated and in the other internally produced, i.e., self generated. [489] Experimental support for Silsbee's hypothesis was forthcoming. Among the research groups to provide support for Silsbee's contention was the research team of Ragnar Holm and Karl W. Meissner.

Holm and Meissner produced mechanical contact junctions between metals which were known superconductors. Such junctions, cooled below the lowest critical temperature of the metals which made up the contact junction, exhibited supercurrents, i.e., they became superconducting. If a similarly constructed contact junction were first cohered, it also became superconducting. The difference was that the critical temperature of the two types of contact junctions (uncohered and cohered) with the same test current were different. Specifically, the critical temperature of the cohered contact junction was higher than that of the uncohered contact junction. This was just what one expected based on Silsbee's hypothesis, because the test current in the cohered contact junction had a higher current density due to its crossing between the two metals through a small diameter metallic fiber or bridge. The higher current density produced a larger magnetic field - for the same test current - and so increased the critical temperature. [490]

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[488] The mercury was formed into a coil by the expedient of putting it inside a glass tube previously formed into the shape of a coil.

[489] F.B. Silsbee; Note on electrical conduction in metals at low temperatures; Bulletin of the Bureau of Standards; Vol. 14; 1918-1919; pp. 301-306.

[490] **Note**, while evidence did accrue in favor of Silsbee's hypothesis, it was still not an open-and-shut case. That is, there would still be many instances wherein Silsbee's hypothesis would be contradicted. However, so great was the intellectual appeal of Silsbee's hypothesis, that the negative evidence would usually be explained away in terms of some presumed nonideal characteristics of the material under investigation. A good example of this can be found in the 1960 paper by Jacques I. Pankove,

J.I. Pankove; Superconducting Contacts; IRE Transactions on Electron Devices; Vol. ED-7; 1960; pp. 137-141.

Being conscious of the coherer phenomenon, Holm and Meissner were also careful to limit the test voltage applied to contact junctions, which had not been cohered, lest the applied test voltage inadvertently caused the junction to cohere during the actual I-V (current-voltage) measurements. More than a quarter century later, in 1958, when Hans W. Meissner duplicated the experiments of Holm & Meissner, the same proscription regarding coherer behavior was likewise voiced anew: “Any possibility of a formation of a [metallic] bridge due coherer action is therefore excluded (see reference 3, p. 30).” [491] Although, I would be willing to bet that very few people - technical or otherwise - in 1958 would truly have understood the previous quotation, especially with regards to knowing what a ‘coherer’ was. The amazing thing about the renewed efforts at examining superconducting contact junctions was that they were still dogged by the uncertainty of whether the experimentally measured currents were real tunnel currents or just artifacts of metallic bridge conduction. This uncertainly became most acute upon the observation of DC supercurrents (significant current flows across the contact junction accompanied by an immeasurably small voltage difference). Ivar Giaever’s 1973 Nobel Prize lecture was a good case in point:

> In our first paper Megerle and I published a curve, which is shown in Figure 13, demonstrating such a supercurrent and also that it depended strongly on a magnetic field. However, I had a ready-made explanation for this supercurrent-it came from a metallic short or bridge. I was puzzled at the time because of the sensitivity to the magnetic field which is unexpected for a small bridge, but no one knew how a 20Å long and 20Å wide bridge would behave anyway. [492]

Note, in the case of a normal tunnel current, i.e., a current which did require a measurable finite voltage to drive it across the contact junction, Giaever was far more certain that they were <u>not</u> a metallic bridge artifact, because these normal tunnel currents were, for the same voltage, proportional to the active area of the MOM structures. Since Giaever formed his junctions by Joule evaporating one metal layer on top of the other through a mask, he had very direct control over

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In this paper, Pankove measured the critical magnetic intensity, H_c, needed to quench (destroy) the superconducting behavior of a superconducting MOM structure made of crossed niobium wires, and found it to be 1/10 the published value for niobium. This discrepancy, he attributed to “…impurities or strains in the wire.”

[491] H. Meissner; Measurements on Superconducting Contacts; Physical Review; Vol. 109; No. 3; February 1, 1958; pp. 686-694. [The coherer quote can be found on p. 687. A similar proscription can also be found on p. 673 of Meissner’s 1960 followup paper,

Idem; Superconductivity of Contacts with Interposed Barriers; Physical Review; Vol. 117; No. 3; February 1, 1960; pp. 672-680.

Note, I have <u>not</u> been able to find any indication that Karl Wilheim Meissner (1891-1959) and Hans Walter Meissner (1922 -) were related to one another.]

[492] Ivar Giaever; Electron Tunneling and Superconductivity; in W. Odelberg (Ed.); <u>Les Prix Nobel</u>; Almqvist & Wiksell International; 1974; pp. 86-102.

the contact area; after the first metal layer was deposited, it was usually either exposed to room air for a fixed time to grow a layer of native oxide or heated in an air furnace to force grow a thicker oxide layer.

Eventually, the general consensus was that the experimentally measured supercurrents were not artifacts due to metallic bridges. Rather, that they were a *bona fide* phenomenon predicted by Brian D. Josephson and called the DC Josephson effect. That this explanation of the observed supercurrents was still not the whole story took some time to come out.

§10. THE ORIGINS OF DC SUPERCURRENTS: TUNNELING vs. METALLIC BRIDGES. - The unwanted metallic bridges, that superconducting MOM structures were heir to, were eventually studied for themselves. One can trace this effort back to Jacques I. Pankove's papers on the nature of the supercurrents in squeezed superconducting MOM structures.[493] Note, Pankove's first two papers cited as their first reference the 1958 *Physical Review* paper by Hans Meissner, thus maintaining a clear paper trail all the way back to the ground breaking work of Heike Kamerlingh Onnes. Pankove utilized the crossed wire technique, made famous by Holm and Meissner, to produce the squeezed MOM structures; the squeezing was simply produced by pressing the two crossed wires against one another with a known amount of force. Pankove's interest in these squeezed superconducting MOM structures arose from the fact that such devices were bistable and could be made to switch quickly from a low resistance to a high resistance state by a suitable control current, which, it was thought, caused the metals to go from the superconducting to the normal state. The hope was that such contrivances could be employed in both analog and digital circuits. In this respect, Pankove's work on these components at RCA Labs, Princeton, New Jersey, in the 1960s presaged the massive, but ultimately unsuccessful effort, launched by IBM to harness the Josephson junction as a commercially viable product; the IBM effort was effectively terminated in 1983.

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[493] J.I.Pankove; Superconducting Contacts; IRE Transactions on Electron Devices; ED-7; 1960; pp. 137-141.

Idem; New Effect at Superconducting Contacts; Physics Letters; Vol. 21; No. 4; June 1, 1966; pp. 406-407. [**Caution**, there are errors in two of the citations contained in the reference section of this paper: “J.I. Pankove, IRE Transactions **PGED-7** (1960) 137.” should read “J.I. Pankove, IRE Transactions **ED-7** (1960) 137.”, and “B.**J**. Josephson, Physics Letters 1 (1962) **261**.” should read “B.**D**. Josephson, Physics Letters 1 (1962) **251**.” In addition, the reader with average patience and eyesight should be forewarned that Fig. 1 of this paper is both incredibly busy and ridiculously small (especially Fig. 1b).]

Idem; Superconducting Contacts in High Magnetic Fields; Physics Letters; Vol. 22; No. 5; September 15, 1966; pp. 557-558. [Note, these appeared to be the only three papers on superconducting devices that Pankove wrote. Concurrent with his transient interest in superconducting devices, there developed a more long term interest in semiconductor devices, especially electro-optical solid state devices such as GaAs injection lasers. This shift in interest can be clearly seen by simply perusing the entries under ‘Pankove’ in the author index of Science Abstracts, Series A from the years 1966 to 1969.]

[494] That both the RCA and IBM efforts failed to yield commercially competitive devices based on Josephson junctions was a testament to the immense chasm separating the research laboratory from the shop floor and the fact that new does <u>not</u> necessarily imply better as has been adequately demonstrated by the dominance of silicon semiconductors devices in the face of all comers.

In the introduction to his 1960 paper, Pankove listed the advantages of a junction made of crossed superconducting wires: 1) Because of the smallness of the junction, the current density through the junction will be very high, even for minute currents. This high current density implied that the critical current density could be reached easily with the normal currents that flowed through the junction. At the critical current density, the superconducting junction will be quenched, i.e., it will behave as if the two wires were normal, as opposed to superconducting, metals. 2) Since the junction was so small, the transition between the superconducting and the normal states, and vice versa, should be very rapid. 3) And finally, due to the superconducting nature of the junction and its minute size with its commensurately small current, the power dissipation should be very low.

Pankove constructed his crossed wire junctions using "…two freshly etched 3-mil-diameter niobium wires…" maintained at 4.2ºK (the critical or transition temperature, T_c, at which niobium becomes superconducting, being 8.70ºK). One might reasonably ask why the wires needed to be "…freshly etched…", and how one would accomplish such etching? However, one would find oneself rebuffed by the lack of any explicit explanation in the paper. A hint can be found, though, in Brian D. Josephson's 1973 Nobel Prize lecture (p. 112), where he tells the story of how Paul Wraight related the fact that one cannot solder niobium using ordinary solder, to the existence of an oxide layer on the surface of the niobium wire. [495] Thus, I believe that Pankove's use of "…freshly etched…" niobium wire had to do with the fact that niobium wire, which had sat around, probably had too thick an oxide layer to allow electron tunneling and so had to be etched to reduce the thickness of the oxide.

It was apparently while observing the I-V plots of some of these crossed wire junctions that Pankove discovered an anomaly which led him to deduce the existence of a new type of DC supercurrent, carried by what what he amorphously referred to in his June 1966 paper as a "…saturable superconductor bridge…". That he was actually referring to a metallic bridge connecting the two metals was also explicitly asserted by N. I. Bogatina and I. K. Yanson in the first paragraph of their 1973 paper in which they investigated the I-V characteristics of such metallic bridges. [496] Pankove's assertion that the

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[494] E.W. Pugh; Technology Assessment; Proceedings of the IEEE; Vol. 73; No. 12; December 1985; pp. 1756-1763.

[495] B.D. Josephson; The Discovery of Tunnelling Supercurrents; in W. Odelberg (Ed.); <u>Les Prix Nobel</u>; Almqvist & Wiksell International; 1974; pp. 106-113.

[496] N.I. Bogatina, I.K. Yanson; The nonlinearity mechanism of the volt-ampere characteristics of point junctions; Soviet Physics JETP; Vol. 36; No. 4; April 1973; pp. 692-696.

supercurrents he observed were anomalous was based on the following observations: 1) The DC supercurrents persisted for bias voltages at least a decade larger than 2Δ.[497] 2) While a portion of the DC supercurrent could be eliminated by quenching the junction, there existed an unquenchable (by current)[498] DC supercurrent in some superconducting crossed wire junctions. 3) This unquenchable (by current) DC supercurrent saturated at high currents. To understand why DC supercurrents having these three characteristics were considered to be anomalous, we need to digress for a brief moment and talk about the DC Josephson effect.

In 1962, a British graduate student in physics wrote a very terse, mathematically intensive, and impenetrable theoretical paper on tunneling in superconducting structures.[499] Among the effects predicted in this paper was the existence of a DC supercurrent in superconducting structures composed of essentially two superconductors separated from one another in such a way that they were loosely coupled. It must be noted that by defining a Josephson junction as two superconducting reservoirs loosely coupled together, the number of admissible structures becomes quite large and is not limited to just MOM structures composed of superconducting metals: 1) MOM structures, in which both metals were superconductors - the traditional, vanilla-flavored Josephson structure; 2) MnMM structures formed by sandwiching a thin layer of a nonsuperconducting metal, say copper or gold, between two superconducting metals (extensively studied by Hans Meissner); 3) Dayem bridges, produced by linking two large pads of the same superconducting metal via a thin narrow bridge ("…2μ long 1/10μ wide") of the same superconducting metal; ….[500]

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[497] 2Δ represents the energy gap found in the ground state of a superconducting metal as predicted by the BCS (Bardeen, Cooper and Schrieffer) theory of superconductivity. In a metal in the normal, i.e., nonsuperconducting, state at T = 0ºK, there is no energy gap between the electrons at the highest occupied energy state (the Fermi level) and the next highest unoccupied energy level. In this situation, an infinitesimal amount of excess energy will be able to promote an electron into the next highest unoccupied state. Once the same metal becomes superconducting, though, a finite energy gap is created between the highest occupied energy state and the rest of the occupied states. As usual there are exceptions, i.e., the so-called gapless superconductors, which are differentiated from the ordinary superconductors by not having an energy gap, 2Δ, in the superconducting state.

[498] The superconducting state of a MOM junction can be destroyed (quenched) by either applying an external magnetic field or, according to Silsbee's hypothesis, by the magnetic field arising from the current through the junction, itself. However, Pankove's use of the term 'quenched by current' refers not to current going through the junction, but to current passing near the junction.

[499] B.D. Josephson; Possible New Effects in Superconductive Tunnelling; Physics Letters; Vol. 1; No. 7; July 1, 1962; pp. 251-253. [That reading this paper was an extremely arduous task for all but the hardiest of souls has been attested to by numerous technical *personae* including Ivar Giaever and Charles Kittel.]

[500] J. Clarke; The Josephson Effect and e/h; American Journal of Physics; Vol. 38; No. 9; September 1970; pp. 1071-1095.

Josephson, himself, attempted to experimentally measure his predicted DC supercurrents, but he was unsuccessful. [501]

According to Josephson's theory, DC supercurrents flowed only when the voltage across the Josephson junction was identically zero. In addition, these current were also predicted to be very sensitive to the presence of external magnetic fields, so sensitive that even the Earth's magnetic field could cause problems if it was not neutralized by a Helmholtz coil. Because of time and space constraints I will not be able to adequately cover the Josephson effects.

The metal filaments, which caused such vexation for the early researchers working on electron tunneling, were both studied and used to advantage only a few years later. In 1975, I. K. Yanson published a conference paper in which he attempted to confirm a theoretical expression for the resistance of such small diameter structures and at the same time used the current passing through these types of metal filaments to study the electron-phonon interaction. [502] Briefly, Yanson constructed the same type of metal-dielectric-metal planar sandwich as Giaever; the dielectric layer thickness was from ~10 to 100 Å and the metal layers were some several thousands of Ångströms thick. In order to produce the this-time-desired metal filaments, the sandwiches were cohered at liquid helium temperatures by one of three methods: 1) applying a voltage, greater than the critical voltage, across the sandwich using a capacitor in series with a current limiting resistor; 2) applying a steady DC voltage across the sandwich using a voltage source with a large internal resistance; or 3) simply using a sandwich which had spontaneously cohered. Note, the nuts-and-bolts experimental details on how the sandwiches were prepared and tested was not to be found in this 1975 conference paper, which was an extremely terse and fragmentary retelling of the events. Rather, this information was gathered by daisy chaining backwards through Yanson's earlier papers.

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[501] B.D. Josephson; The Discovery of Tunnelling Supercurrents; in W. Odelberg (Ed.); Les Prix Nobel; Almqvist & Wiksell International; 1974; pp. 106-113. [As an example of an I-V curve containing a DC supercurrent, Josephson presented a curve by Nicol, Shapiro and Smith taken using a MOM superconducting structure. **Warning**, in citing the paper from which this curve was copied, Josephson incorrectly identified it as "…reference 6).". The correct citation should have read "reference 12).", which was the following paper,

J. Nicol, S. Shapiro, P.H. Smith; Direct Measurement of the Superconducting Energy Gap; Physical Review Letters; Vol. 5; No. 10; November 15, 1960; pp. 461-464.]

[502] I.K. Yanson; Non-linear effects in electrical conductivity of point contacts and electron-phonon interaction in normal metals.; in Matti Krusius, Matti Vuorio (Eds.); Proceedings of the 14th International Conference on Low Temperature Physics, Otaniemi, Finland, August 14-20,1975, Vol. 3, Low Temperature Properties of Solids; North-Holland Publishing Co.; 1975; pp. 506-509. [The Library of Congress call number is QC 278 I498.]

Yanson's first paper on this subject appeared in 1973. [503] By way of an introduction to this paper, Yanson mentioned that various other researchers had been studying these "…narrow conducting bridge[s]…" formed when MOM (Metal-Oxide-Metal) sandwiches were broken down due to the application of excessive voltage. Of particular interest to these researchers was the resistance of the metallic bridges as a function of the applied voltage used to measure their resistance. Yanson mentioned that the bridge current versus voltage (I-V) plot was nonlinear if one or both of the metals making up the MOM structure were in its superconducting state as opposed to its normal or nonsuperconducting state, where the I-V plots reverted to being linear. Before continuing, it is incumbent upon me to remark that Yanson made <u>no</u> mention of the fact that the phenomenon he was studying was an example of a coherer; the word 'coherer' did <u>not</u> appear in this 1973 paper, the 1974 paper we will review shortly or in the previously cited 1975 conference paper. The usual explanation for the nonlinearity in such I-V plots was, as one might expect, of a thermal nature. As a crude analogy, consider the tungsten filament of the common incandescent light bulb. For small voltages («110 VAC) the resulting I-V plot would be visibly linear. However, as the applied voltage was increased the resulting increase in the current would cause the filament to heat up. Since like most metals, tungsten has a positive temperature coefficient of resistance ($1/R\ \partial R/\partial T > 0$), its hot resistance will be greater than its its cold resistance, and this will cause the resulting currents to be less than they would be if there was no self-heating or if the filament was externally cooled in such a way as to maintain its temperature at ambient.

Yanson's next paper in 1974 dealt almost exclusively with the use of the cohered sandwiches being used to study electron-phonon interactions. [504] It was in this paper that Yanson provided the reader with the only detailed *récipé* of how he created the conducting bridges (see section 3. EXPERIMENTAL PROCEDURE of this 1974 paper). Among the details made public by Yanson was his use of the organic compound adenine in the formation of the oxide layer of the MOM structure. A small amount of adenine was apparently always included in the oxide layer to prevent the formation of spontaneous shorts (bridges). The startled reader might well ask why adenine ($C_5H_5N_5$), an aromatic heterocyclic, almost planar, organic molecule of the class purine and most famous as one of the five building blocks (uracil, thymine, cytosine, adenine and guanine) of nucleic acids such as DNA and RNA, had this ability to prevent shorts in MOM structures and who first discovered this useful property? A question which Yanson conveniently forgot to answer. The nature of these

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[503] N.I. Bogatina, I.K. Yanson; The nonlinearity mechanism of the volt-ampere characteristics of point junctions; Soviet Physics JETP; Vol. 36; No. 4; April 1973; pp. 692-696. [The journal *Soviet Physics JETP* is a direct translation of the Russian language journal *Zhurnal Éksperimental'noi i Teoreticheskoi Fiziki*.]

[504] I.K. Yanson; Nonlinear effects in the electric conductivity of point junctions and the electron-phonon interaction in normal metals; Soviet Physics JETP; Vol. 39; No. 3; September 1974; pp. 506-513.

spontaneous bridges was also not made clear. That is, were they the result of the MOM junction being inadvertently cohered by perhaps accumulate static charges, or were these bridges the result of spontaneous growth of metal whiskers?

During the Second World War, the makers of military radios experienced failures in their equipment of a novel type: the air dielectric, variable capacitors used for tuning the radios to different frequencies were found to have spontaneously shorted out. After much head scratching, it was discovered that microscopically thin metal whiskers were growing out perpendicularly from the surface of the capacitor plates. Eventually these whisker grew long enough that they reached the opposite plate and so shorted out the capacitor. The whiskers originated from and were composed of cadmium, which had been electroplated onto the capacitor plates to prevent corrosion. Physically, a typical whisker was between 0.00001 to 0.00005 inches in diameter, could be as long as 0.040 inches, and were remarkably straight. Electrically, "…the resistance of one crystal [whisker], approximately .020 in. long and .00003 in. diameter, is of the order of magnitude of 300 ohm." [505] Howard L. Cobb, who first chronicled these events and observations, mentioned that, at the time, there were precious few facts to be had on the subject of the growth of metal whiskers. In fact, research on this subject did not start in earnest until the channel filters, used in the Bell Telephones multi-channel telephone line, began to fail due to shorts caused by the zinc whiskers growing out of the zinc plating used on the electronic components in the filters as related in a 1951 article coauthored by Karl G. Compton. [506] Compton *et al.*, as a result of their literature search, found that the only other article on the subject of metal whisker growth was the 1946 article by Cobb. With such a dearth of background information, Compton *et al.* decided that they had no choice but to initiate the study of the topic themselves. Their results, while interesting, were equivocal. If these metal whiskers had simply remained only a nuisance to electronic equipment, probably not much more basic research would have been done on them. But in 1952, W. Conyers Herring and John K. Galt published the results of their investigation into the mechanical strength of tin whiskers "…grown from a tin-plated surface…". What they found was that the tensile strength of these whiskers was over 1000 time greater than that of ordinary bulk tin crystals. [507] The rest, as they say, is history. [508]

An objection to assuming that whisker growth was the mechanism behind spontaneous cohering of MOM structures might go along the following lines. The

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[505] H.L. Cobb; Cadmium Whiskers; The Monthly Review - American Electroplaters' Society; Vol. 33; January 1946; pp. 28-30, 95.

[506] K.G. Compton, A. Mendizza, S.M. Arnold; Filamentary Growths On Metal Surfaces - "Whiskers"; Corrosion - National Association of Corrosion Engineers; Vol. 7; October 1951; pp. 327-334.

[507] [W.]C. Herring, J.K. Galt; Elastic and Plastic Properties of Very Small Metal Specimens; Physical Review; Vol. 85 (2nd Series);1952; pp. 1060-1061.

[508] S.S. Brenner; Metal "Whiskers"; Scientific American; Vol. 203; No. 1; 1960; pp. 64-72.

growth of metal whiskers found in radio and telephone equipment was found to take an amount of time on the order of weeks or months. The problem with this argument is that the length of the whiskers needed to short out radio or telephone equipment is on the order of millimeters. Bridging the oxide in the case of MOM structures, on the other hand, would only require whiskers on the order of 100 Å, and so the time for this growth would likewise be significantly less.

Another question left unanswered by Yanson had to do with how the width (diameter) of the bridges depended on the voltage and current used to coherer the MOM sandwiches? A partial answer to this question can be found in a paper by Angelika Székely. [509] As much as I would like to discuss the contents of this paper - having spent the time translating it - I have run out of time and space to do so.

§11. FIELD EMISSION X-RAY TUBES. - At the same time the theoretical work was progressing, experimental work on field emission moved away from the use of low voltages applied to air gaps in the 100-1000 Å range, and began to focus more on macroscopic vacuum gaps across which tens or hundreds of thousands of volts could be applied. The main impetus for this shift in experimental system was the ready availability of commercially made high quality x-ray tubes. In addition, the accessibility of the high vacuum technology used in making these high vacuum x-ray tubes, allowed researchers to construct modified x-ray tubes specifically for investigating field emission. Until the advent of readily available high vacuum systems, any electrical conduction through a vacuum between electrodes of large separation could just as well have been ascribed to gaseous discharge due to incomplete evacuation of the gas as to field emission. These newer field emission systems were also obviously much easier to handle than the Michelson interferometers, precision lead screws, etc. of the Earhart type of contrivance.

Since we are on the topic of field emission x-ray tubes, I should like to backtrack for a moment and discuss briefly the work of Julius Edgar Lilienfeld on the field emission x-ray tube. As was stated earlier, the Coolidge x-ray tube, introduced in 1913, quickly usurped the up-to-then sacred position occupied by the Hittorf-Crookes gas x-ray tube. What I neglected to mention was that there was a third x-ray tube candidate, the field emission x-ray tube of J. E. Lilienfeld. Lilienfeld's original research interest appeared to be thermionic vacuum tubes; his having been a student of Emil G. Warburg, no doubt, contributed to his interest in conduction in rarefied gases. His later work on the field emission x-ray tube developed as a natural offshoot of his earlier electron tube work, his first

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[509] A. Székely; Über die Art des Elektrizitätsüberganges zwischen Metallen, die sich lose berühren [On the types of electrical conduction between metals which are in loose contact].; Zeitschrift für Physik; Vol. 22; February-March 1924; pp. 51-69.

attempts (circa 1912) at designing a thermionic x-ray tube and last, but not least, his association with Franz Rother.

In 1922, Lilienfeld published a paper describing his field emission x-ray tube. [510] As previously mentioned, the modern version of the diffusion pump was extant by 1920, and so really 'hard' vacuums were available to researchers from that time on. Lilienfeld took advantage of this technological breakthrough to build cold cathode x-ray tubes. Besides pumping down the tubes, Lilienfeld also baked the electrodes - and probably the glass walls of the vessel, too - during the course of the evacuation until the vacuum stabilized. As an added precaution, he also never operated the tubes in any manner that would cause the temperature of their components parts to becomes equal to or greater than the bake out temperature. Tubes prepared in this manner were found to exhibit conduction when a large DC voltage was applied across their anode and cathode. The size of the field emission current depended on the shape of the electrodes, the distance between the electrodes and the metal out of which the electrodes were constructed. The field emission current was essentially <u>in</u>dependent of both the temperature, provided it did not approach the point at which thermionic emission began, and the pressure, provided it was below the point of Paschen type of discharges. Note, Lilienfeld did not refer to the process as field emission, instead he called this process "…autoelektronische [autoelectronic]…". Even though he was using state of the art vacuum techniques, Lilienfeld still felt that he needed to prove that the discharge he was seeing was qualitatively different from residual gas ionization. To this end, he pointed out that the cathode did not appear to undergo any heating nor did it suffer any type of disintegration (sputtering) even after a hundred hours of operation. The absence of both these effects implied the absence of positive ions (from residual gases).

Lilienfeld's enthusiasm for his field emission x-ray tube notwithstanding, it was not commercially viable. Perhaps one of its main problems was reproducibility. Four years after Lilienfeld's paper, a General Electric researcher, B. S. Gossling, reinvestigated these tubes. [511] His results demonstrated that the tube exhibited irregular behavior coupled with large spontaneous excursions at high field emission currents and/or voltages. Most of these irregularities came from deficiencies in materials processing, especially of the electrodes, the field emission current being particularly susceptible to surface conditions. In fact, field emission x-ray tubes would not make their way onto the commercial scene until the 1960s when they were adapted to flash radiography work (see APPENDIX F). Lilienfeld's research interest in field emission waned after the 1920s, and his later research, after he came to the American Virgin Islands in 1935, was

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[510] J.E. Lilienfeld; Die Röntgenstrahlung der Kathode bei der autoelektronischen Entladung [X-rays from the cathode during the autoelectronic discharge].; Physikalische Zeitschrift; Vol. 23; 1922; pp. 506-511.

[511] B.S. Gossling; The Emission of Electrons under the Influence of Intense Electric Fields; Philosophical Magazine [and Journal of Science]; Vol. 1 (7th Series); No. 3; March 1926; pp. 609-635.

concerned with the study of anodically formed dielectric layers on aluminum. These insulating or blocking layers were essential to the operation of electrolytic rectifiers and more importantly electrolytic capacitors.

It also must be pointed out that in 1930 and 1933, Lilienfeld was issued two US patents for a solid state device resembling the modern field effect transistor.[512] The first patent gave a very crude description of the proposed field effect device. For this reason, I shall concentrate on the description provided by the second patent, which was more detailed in both the origins and the construction of this device. This device consisted of an aluminum base, the top surface of which had had a layer of aluminum oxide (Al_2O_3) grown on it to a thickness of ~10^{-4} mm (1000 Å). On top of the aluminum oxide layer there was subsequently deposited a thin layer of a compound semiconductor such as cuprous sulfide (Cu_2S) or cuprous oxide (Cu_20); a metal pad was attached to either end of the semiconductor stratum so that current could be made to flow through it. If the semiconductor channel was thin enough, then its conductivity, which was modulated by applying the proper potential to the aluminum base electrode, could be controlled and along with it the current flow.

Lilienfeld mentioned in his second patent that the aluminum oxide layer acted as a very high quality insulator, which had the added advantage that it was self healing in the event of a puncture due to too great an electric field being applied across it. All of this insight into the properties of aluminum oxide was garnered, no doubt, during Lilienfeld's tenure working on electrolytic capacitors. With this insulating layer interposed between the aluminum base (gate) electrode and the semiconductor channel, one could apply large enough voltages to the gate so that the resulting electric field would modulate the channel conductivity. As pointed out in a 1964 article reviewing Lilienfeld's work, the cuprous sulfide layer most certainly behaved as a P-type semiconductor due to the inevitable presence of trace amounts of cupric sulfide (CuS): pure cuprous sulfide being an insulator, while cupric sulfide was almost metallic in its conductivity.[513] Cuprous

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[512] Julius E. Lilienfeld; Method and Apparatus for Controlling Electric Currents; US Patent No. 1,745,175; January 28, 1930.

Julius E. Lilienfeld; Device for Controlling Electric Current; US Patent No. 1,900,018; March 7, 1933.

[513] Anon.; Obituary: Julius E. Lillienfeld [sic]; Physics Today; Vol. 16; No. 11; November 1963; p. 104.

V.E. Bottom; Invention of the Solid State Amplifier; Physics Today; Vol. 17; No. 2; February 1964; pp. 60-62.

J.B. Johnson; More on the Solid-State Amplifier and Dr. Lilienfeld; Physics Today; Vol. 17; No. 5; May 1964; pp. 60-62. [J.B. Johnson was, of course, the person responsible for the concept of Johnson noise. As he mentioned in his article, he also did work with field emission early in his professional career before his landmark work on noise in active and passive components. More to the point with respect to the subject of this appendix, he gave a brief history of the development of field emission which corroborated much of what I have been saying. Consider the following examples: "The discovery of field emission of electrons has been attributed by some [Good & Müller] to R.W. Wood (1897), I think with very scant justification. The real discovers were probably three men [Earhart, Kinsley and Hobbs - see, his footnote #9] who oxide, on the other hand, would have acted as a defect semiconductor, see APPENDIX G. While Lilienfeld's device saw no commercial application, his patents precluded John Bardeen and also Walter H. Brattain & Robert B. Gibney from claiming "no prior art" in the their respective patents on their versions of the field effect transistor granted in 1950. [514]

The theoretical work on tunneling and field emission attained its most persistent explanatory form in the Fowler-Nordheim theory. [515] Note, in addition to being the source of the current paradigm on tunneling, the aforementioned paper was my starting point in rediscovering the contributions of Robert Francis Earhart with respect to tunneling. Specifically, this paper, which was basically a theoretical look at the process of tunneling, contained in its first page, references to a number experimental and theoretical articles on tunneling. When I consulted two of these papers, [516] I found that both introduced their respective histories of electron tunneling with Earhart's 1901 *Philosophical Magazine* article.

§12. THE UNREMEMBERED. - It should be clear by now that Earhart and Rother can be legitimately claimed to be the 'Fathers' of the STM, but for reasons unclear to me their names and accomplishments do not grace any books, papers or monographs on the subject of STMs to my knowledge. [517] Earhart's method

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worked with Michelson at Chicago, on problems suggested by Millikan, in the early 1900's. They studied the starting voltage of current flow across very small air gaps measured with interferometers." Johnson also gave credit to J.J. Thomson for correctly interpreting the experimental work of Earhart *et al.* in terms of the electrons being dragged out of the metal electrodes against the image force. What Johnson failed to do, however, was to realize that what Earhart *et al.* actually observed were 'vacuum sparks', and that not until 1911 did Rother postulate and then experimentally prove that by reducing the voltage across the electrodes, one could suppress the 'vacuum arcs' and measure the resulting constant field emission currents.]

[514] John Bardeen, Bell Telephone Laboratories, Inc.; Three-Electrode Circuit Element Utilizing Semiconductive Materials; US Patent No. 2,524,033; October 3, 1950.

Walter H. Brattain, Robert B. Gibney, Bell Telephone Laboratories, Inc.; Three-Electrode Circuit Element Utilizing Semiconductive Materials; US Patent No. 2,524,034; October 3, 1950.

[515] R.H. Fowler, L. Nordheim; Electron Emission in Intense Electric Fields; Proceedings of the Royal Society (London); Vol. 119 (Series A); 1928; pp. 173-181. [For a very informative exposition on the history, successes and shortcomings of the Fowler-Nordheim theory see,

Leonard B. Loeb; Fundamental Processes of Electrical Discharge in Gases; John Wiley & Sons, Inc.; 1939; pp. 471-475.]

[516] O.W. Richardson; On the Extraction of Electrons from Cold Conductors in Intense Electric Fields; Proceedings of the Royal Society (London); Vol. 117 (Series A); 1928; pp. 719-730.

R.A. Millikan, C.F. Eyring; Laws Governing the Pulling of Electrons Out of Metals by Intense Electrical Fields; Physical Review; Vol. 27; January 1926; pp. 51-67.

[517] See, for example,

C.B. Duke; Tunneling in Solids; Academic Press; 1969. [This book was an exhaustive compendium of all known tunneling phenomenon up to and including 1969, but there was no mention of R.F. Earhart, P.E. Shaw, C. Kinsley or G.M. Hobbs. Note, this book was actually Vol. 10, Supplement 1 of: Frederick Seitz, David Turnbull, Harry Ehrenreich (Eds.); Solid State Physics; Academic Press. Many libraries list Duke's book under the title Solid State Physics and not Tunneling in Solids.

of controlling and measuring the separation between closely spaced electrodes, together with Rother's realization that there was a phenomenon (field emission) 'underneath' the rather annoying 'vacuum sparks', surely deserved much wider dissemination that they have heretofore received. To complete this process of familiarization I will now present the biographies, such as I could find, of these two forgotten scientists.

Earhart's name did not appear in such biographical compendiums as World Who's Who in Science or American Men & Women of Science.[518] The paucity of biographical information about him in the open literature forced me to look elsewhere for biographical information on his life.[519]

Robert Francis Earhart was born in Toledo, Iowa on February 2, 1873.[520] His higher education consisted of Northwestern University (18??-1893), BS; Johns Hopkins University (1897-98), degree conferred, unknown; University of Chicago (1898-1900), PhD; between 1893 and 1897 he worked as an electrician for the Peoples Power Co., Illinois. After attaining his doctorate, Earhart held a couple of teaching jobs before finally settling down to a permanent teaching post at the Ohio State University (OSU), Columbus, Ohio. He remained at OSU from 1903 to 1931, when he retired, rising to the rank of full professor by 1912. He married [date unknown] and had one daughter and four sons, all of whom

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While the names of Earhart and Rother did not grace the pages of specialized texts on tunneling, Earhart's name did appear - albeit only in a brief footnote - in a well regarded history of physics,

Sir Edmund [Taylor] Whittaker; A History of the Theories of Aether and Electricity, Vol. II, The Modern Theories, 1900-1926; Humanities Press; 1973; p. 236, footnote 7.

In the footnote, Whittaker mentioned that the study of conduction between closely spaced electrodes originated with Earhart's examination of short sparks. In footnote 8 of the same page, the credit for the first theoretical explanation of this phenomena was attributed in the following curious manner, "A first approximate theory was given by W. Schottky, *ZS. f. P.* xiv (1923), p. 63, following on J.E. Lilienfeld, *Phys. ZS.* xxiii (1922), p. 306." **Warning**, this citation contains an error: the starting page should be 506 not 306. J.J. Thomson's priority in this matter seemed also to have been overlooked by Whittaker. In addition, no attention was directed to fact that what Earhart actually observed were 'vacuum sparks', and that this particular phenomenon has not yet been accounted for theoretically.]

[518] Allen G. Debus (Ed.); World Who's Who in Science; A.N. Marquis Co.; 1968.

Jaques Cattell Press (Ed.); American Men & Women of Science; R.R. Bowker Co.; 1986.

[519] All the biographical information on Earhart was obtained from the Ohio State University's University Archives. I wish thank Miss Bertha L. Ihnat [pronounced, ee-not] of their University Archives for looking up the information, xeroxing it and sending it to me in a most efficacious manner.

[520] There seems to be some confusion as whether Earhart was born in Toledo, Iowa or Toledo, Indiana. The biographical information from the OSU University Archives consisted of the following: 1) a June 5, 1965 questionnaire from the editor, Hans Salié, of J.C. Poggendorff's Biographisch-Literarisches Handwörterbuch, Vol. VIIb [Summary of the Years 1932 to 1962] which was filled out by one of Earhart's sons, Daniel S. Earhart, 2) an obituary notice from p. 7 of the May 1946 edition of The Ohio State University Monthly, and 3) p. 83 from The Ohio State Centennial History of the College of Mathematics and Physical Sciences. Two of these items say he was born in Toledo, Iowa and one says Toledo, Indiana.

graduated from OSU. An examination of the Science Abstracts, Series A revealed that his scientific papers spanned the time period, 1901 - 1933, and were mostly concerned with gas discharges. During his tenure at OSU, Earhart kept in contact with prominent members of the scientific community both at home and abroad; he made a number of trips to Europe for this purpose at his own expense. The following table contains a list of the twenty-four citations to Earhart's work in Science Abstracts, Series A - not all these citations were papers by Earhart, some were just abstracts of papers by other workers in the field who happened to mention Earhart's name. Papers by Earhart are designated by an asterisk next to the Abstract No.

TABLE 1E

YEAR	**SCI. ABSTS. Vol.**	**ABST. No.**
1901	4A	514*
1903	6A	248*
1904	7A	2965*
1906	9A	355, 931, 1106
1907	10A	98*,461,924
1908	11A	1467*,2008
1909	12A	1741*
1910	13A	971*
1911	14A	382*
1912	15A	1087*
1913	16A	853*
1914	17A	1099*,1719*
1915	18A	1096
1916	19A	934*
1917	20A	1367*
1919	22A	1537
1929	32A	1623*
1933	36A	1989*

After retiring in 1931, Earhart devoted himself to writing a general physics book for engineering students, this subject was apparently his specialty having established by his own dint the curriculum for the degree of Bachelor of Engineering Physics while tenured at OSU. Unfortunately, the economic climate at the time was not very good, this being the era of the Great Depression, as a result this book, which he coauthored with Alvin H. Nielsen of the University of Tennessee, was not published until 1941, and even then it fell on hard times due to the nation's preoccupation with the Second World War.[521] Undaunted by all

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[521] According to,

this, Earhart did his part to help the war effort by writing technical manuals for the Armed Forces. On April 4, 1946, Dr. Robert Francis Earhart died in Columbus, Ohio after a heart attack suffered in the hotel where he lived; his wife had died the previous August (8/24/45).

The biographical sketch I shall present of Franz Rother will be decidedly emaciated. My only sources of information on Rother are Science Abstracts, Series A for his scientific achievements and J. C. Poggendorff's Biographisch-Literarisches Handwörterbuch Der Exakten Naturwissenschaften [née J. C. Poggendorff's Biographisch-Literarisches Handwörterbuch für Mathematik, Astronomie, Physik, Chemie und verwandte Wissenschaftsgebiete] for both scientific and biographical information. Examination of Science Abstracts, Series A from 1911 (Vol. 14A) to 1934 (Vol. 37A) revealed that the first twenty years of Rother professional life were devoted to the study of emission of electrons from cold metals, especially between closely spaced electrodes *à la* Earhart's apparatus. At the same time, Rother also studied the properties of the field emission x-ray tube designed by J. E. Lilienfeld.

It is interesting to note that both Earhart and Rother wrote their respective PhDs on the conduction between closely spaced cold metal electrodes. Earhart's thesis defined the apparatus used to control and measure the spacing between the electrodes, but the conduction phenomenon he observed at the smallest separations were due to 'vacuum sparks'. Rother's thesis verifies Earhart's original work, but went on to uncover the electron tunneling and/or field emission preceding the 'vacuum spark'; Rother, in fact, was the first researcher to measure the field emission current flowing between closely spaced cold metal electrodes. The conduction currents indirectly observed (via the voltage drop across the electrodes) by Earhart, Shaw, Kinsley, Hobbs and Hoffmann were large in magnitude and transient, just what one would expect from a 'vacuum spark'. Rother's intuitive leap was to realize that if he reduced the applied

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Hans Salié (Ed.); J.C. Poggendorff's Biographisch-Literarisches Handwörterbuch Der Exakten Naturwissenschaften, Vol. VIIb [Summary of the Years 1932 to 1962], Part 2; Akademie-Verlag; 1968; p. 1181.

Earhart's textbook was not published until 1941. However, according to a letter from one of Earhart's sons, Daniel S. Earhart, to Hans Salié, in reference to a biographical questionnaire about Robert F. Earhart, the book was actually published in 1939. In an effort to clear up this point, I obtained a copy of the book via interlibrary loan from the Ohio State University main library. Due to the difficulty in finding this book, let me include its Library of Congress call number: QC 21 .E12.

Robert Francis Earhart, Alvin H. Nielsen; College Physics for Engineers; Edwards Brothers, Inc.; 1941; 428 p. [A cursory examination of this text revealed five references to quantum mechanical phenomena: Planck's discretization of the black-body oscillators, the photoelectric effect, the Bohr atom, an exceedingly brief mention of matrix and wave mechanics, and lastly the Gurney, Condon & Gamow theory of (alpha) radioactive decay - in fact, Earhart erroneously referred to it as solely Gamow's theory. Although this theory was cited, there was no attempt made to contrast the nonclassical nature of quantum mechanical tunneling, nor was the relationship between tunneling and field emission commented on. In short, it was difficult to tell whether or not Earhart, himself, accepted the idea of tunneling, which played such a major part in the results of his work.]

voltage across the electrodes, the ‘vacuum sparks’ would cease, and only the underlying steady field emission currents would remain. By this simple sounding artifice, together with a cleverly designed current measuring contrivance able to measure down to ~10^{-14} A, Rother was able to be the first person to actually obtain an I-V curve of this conduction process. Later refinements of his whole apparatus enabled him to produce the complete I-V curves having the exponential dependence expected from a field emission process.

From about 1933 onwards, Rother’s interest in the emission of electrons from cold metals was redirected towards the photoelectric effect. The late 1920s and the early to mid 1930s witnessed a renaissance of sorts with respect to the photoelectric effect. Most physics textbooks give the erroneous impression that this phenomenon was bludgeoned into submission by the combined efforts of Albert Einstein’s theoretical virtuosity and Robert Andrews Millikan’s experimental acumen. The truth of the matter was that the photoelectric effect was far from being wrung dry of mystery, even by the likes of Einstein and Millikan, see APPENDIX D.

The following table contains a complete enumeration of entries under Franz Rother’s name in the Science Abstracts, Series A,

TABLE 2E

YEAR	SCI. ABSTS. Vol.	ABST. No.
1911	14A	1385
1915	18A	341
1920	23A	1642
1923	26A	741
1924	27A	1123
1926	29A	2940
1929	32A	1958
1931	34A	1287
1933	36A	3258
1934	37A	391-2,1757,4748

Franz Rother was born in Nürnberg (a.k.a. Nuremberg) on May 15, 1887. He received his PhD in 1914 from the University of Leipzig under the direction O. Wiener and H. Scholl. From the time he graduated until 1923, he held various teaching positions at the University of Leipzig. In 1923, he entered industry as a Technical Director at Reiniger, Gebbert & Schall A. G. in Erlangen, where Erlangen is a city just north of Nürnberg. His stay in industry seemed to have been rather abbreviated, since in 1926 he apparently returned to the Physics Institute of the University of Leipzig. From there he journeyed to Berlin in 1928 and became a guest at the Institute for Radiology at the University of Berlin. Although he continued to publish scientific papers up to and including 1934, after 1934, "Weitere Daten nicht bekannt [Further information is not known]." [522]

§13. MODERN TIMES, TUNNELING HITS ITS STRIDE. - As long as the study of tunneling was an end in itself, the model systems utilized by researchers remained of the x-ray tube and MOM structure type. But after the advent of the transistor in 1948 and the concomitant rise of solid state physics as a separate, distinct and commercially important field of scholarship, people's attention started to focus on the problems related to the scaling of devices to smaller and smaller sizes. With the insatiable striving for miniaturization came the need to be able to quantify the properties of these small pieces of metal or semiconductor. In particular, the quantification of their surfaces became of paramount importance due to the increasing influence of the surface on the behavior of small volume electronic devices. At the same time as the semiconductor revolution was taking place, the field of tribology was also coming of age, and people were looking for better ways to quantify, among other things, the roughness of machined surfaces.

These problems and others like them inspired Russell D. Young in 1966 to try to design a noncontact surface probe. In order to sense the surface without touching it, Young decided to have his probe operate by sensing tunnel current, this approach, of course, restricted the composition of the surfaces his probe could examine to those made of metal or semiconductor. His first design attempt was imminently impractical, but it did serve as a test bed and valuable learning experience. [523] His next attempt, unveiled in 1972, yielded a practical device, which again sensed the surface via electron tunneling and in addition could scan the surface in x and y directions; the sample was brought into proximity of the metal field emission tip by means of a differential screw, the fine adjustment of the tip in the x, y and z directions was accomplished by three separate piezodrivers. Young christened this surface probe, the Topografiner. [524] In normal use, the Topografiner was operated under high vacuum and the electrolytically etched field emission tip was 'flown' over the surface to be examined at 200 Å with the tip bias at -50 to -100 V.

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[522] Rudolph Zaunick, Hans Salié (Eds.); J. C. Poggendorff's Biographisch-Literarisches Handwörterbuch Der Exakten Naturwissenschaften, Vol. 7a, Part 3: L-R; Akademie-Verlag; 1959; p. 827.

[523] R.D. Young; Field Emission Ultramicrometer; Review of Scientific Instruments; Vol. 37; No. 3; March 1966; pp. 275-278.

[524] R. Young, J. Ward, F. Scire; The Topografiner: An Instrument for Measuring Surface Microtopography; Review of Scientific Instruments; Vol. 43; No. 7; July 1972; pp. 999-1011.

Idem; Observation of Metal-Vacuum-Metal Tunneling, Field Emission, and the Transition Region; Physical Review Letters; Vol. 27; No. 14; October 4, 1971; pp. 922-924.

Young’s main improvement over Earhart’s apparatus was his use of piezodrivers in place of the lead screw arrangement favored by Earhart. Not only are piezodrivers smaller and cheaper, but they offer better spatial resolution. And, of course, Earhart’s device could not scan.

It should be noted that Young’s accomplishment using piezodrivers, great though it was, paled in comparison to some slightly earlier work in which the piezoelectric crystals were used to sense small displacements rather than to affect such movements. In the mid to late 1950s, Joseph Weber began to analyze, design and construct gravity wave detectors. In the end, the detector he decided on consisted of a 1.5 ton aluminum cylinder, 5 ft long X 2 ft in diameter; the cylinder had quartz strain gauges (piezoelectric crystals) cemented around its equator; and the cylinder with its gauges was suspended about its equator via a loop of wire, the ends of the wire were attached to a cross piece which rested on two vibration isolation columns to attenuate any environmental vibrations. The vibration isolation columns, which consisted of alternating layers of steel and rubber plates, is employed today in STMs for this same purpose - for STMs the vibration isolation column usually consists of alternating layers of steel plates and Viton® O-rings, the Viton® O-rings are UHV (Ultra High Vacuum) compatible. [525] The cylinder + strain gauges + cross piece + vibration isolation columns + rolling base was housed inside a vacuum chamber to protect it from acoustical vibrations in the air. The aluminum cylinder acted as an antenna to detect gravity waves by means of its change in length under the action of such waves. This detector together with its electronics was supposed to be able to sense displacements on the order of 10^{-14} cm. The details of exactly how all this was done is outside the scope of this thesis, but the interested reader can consult the U.S. patents taken out by Weber, Forward and Zipoy. [526]

The piezo-driven apparatus of Young *et al.* inspired other workers to try achieve tunneling at even closer distances. Most notable among this group was Edgar Clayton Teague, who studied tunneling taking place between gold

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[525] The idea of making a sandwich out of alternating layers of rigid plates and rubber rings or plates, for the purpose of vibration isolation, can actually be traced back to, at least, 1900, see,

P.E. Shaw; The Improved Electric Micrometer; Proceedings of the Royal Society (London); Vol. 76 (Series A); August 4, 1905; pp. 350-359. [In particular, see Figure 6, p. 352 and its accompanying text.]

[526] Although Weber’s detector was constructed around 1960, most of the corresponding US patents were not submitted (filed) until the mid-1960s and the actual patents were not granted until the early-1970s. See,

Joseph Weber, Hyman Hurvitz; Amplifier with Feedback Particularly Useful with a Gravity Wave Detector; US Patent No. 3,554,033; January 12, 1971.

Joseph Weber, David M. Zipoy, Robert L. Forward, Hughes Aircraft Co.; Detector of Dynamic Gravitational Force Gradient Fields; US Patent Nos. 3,722,284, 3,722,289 & 3,722,290; March 27, 1973.

Note, besides the gravity wave detectors, Weber was also responsible for ground breaking research into the use of stimulated emission for the purposes of amplification. See,

Joan Lisa Bromberg; The Laser in America, 1950-1970; MIT Press; 1991.

electrodes in a vacuum at various electrode spacings down to about 20 Å. [527] While the piezodriver was becoming the method of choice to affect motion requiring Ångström resolution, it was by no means the only way of achieving these incredibly minute motions. W. A. Thompson and S. F. Hanrahan used the nonzero coefficient of thermal expansion or contraction of metals to achieve stable and repeatable motions with Ångström resolution; [528] and R. J. Walko utilized magnetic attraction coupled with a restoring forced provided by a metal spring to study the damage to field emission tips just touching a 'flat' metal surface. [529]

As I was completing this thesis, I stumbled across yet another example of 'parallel evolution' in the field of precursors to the STM. In the mid to late 1970s, a group of researchers in the Netherlands was investigating electron-phonon interactions via an apparatus which had a startling resemblance to the modern STM of Binnig and Rohrer. The apparatus of Jansen, Mueller and Wyder was used to bring an electrolytically sharpened "…spear…" into the lightest contact possible with a larger piece of the same or a different metal called the "…anvil…". The approach mechanism, which had to have a resolution somewhat better than 100 Å consisted of a differential screw for coarse adjustment and a piezoelectric stack for the final approach; the whole apparatus could be immersed in a Dewar flask so as to bring its temperature down around 1.2ºK. The use of vibration isolation coupled with operating the apparatus at night to further reduce mechanical and acoustical noise pickup completed the

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[527] E.C. Teague; Room temperature Gold-Vacuum-Gold Tunneling Experiments; American Physical Society Bulletin; Vol. 23; No. 3; March 1978; p. 290. [Note, this was only an abstract of a poster session and as such did not contain much information beyond a very abbreviated explanation of what was done. More detailed information can be found in Teague's 1978 PhD Thesis,

E. Clayton Teague; Room Temperature Gold-Vacuum-Gold Tunneling Experiments; North Texas State University; 1978; 229 p. **Note**, Teague revealed that, when the voltage difference across the two gold electrodes approached ~2-3 V @ 30 Å electrode separation, breakdown occurred, i.e., the current increased seemingly without bound. Although Teague did not mention it, this was coherer-like behavior and the system appeared to have a 'critical voltage' of around 2-3 V, see Fig. 37, p. 140 in his thesis.

[528] W.A. Thompson, S.F. Hanrahan; Thermal drive apparatus for direct vacuum tunneling experiments; The Review of Scientific Instruments; Vol. 47; 1976; pp. 1303-1304.]

[529] Robert J. Walko; Lattice Damage by Mechanical and Electrical Contact Investigated by Field Ion Microscopy; Pennsylvania State University; 1974. [Note, Walko was not the first person to use a magnetic field coupled to a spring for use in moving contacts smoothly and precisely over distance measured in Ångströms. As earlier examples of this approach, see,

G. Hoffmann; Elektrizitätsübergang durch sehr kurze Trennungastrecken [Passage of electricity across very minute air-gaps]; Physikalische Zeitschrift; Vol. 11; 1910; pp. 961-967. Or see Science Abstracts, Series A; Vol. 14A; 1911; Abstract No. 122.

Idem; Der Elektronenaustritt aus Metallen unter Wirkung hoher Feldstärken [Electron emission from metals under the influence of high electric fields]; Zeitschrift für Physik; Vol. 4; 1921; pp. 363-382.

R. Deaglio; Einfluß der Wasserhäute auf den Voltaeffekt [Influence of Water Films on Contact Potentials (Volta effect)]; Zeitschrift für Physik; Vol. 51; 1928; pp. 279-286. Or see Science Abstracts, Series A; Vol. 32A; 1929; Abstract No. 594.]

analogy between this work and that of Binnig and Rohrer on the STM.[530] A detailed discussion of what Jansen *et al.* were doing and why can be found in this appendix and in APPENDIX A. It turns out that their results may help solve the question of how MOM diodes function?

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[530] A.G.M. Jansen, F.M. Mueller, P. Wyder; Direct Measurement of α^2F in Normal Metals using Point-Contacts: Noble Metals; in D.H. Douglass (Ed.); Superconductivity in d- and f-Band Metals; Plenum Press; 1976; pp. 607-623.

Idem; Direct measurement of electron-phonon coupling $\alpha^2F(\omega)$ using point contacts: Noble metals; Physical Review B, Solid State; Vol. 16 (3rd Series); No. 4; August 15, 1977; pp. 1325-1328.

Idem; Normal Metallic Point Contacts; Science; Vol. 199; March 10, 1978; pp. 1037-1040. [I wish to thank Dr. Vallorie Peridier and Dr. Thomas E. Sullivan for having encouraged me to read a series of articles on heat transfer in micro-scale objects, which ultimately led me to the articles of Jansen *et al.*]

APPENDIX F - 'VACUUM ARC, SPARK or DISCHARGE' PHENOMENA, a.k.a. METAL VAPOR ARC or just plain ARC PHENOMENA

> "It is of great advantage to the student of any subject to read in the original memoirs on that subject, for science is always most completely assimilated when it is found in its nascent state. Every student of science should, in fact, be an antiquary in his subject."
>
> \- James Clerk Maxwell

§1. INTRODUCTION: AN ARC BY ANY OTHER NAME… - In discussing the history of the STM (Scanning Tunneling Microscope) in APPENDIX E, the phenomena of vacuum sparks (a.k.a. vacuum arcs) came to the fore. A necessarily brief but succinct history was then presented. In this appendix, I wish to delve more deeply into the characteristics and possible microscopic mechanism of this phenomena. The bulk of the work undertaken in an effort to elucidate this phenomena was performed by two groups, one on the east coast (New Jersey) and the other on the west coast (Oregon) of the United States; the east coast group, working out of Bell Telephone Laboratories in Murray Hill, NJ, was headed by Lester H. Germer, while the west coast group, composed of W. P. Dyke, J. K. Trolan, W. W. Dolan, *et al.* was affiliated with the Physics department of Linfield College, McMinnville, Oregon. Because of the sheer volume of work produced by these two groups, a separate appendix had to be set aside to do justice to their efforts.

But before reviewing the work on 'vacuum arcs', it would be useful to have some sort of definition for the term 'vacuum arc'. To this end, a little bit of history will go a long way towards making the terminology, at least, seem logical and perhaps even natural.

Around 1809, Sir Humphry Davy discovered that if he touched together two carbon (actually wood charcoal) rods, each connected to one pole of a large battery (consisting, in his case, of 2000 Voltaic cells), and then slightly separated them, a brilliant steady flame commenced to burn at the point of separation. This flame was called a "Voltaic arc", "electric arc" or just simply an "arc". While the above statements are factual, they are by no means complete. For example, Davy did indeed do much significant work with the electric arc, but he was not necessarily the discoverer of this phenomenon. Around 1900, Hertha Ayrton wrote an exhaustive and lucid treatise on the subject of the electric arc.[531] The first chapter of her book was devoted to the history of the arc's discovery. To this end, she surveyed all the pertinent scientific literature both published and unpublished of the period in question: 1800 to 1810. What she found can be best summarized in her own words, "Hence it is impossible to say when and by whom the arc was really discovered." She also provided the logic behind the term 'arc'. It appears that the early researchers, e.g., Davy, produced their electric arcs between two horizontal electrodes, which were then separated as far apart as possible without extinguishing the arc. The resulting electric arc had the shape of an arch with its apex situated midway between the two electrodes. Hence, the appellation 'electric arc' actually referred to its shape. Mrs. Ayrton also mentioned that what distinguished an arc from a spark was that the later was a transient phenomenon, whereas the arc was essentially a steady spark. Finally, according to Mrs. Ayrton, the fact that "…well-burned charcoal…" was a good conductor of electricity was first happened upon by Joseph Priestly; well-burned charcoal proved to be an indispensable material out of which to build the electric arc electrodes due to its excellent refractory properties.

The conditions for striking such an arc were as follows: a source of DC EMF of 45-60 Volts with a current capacity of 5-10 Amperes; if an AC source of EMF was employed the voltage needed only to be 30-35 Volts. A ballast resistor, either in the form of an external ~1 Ω resistor or simply the internal resistance of the source of EMF, had to be present to stabilize the arc, otherwise it would short circuit the power source. These conditions gave rise to an arc of 400-800 candle power, which was far brighter than any other known source of light. Examination of the carbon rods after sustained operation with a DC source revealed a crater at the tip of the anode. Apparently the carbon at the anode tip was being vaporized by the arc; the cathode showed little erosion, indicating that the high temperatures were localized at the anode. From this observation Jules Louis Gabriel Violle concluded that the temperature of the arc - at least at the anode crater - must be around 3500ºC, the temperature at which carbon was volatilized. Note, this erosion could be minimized by operating the arc in a nonoxidizing atmosphere or simply restricting the access of fresh air. The light produced by the arc also came from the anode crater, again attesting to the enormous temperatures which must have existed there. And lastly, the arc was observed to possess a back or opposing EMF.[532] Note, this back or opposing EMF, which was largest when the arc was quiet as opposed to when it hissed,

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[531] Hertha Ayrton; The Electric Arc; "The Electrician" Printing and Publishing Co.; ~1900; pp. 19-27. [Hertha Marks Aryton (née Phoebe Sarah Marks) was a remarkable person. A brief biography of her can be found in the following reference,

Marilyn Bailey Ogilvie; Women in Science, Antiquity through the Nineteenth Century; MIT Press; 1986; pp. 32-34.]

[532] Silvanus P. Thompson; Elementary Lessons in Electricity and Magnetism; The Macmillan Co.; 1921; pp. 463-473.

was a manifestation of both the negative resistance characteristic of the I-V curve of the arc and a less well understood propensity, which indeed mimicked the behavior of a rather large inductor, and probably was related to the dynamics of the cratering of the anode.[533]

Around 1896-97, three independent researchers (Henry A. Rowland, Sidney D. Rowland and Robert W. Wood) reported that they had produced an electrical discharge in an evacuated vessel that had many of the same properties as the normal arc, then associated with arc lamps. Because they had all obtained this discharge in a vacuum, the term ‘vacuum arc’ naturally was associated with this phenomenon. Like the normal arc, only the anode of the ‘vacuum arc’ experienced a loss of material. As was shown by R. E. Loving in 1905, the light from the ‘vacuum arc’ originated solely from the anode, as was the case with the normal arc. The main difference between the ‘vacuum arc’ and the normal arc was, that the normal arc was struck by first bringing the electrodes into contact and then separating them, whereas the ‘vacuum arc’ was struck by simply applying the volt (~50,000-100,000 V) across metal electrodes separated by a fixed distance of ~1 millimeter in a moderate vacuum.

Continuous steady luminous discharges in gases (glow discharges) submitted themselves to quantification in 1889 under the auspices of Paschen’s law. After Paschen’s law was verified, further work revealed that there was a minimum gas breakdown voltage for each gas. This minimum voltage depended <u>only</u> on the identity of the gas and no other parameters. In 1901, Robert Francis Earhart discovered that he could get a significant electrical discharge, which violated Paschen’s law, between very closely spaced electrodes in dust-free dry air, i.e., he was able to obtain electrical discharges at voltages well below the minimum breakdown voltage of the gas enveloping these electrodes separated by a distance equal to a few wavelengths of visible light. The character of this discharge was shown to be <u>in</u>dependent of the identity of the gas surrounding the electrodes, i.e., it was not the normal glow discharge or even Townsend discharge. Eventually it was realized that this discharge was actually a ‘vacuum arc’. A ‘vacuum arc’, it must be added, that could form even in air, or any other

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[533] The negative resistance characteristic of the arc allowed it to act as an oscillator as was independently discovered by Elihu Thomson and W.D. Duddell around 1892. Duddell’s “singing arc” was perhaps the most startling demonstration of the utilization of the negative resistance character of the arc. Duddell took a normal DC arc lamp and attached a series LC circuit in parallel with the carbon electrodes. Provided that the inductor (L) and capacitor (C) were large enough that their resonant frequency was in the audible range, the modified DC arc would ‘sing’ at this frequency. A few years after Duddell’s description of his “singing arc”, Valdemar Poulsen modified and adapted it for the production of pure sinusoidal radio frequencies. The Poulsen arc transmitter became the first high powered (>100 kW, input) continuous wave (CW) radio frequency transmitters. Up to this time, the only transmitters were the so-called spark transmitters which produced trains of damped radio frequency sinusoids. For further information on these arc transmitters see,

Donald McNicol; <u>Radio’s Conquest of Space</u>; Murray Hill Books, Inc.; 1946; pp. 70-73.

John H. Morecroft *et al.*; <u>Principles of Radio Communication</u>; John Wiley & Sons, Inc.; 1933; pp. 713-724.

gas for that matter, at one atmosphere of pressure. Later in this appendix, we shall see how during the 1950s Lester H. Germer rediscovered ‘vacuum arcs’ in air at atmospheric pressure. Because these discharges were transient in nature, the term ‘vacuum arc’ was actually a misnomer. To be exact they should be referred to as ‘vacuum sparks’, but we shall continue to employ the incorrect nomenclature out of sloth. [534]

Finally, arcs are also produced as part of the natural progression in gas discharges at low pressures. The stages of a discharge in a gas at low pressures are: ionization chamber, Townsend, breakdown, glow discharge, and lastly the arc. These stages cover the range from high voltage & low current (ionization chamber stage) to very low voltage & very high current (arc stage).

We are now ready to relate the modern history of the ‘vacuum arc’. By modern I mean the discoveries relating to this phenomenon after the Second World War.

§2. LESTER H. GERMER: ‘VACUUM ARCS’ VIA TELEPHONE EXCHANGE SWITCHING RELAYS. - Due to the mind boggling amount of information unearthed by Germer *et al.*, a top down approach is prudent, and also conducive to the continued mental health of the writer and reader of this tract. In the mid to late 1920s, Clinton Davisson and Lester H. Germer, while working at Bell Telephone Laboratories, became famous for their experimental verification of the wave nature of the electron by showing that a low energy electron could be diffracted by a face of a single crystal of nickel. In honor of their justifiably heroic efforts and results, this experiment today bears their names.

While Lester H. Germer (1896-1971) is probably best known to the science community for his work on the Davisson-Germer experiment, [535] his

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[534] In a recent book on ‘vacuum arcs’ as they pertain to current interruption in power grids,
J.M. Lafferty (Ed.); Vacuum Arcs, Theory and Application; John Wiley & Sons; 1980; p. v.
the editor makes the following observation: “The term “vacuum arc” is a misnomer. What is really described in this book is a “metal vapor arc in a vacuum environment.” But since “vacuum arc” is in common usage and has been accepted in the literature, it is retained here.” Which provides further proof that the term ‘vacuum arc’ is indeed a protean moniker if ever there was one.

[535] The Davisson-Germer experiment was one of the most famous empirical achievements of this century. It was complemented by the electron transmission diffraction experiments of G.P. Thomson. Together, these endeavors verified Prince Louis Victor de Broglie’s theoretical considerations about the wave-particle duality of matter particles (particles with a finite rest mass), for which he received the Nobel Prize in physics in 1929; the wave-particle duality of the photon - a massless particle mediating electromagnetic forces - had been grudgingly accepted slightly earlier due to the work of Einstein and Millikan. As one might reasonably expect, such Herculean efforts did not go unrewarded. In 1937, Thomson and Davisson were awarded the Nobel Prize in physics for their work proving the wave-particle duality of matter particles. But what about Germer? After all it was called the Davisson-Germer experiment. The only time I saw mention made of this oversight was in a book by Walter Moore,

work on contact erosion is equally impressive even though nowhere as well known. When Germer first became interested in telephone relay contact erosion, I do not know. What I do know is that beginning after WWII and ending only a few years before his death, Germer produced a relentless and continuous stream of papers on the subject of contact erosion. The following table lists the entries in Science Abstracts, Series A (Physics) found under the author name, L. H. Germer.

Walter Moore; Schrödinger, Life and Thought; Cambridge University Press; 1989; pp. 281-292.

Moore mentioned the fact that the experimental verification of the wave-particle duality of matter particles was actually an effort attributable to quite few investigators: C.J. Davisson & L.H. Germer, G.P. Thomson & A. Reid, P.H.E. Rupp, and S. Kikuchi. He also pointed out that there had been thought given to giving the prize to Germer also, but for some unexplained or unexplainable reason nothing came of it.

A comprehensive firsthand review of the initial and follow up experimental work on matter waves can be found in the following article,

S. Kikuchi; Beugung der Materiestrahlen [Diffraction of Material Waves].; Physikalische Zeitschrift; Vol. 31; No. 17; September 1, 1930; pp. 777-791.

TABLE 1F

YEAR	SCI. ABS. Vol.	ABST. No.
1945	48	-
1946	49	-
1947	50	-
1948	51	3352
1949	52	-
1950	53	1771
1951	54	6989, 9507
1952	55	1027, 5799
1953	56	-
1954	57	4562, 9270[536]
1955	58	7068, 7075
1956	59	2134, 2135
1957	60	-
1958	61	-
1959	62	5753
1960	63	4613, 19762, 21250
1961	64	1458, 4085, 20658
1962	65	8894, 19127, 21558, 23921-22
1963	66	1378
1964	67	-
1965	68	-
1966	69	23769, 30704, 30842, 30918
1967	70	1288, 1290, 29285, 37008
1968	71	26107
1969	72	12544, 19679
1970	73	2462, 34080, 47085, 68245
1971	74	12580, 36337

For reasons unknown to me, not all of Germer's papers in the time frame, 1945-1971, were abstracted in Science Abstracts, Series A - at least, I could not find them using the author index. Because of this deficiency, and in an effort to convey the massive scope of the Germer's work on this subject, I have constructed the following table, which contains citations to his articles from 1945 to 1960. Those articles missing from Science Abstracts, Series A were found by starting with Germer's most recent articles, as found in Science Abstracts, Series

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[536] Of the six part series of articles entitled, Arcing at Electrical Contacts on Closure, part V was written by P. Kisliuk; parts I-IV & VI were authored or coauthored by Germer.

A and using the citations therein or from references provided by the papers of other authors in the field, e.g., W. P. Dyke, J. K. Trolan, W. W. Dolan, *et al.* For reasons which will be explained later, Table 2F stops at 1960.

TABLE 2F

[1] L.H. Germer, F.E. Haworth; A Low Voltage Discharge between Very Close Electrodes; Physical Review; Vol. 73 (2nd Series); January-June 1948; p. 1121. [Or see Science Abstracts, Series A; Vol. 51A;1948; Abstract No. 3352.]

¶[2] J.J. Lander, L.H. Germer; The Bridge Erosion of Electrical Contacts. Part I.; Journal of Applied Physics; Vol. 19; October 1948; pp. 910-928.

[3] L.H. Germer, F.E. Haworth; Erosion of Electrical Contacts on Make; Journal of Applied Physics; Vol. 20; November 1949; pp. 1085-1109. [Or see Science Abstracts, Series A; Vol. 53A;1950; Abstract No. 1771.]

[4] L.H. Germer; Arcing at Electrical Contacts on Closure. Part I. Dependence upon Surface Conditions and Circuit Parameters; Journal of Applied Physics; Vol. 22; No. 7; July 1951; pp. 955-964. [Or see Science Abstracts, Series A; Vol. 54A;1951; Abstract No. 6989.]

[5] L.H. Germer; Arcing at Electrical Contacts on Closure. Part II. The Initiation of an Arc; Journal of Applied Physics; Vol. 22; No. 9; September 1951; pp. 1133-1139. [Or see Science Abstracts, Series A; Vol. 54A; 1951; Abstract No. 9507.]

[6] L.H. Germer; Heat Dissipation at the Electrodes of a Short Electric Arc; Bell System Technical Journal; Vol. 30; October 1951; pp. 933-944. [Or see Science Abstracts, Series A; Vol. 55A; 1952; Abstract No. 1027.]

[7] L.H. Germer, J.L. Smith; Arcing at Electrical Contacts on Closure. Part III. Development of an Arc; Journal of Applied Physics; Vol. 23; No. 5; May 1952; pp. 553-562. [Or see Science Abstracts, Series A; Vol. 55A; 1952; Abstract No. 5799.]

[8] L.H. Germer; Arcing at Electrical Contacts on Closure. Part IV. Activation of Contacts by Organic Vapor; Journal of Applied Physics; Vol. 25; March 1954; pp. 332-335. [Or see Science Abstracts, Series A; Vol. 57A; 1954; Abstract No. 4562.]

[9] P. Kisliuk; Arcing at Electrical Contacts on Closure. Part V. The Cathode Mechanism of Extremely Short Arcs; Journal of Applied Physics; Vol.

25; July 1954; pp. 1133-1139. [Or see Science Abstracts, Series A; Vol. 57A; 1954; Abstract No. 9270.]

[10] W.S. Boyle, P. Kisliuk, L.H. Germer; Electrical Breakdown in High Vacuum; Journal of Applied Physics; Vol. 26: No. 6; June 1955; pp. 720-726. [Or see Science Abstracts, Series A; Vol. 58A; 1955; Abstract No. 7068.]

[11] W.S. Boyle, L.H. Germer; Arcing at Electrical Contacts on Closure. Part VI. The Anode Mechanism of Extremely Short Arcs; Journal of Applied Physics; Vol. 26; May 1955; pp. 571-574. [Or see Science Abstracts, Series A; Vol. 58A; 1955; Abstract No. 7075.]

[12] L.H. Germer, W.S. Boyle; Anode and Cathode Arcs; Nature (London); Vol. 176; November 26, 1955; p. 1019. [Or see Science Abstracts, Series A; Vol. 59A; 1956; Abstract No. 2134.]

[13] L.H. Germer, W.S. Boyle; Two Distinct Types of Short Arcs; Journal of Applied Physics; Vol. 27; No. 1; January 1956; pp. 32-39. [Or see Science Abstracts, Series A; Vol. 59A; 1956; Abstract No. 2135.]

¶[14] L.H. Germer, J.L. Smith; Activation of Electrical Contact by Organic Vapors; Bell System Technical Journal; Vol. 36; 1957; pp. 769-812.

¶[15] L.H. Germer; Physical Processes in Contact Erosion; Journal of Applied Physics; Vol. 29; No. 7; July 1958; pp. 1067-1082.

[16] L.H. Germer; Electrical Breakdown between Close Electrodes in Air; Journal of Applied Physics; Vol. 30; No. 1; January 1959; pp. 46-51. [Or see Science Abstracts, Series A; Vol. 62A; 1959; Abstract No. 5753.]

[17] E.J. Scheibner, L.H. Germer, C.D. Hartman; Apparatus for Direct Observation of Low-Energy Electron Diffraction Patterns; The Review of Scientific Instruments; Vol. 31; No. 2; February 1960; pp. 112-114. [Or see Science Abstracts, Series A; Vol. 63A; 1960; Abstract No. 4613.]

NOTE, those citations not found in the author index of the Science Abstracts, Series A are prefixed with a '¶'. All those which can be found in the author index of the Science Abstracts, Series A are postfixed with the abstract number.

The 'Big Picture' of the research by Germer as told by the above tables goes as follows. From 1948 to 1959, Germer and his associates assiduously investigated the various mechanisms that led to contact erosion under the following normal operating conditions: 1) the opening of current carrying contacts, and 2) the closing of contacts with a steady DC voltage impressed across them. These predominantly experimental investigations produced 15 papers for a total of some 175 pages. Most of the articles, however, are concerned with the arcs created during closure; only [2] is devoted to bridge formation on contact opening. Although, article [2] is entitled Part 1, I was unable to find any of the succeeding parts. Perhaps the later parts of the bridge formation article were penned by someone other than J. J. Lander or L. H. Germer.

Germer's research on the erosion of contacts during closure eventually revealed that the arc was formed before the contacts touched. This was a significant finding, since the acknowledged expert in the field of switch contacts, Ragnar Holm, believed that closure arcs occurred only when opposing asperities touched, causing the voltage across the contacts to go to zero momentarily, and then vaporized, due to Joule heating, as the contacts approached one another.[537] Germer was able to discern two types of closure arcs: anode arcs and cathode arcs. Anodes [Cathode] arcs are characterized by the loss of electrode material from the anode [cathode] with the lost material usually ending up on the opposite surface of the cathode [anode]. The anode arcs resembles closely the 'vacuum arcs or sparks' discussed in APPENDIX E, in that it is the anode which suffers erosion. The similarity between anode arcs and 'vacuum arcs' notwithstanding, both anode and cathode arcs are 'vacuum arcs', in the sense that neither is due to gas discharge, i.e., Paschen's law, both are initiated by field emission, and each can carry significant amounts of current.

With their understanding that the source of the positive ions, which allowed the arcs to carry currents far in excess of what was predicted by the Fowler-Nordheim law, were monolayers of tenaciously held gas molecules on the surface of the electrodes, Germer *et al.* turned, in 1960, to the study of these monolayers. To study these monolayers, Germer returned to the low energy electron diffraction technique that he helped pioneer with Clinton Davisson. From 1960 onwards, Germer *et al.* dedicated themselves to designing and building the required apparatus, and then utilized it to explore the structure of the

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[537] Ragnar Holm; Electric Contacts; Hugh Gehers; 1946; p. 280. [**Note**, in the 4th edition of his book,

Ragnar & Else Holm; Electric Contacts, Theory and Application, 4th Ed.; Springer-Verlag; 1967; p. 276-277.

Holm acknowledges Germer's findings about the closure arc occurring before any physical contact of the contacts. And, in a gentlemanly display of good form, Holm adds that it was his theory which was overthrown by Germer's results.

In introducing Germer's work, Holm starts out by discussing Paschen's law, and then demonstrates how Germer's results - in particular, the arcing at voltages below the Paschen's law minimum voltage - are inconsistent with this law. In what is one of the rare lapses in this remarkable book, Holm does not mention the work of Peace, Strutt and, most importantly, Carr on Paschen's law or the seminal work of Earhart, Shaw, Kinsley, Hobbs, Almy, Williams, Carter, Hoffmann, Rother and Rohmann on conduction between closely spaced electrodes. The work of Carr is, as we've seen in APPENDIX E, crucial to formulating Paschen's law for the case where one or both of the electrodes is nonplanar; the usual V (voltage) versus P*d (gas pressure*electrode separation) plots of Paschen's law with their V shape are for planar electrodes only.]

gas monolayers and the influence of these layers on the underlying metal substrate, i.e., surface reconstruction due to the overlying gas monolayer. From 1960 to his death in 1971, Germer authored or coauthored 20 papers on the subject of gas adsorption on metal crystals.

Having considered the ‘Big Picture’ with respect to Germer’s work, the next thing is to examine it in more detail. However, because of time and space constraints, I shall not detail the work from 1948-1959 directly involving observations of contact arcing and its causes; the low energy electron diffraction work (1960-1971), although important, will also not be covered.

§3. WALTER P. DYKE: ‘VACUUM ARCS’ VIA FIELD EMISSION TIPS. - With the analytical tools provided by Erwin Schrödinger’s formulation of wave mechanics in 1926, Oppenheimer, Fowler & Nordheim, Gurney & Condon and Gamow laid the theoretical groundwork for tunneling in 1928. On the experimental side, the introduction (circa 1920) of the Gaede/Langmuir diffusion pump, together with the existing cryogenic capabilities, allowed for vacuums which were both high and clean. Or so it was thought. Even with all these technical advances, the only field emission currents that were reasonably well behaved were small currents; at the higher, commercially useful currents, instabilities appeared which invariably led to ‘vacuum arcs’ which resulted in irreversible changes (melting, deformation, etc.) of the field emitter tips and counterelectrodes.[538] This behavior, or lack of it, at high currents was confusing to workers in the field. On the one hand, they were reasonably sure that their vacuum technique was good, but on the other hand, the high current instability reminded them of the irregular conduction shown by field emission under mediocre vacuums such as were available at the turn of the century. Since the vacuums they were ‘pulling’ were state-of-the-art, there was no easy way to check the theory that the instabilities were being caused by too much residual gas.

W. P. Dyke *et al.*, however, thought that they had a way of circumventing the contamination problem of field emission instability. Their idea was composed

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[538] Problems with ‘vacuum arcs’ were not restricted to industrial applications such as field emission x-ray tubes, they also affected research applications. The first available technique for observing atoms directly was the FIM (Field Ion Microscope) invented by Erwin W. Müller in 1951. The FIM used a microscopically sharp tungsten tip to affect field ionization of an imaging gas, e.g., helium. The tip was usually formed by electrolytically etching a point on the end of a fine tungsten wire. Once the wire was installed in the FIM and the system was pumped down and baked out, the tungsten tip was heat cleaned, to remove surface contaminants, and ‘flashed’, to remove any surface asperities. During the ‘flashing’ procedure, a large transient positive potential was applied to the tip causing preferential field desorption (field ionization at the surface of the tip) of any tungsten asperities; this yielded a smooth single crystal surface suitable for imaging. Unfortunately, the ‘flashing’ process was prone to vacuum arcing, which in the absence of a current limiting resistor could totally destroy the tip. See,

Erwin W. Müller, Tien Tzou Tsong; Field Ion Microscopy, Principles and Applications; American Elsevier Publishing Co., Inc.; 1969; p. 126.

of two parts. [539] The first part consisted of a state-of-the-art pumped field emission tube whose anode could be heat cleaned from behind with a thermionic filament, so as to liberate its surfaces of adsorbed gas and, at the same time, smooth out any overly sharp asperities on its front surface which would be facing the field emission tip (cathode). The field emission tip was prepared in such a way that, when observed in the FEM (Field Emission Microscope) mode, its apex appeared to be a single tungsten crystal. The second part of their scheme involved operating this field emission tube in the pulsed, as opposed to the continuous, mode. Appropriate adjustment of the shortness of the pulse width assured that during its application no positive ions originating from the anode could reach the field emission tip (cathode), and cause a premature 'vacuum arc' or some other artifact. These precautions would not, of course, prevent artifacts from arising due to positive ions generated on or near the surface of the field emission tip itself. Such unavoidable positive ions arise by the now accepted process of field ionization by electron tunneling from neutral surface or adsorbed gas atoms. [540]

By slowly increasing the amplitude of the applied voltage pulse Dyke *et al.* were able to gradually increase the field emission current. Initially, the current-voltage characteristics followed the standard one dimensional Fowler-Nordheim

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[539] W.P. Dyke, J.K. Trolan; Field Emission: Large Current Densities, Space Charge, and the Vacuum Arc; Physical Review; Vol. 89; No. 4; February 15, 1953; pp. 799-808.

W.P. Dyke, J.K. Trolan, E.E. Martin, J.P. Barbour; The Field Emission Initiated Vacuum Arc. I. Experiments on Arc Initiation; Physical Review; Vol. 91; No. 5; September 1, 1953; pp. 1043-1054.

W.W. Dolan,W.P. Dyke, J.K. Trolan; The Field Emission Initiated Vacuum Arc. II The Resistively Heated Emitter; Physical Review; Vol. 91; No. 5; September 1, 1953; pp. 1054-1057.

[540] In the FEM (Field Emission Microscope), electrons are emitted from the pointed cathode by the process of field emission, wherein they tunnel through the confining potential barrier at the metal surface. Once outside the cathode, these electrons are accelerated through the vacuum by the strong electric field between the cathode and anode until they impinge on the phosphor coated anode, and give up their energy as light. By doing an inverse mapping from the image on the phosphor coated screen back to the field emission tip, a picture of the tip surface can be reconstructed. While the resolution of the FEM is very good, it is not good enough to allow the imaging of individual atoms and for this the FIM (Field Ion Microscope) is necessary.

Both the FEM and the FIM were discovered by Erwin W. Müller in 1937 and 1951, respectively. And while he was able to elucidate the mechanism underlying the functioning of the FEM, he was unsuccessful in his bid to uncover the exact method by which the FIM worked. In the FIM, the tip is the anode and the phosphor screen is the cathode, and the vacuum between these two electrodes is slightly backfilled with helium; backfilling with helium is easily accomplished by simply surrounding the glass vessel, containing the electrodes, by a plastic bag filled with helium and waiting a few hours for enough helium to diffuse through the glass. When a high voltage is subsequently applied, the helium atoms near the positive tip are ionized, i.e., lose an electron to the tip - a kind of 'reverse field emission' by electron tunneling according to the theory of Mark G. Inghram and Robert Gomer, and the resulting positive ion now follows the electric field lines to the phosphor screen where it gives up its kinetic energy in the form of light.

M.G. Inghram, R. Gomer; Mass Spectrometric Analysis of Ions from the Field Microscope; Journal of Chemical Physics; Vol. 22; July-December 1954; pp. 1279-1280.

Robert Gomer; Field Emission and Field Ionization; Harvard University Press; 1961; pp. 64-71.

model, i.e., a plot of $\log_e(I)$ versus 1/V yielded a straight line, where I and V were the current and voltage, respectively. At sufficiently high voltages, the effects of space charge became evident as a deviation from the Fowler-Nordheim plot indicated that the current was less than one would expect for the applied voltage. Still further increases in the applied voltage resulted in the appearance of the 'vacuum arc'. At the initiation of the 'vacuum arc', the I-V characteristics were just what one would expect based on Fowler-Nordheim model in the presence of space charge. But once the 'vacuum arc' became more fully developed, the current began to increase enormously and the voltage dropped precipitously; without a current limiting resistor in series with the pulsed power supply feeding the field emission tube, the field emission tip would be completely vaporized. By keeping the pulse width of the voltage applied to the field emission tube short enough, Dyke *et al.* were able to initiate 'vacuum arcing' and watch it start to develop without it outright destroying the emission tip. Thus, this technique allowed them to investigate the onset of 'vacuum arcing' over and over again with the <u>same</u> emission tip, and without the worry that the explosive breakdown was being caused by bombardment of the emission tip by positive ions originating at the anode.

At the end of their research Dyke *et al.* presented their criterion for the appearance of the 'vacuum arc'. For their criterion, they wanted a single parameter, either a critical voltage or current density. The voltage was, of course, known, since they set its amplitude themselves. The current density at the emitter tip was another matter, though. Because they had no way of measuring it directly, they were forced to estimate it by way of a rather involved mix of theories, assumptions and empirical measurements. When they compared the voltages and the current densities at the initiation of the 'vacuum arc' in a number of different emitter tips, only the currents densities showed a correlation, i.e., they were in rough agreement whereas the voltages were not. Therefore, the criterion for the onset of 'vacuum arcing' was a critical value of the current density of the emitter tips.

§4. K. D. FROOME: OSCILLATIONS IN CATHODE SPOTS, THE CONVERSE COHERER. - One of the most interesting and easy to observe phenomenon associated with high current electron emission from electrodes are cathode spots. The amount of technical and scientific literature on this subject is enormous and will not be considered here.

However, there is one facet of cathode spot behavior which may have some relevance to the coherer phenomena. Coherers are characterized by their ability to undergo 'vacuum arcing' in response to the presence of RF energy. Froome has observed the converse process in cathode spots: namely, 'vacuum arcing' causing the production of RF energy, specifically microwaves. [541]

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[541] K.D. Froome; An 8-Volt Cold-Cathode Mercury Arc emitting Microwaves.; Nature; Vol. 179; No. 453; February 2, 1957; pp. 267-268. [I wish to express my thanks to Dr. Thomas E.

§5. APPLICATIONS. - As has been mentioned over and over in this thesis, 'vacuum arcs' are usually seen as something to be avoided at all costs. However, it turns out that 'vacuum arcs' have been harnessed commercially in the field of flash radiography.[542] In the study of, for example, interior ballistics there was the need to be able to take a flash x-ray picture of a projectile at some or many points in its travels up the barrel of the gun. Consider the interior ballistics of a howitzer. One would like to be able to follow the motion of a shell from the moment of ignition of the powder charge to the point at which the shell exited the barrel. The only way to accomplish this feat was by flash radiography. The same thing holds true at the other end of the shell's trajectory when it was penetrating its target, i.e., the study of terminal ballistics. The problem with using Coolidge type x-ray tubes for flash radiography was their writing rate. Because of the speed of the projectile, the x-ray tube must be turned on rapidly or be on continuously and gated using a mechanically driven shutter, and at the same time it must produce enough x-rays in the short time it 'flashed' to record the desired image on the photographic film. In addition, good resolution required a point x-ray source, since there was no easy and convenient way to focus the rays. Summarizing the requirements for a flash x-ray source we have that it must be fast, intense and as close to a point source as is possible.

It turns out that a cold cathode x-ray tube driven hard enough to form a 'vacuum arc' - what Gustave Thomer calls a "vacuum discharge" - satisfies the speed, intensity and constricted spatial extent requirements. As was discovered in 1896-97 by Henry Augustus Rowland, Sydney D. Rowland and Robert William Wood, the x-rays from a tube operated in the 'vacuum arc' *régime* come from a very small area on the surface of the cathode. And as was shown by Robert Millikan and Ralph Sawyer, the 'vacuum arc' could be made to carry as much current as one wanted by paralleling the electrodes with a large enough capacitor.

Following this line of reasoning a number of flash x-ray tubes utilizing 'vacuum arc, spark or discharges' were tried. These included the flash x-ray tube

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Sullivan for bringing my attention to the fact that Froome had done work relating cathode spots and RF oscillations. Dr. Sullivan had heard Dr. Henry Gray casually mention this in a talk that he was giving at a conference. Dr. Gray's citation was rather terse: Froome, 1938. In fact, it turned out that the article was actually published in 1957. **Warning**, the author index of the Science Abstracts, Series A does <u>not</u> have an entry for this paper. The way I found this article was indirectly: it was listed as a reference in a paper on vacuum breakers,

M.P. Reece; The Vacuum Switch, Part I. Properties of the Vacuum Arc; Proceedings of the IEE; Vol. 110; No. 4; April 1963; pp. 793-802.]

[542] Gustav Thomer; History of Flash Radiography; in Lawrence E. Bryant, Jr. (Ed.); <u>Proceedings of the Flash Radiography Symposium</u>; The American Society for Nondestructive Testing; 1977; pp. 1-14.

of K. H. Kingdon and H. E. Tanis, Jr. which used a liquid mercury cathode. [543] The culmination of these efforts was the commercially marketed 'Micronex' system by Westinghouse Electric and Manufacturing Co. based on the work of Charles M. Slack and Louis F. Ehrke. [544] Note, these 'vacuum arc' flash x-ray tubes produced very brief pulses of x-rays for the following reason. The tube action was initiated by field emission; the field emitted electrons produced a few positive ions from the ionization of the residual and surface adsorbed gas, which were attracted to the cathode, and because of their positive charge and low mobility were able to aid in the production of more field emitted electrons; and, of course, these new electrons gave rise to even more positive ions; etc. As the electron current increased, but before the discharge had changed into a full blown arc with its attendant low voltage drop, was when the hard x-rays were produced. By the time the discharge was in its arc mode the voltage drop through which the electrons were accelerated on their way to the anode was so small that the resulting x-rays had essentially no penetrating power. This self limiting action was what gave rise to the x-ray pulse or flash.

These 'vacuum arc' flash x-ray tubes still suffered from limited lifetime due to the inevitable erosion of the electrodes. A solution to this problem involved building a flash x-ray tube which functioned solely in the field emission mode. Because of the reduced current from the cathode tip in this mode, the idea was hit upon to use an array of cathode tips, but just a single anode. This idea was the brainchild of W. P. Dyke and the researchers at the Field Emission Corporation, McMinnville, Oregon. [545]

An even more ubiquitous application of 'vacuum arcs' was in high voltage vacuum circuit breakers. All power transmission grids require some means of interrupting the flow of current. Initially this was accomplished by oil and/or air blast breakers (switchgear). But in the mid 1920s, Royal W. Sorensen and Hallan [Hallam] E. Mendenhall showed that a vacuum switch could successfully interrupt AC currents up to 926 amperes @ 41,594 volts. [546] The impetus for this idea apparently originated from the work by Robert A. Millikan on field

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[543] K.H. Kingdon, H.E. Tanis; Experiments with a Condenser Discharge X-Ray Tube; Physical Review; Vol. 53 (2nd Series); January 15, 1938; pp. 128-134.

[544] C.M. Slack, L.F. Ehrke; Field Emission X-Ray Tube; Journal of Applied Physics; Vol. 12; February 1941; pp. 165-168.

[545] W.P. Dyke; Advances in Field Emission; Scientific American; Vol. 210; No. 1; January 1964; pp. 108-116,118. [W.P. Dyke graduated from Linfield College, McMinnville, Oregon and then obtained his doctorate in physics from the University of Washington in 1946. That same year he returned to teach physics at Linfield College. In 1955, he created and became the director of the Linfield Research Corporation, which was a nonprofit research organization. Dyke founded the Field Emission Corporation (FEC) in 1958. W.P. Dyke and Francis M. Charbonnier were respectively the president and vice president of FEC until the company was bought by Hewlett-Packard in 1973 and renamed the McMinnville Division of Hewlett-Packard; Charbonnier received his doctorate in physics from the University of Washington in 1952.]

[546] R.W. Sorensen; Vacuum Switching Experiments; Transactions of the American Institute of Electrical Engineers; Vol. 45; January-December 1926; pp. 1102-1107.

emission. Millikan showed that by carefully heating the surface of the electrodes while they were under vacuum, the minimum voltage to obtain discharges increased dramatically, most likely because this process removed adsorbed gases from the electrode and the glass envelope surfaces.[547] Note, conventional wisdom of the time said that the idea of a vacuum circuit breaker would not work, even if the adsorbed gases were removed. Not only did the prototype vacuum breakers work, but surprisingly their electrodes did not suffer any significant erosion and the interruptions always occurred within the first half-cycle of the power line frequency after the electrodes separated.

After Sorensen and Mendenhall had demonstrated the feasibility of the vacuum interrupter, the patents rights to it were acquired by the General Electric Company. However, the gulf between feasibility and practicality turned out to be rather large. The prototype had two main problems which ruled out any reasonable reliability: 1) the fragility of the glass-to-metal seals, and 2) the gas content of the electrodes.[548] The glass-to-metal seal problem was eventually solved by Albert W. Hull sometime around 1950 with his discovery of the alloy, Fernico, whose thermal expansion coefficient was perfectly compatible with glass.

The problem of obtaining gas free electrodes was more resistant to solution. Refractory metals such as sintered tungsten could be made relatively gas free by prolonged heating in vacuum, but their high melting point made them unsuitable for vacuum interrupters due to excessive current chopping. Briefly, the phenomenon of current chopping is as follows. When the vacuum interrupter electrodes are separated, while an alternating current is flowing through them, a ‘vacuum arc’ is struck which carries the current between the now separated electrodes. As the alternating current approaches a zero crossing, the ‘vacuum arc’ goes out and stays out even as the current and voltage build up on the other side of the zero crossing thus interrupting the circuit. However, it turns out that the ‘vacuum arc’ always goes out at a finite value of current, i.e., it is extinguished before the current is identically zero. This propensity is referred to as ‘chopping the current’, and it is an undesirable property in that it leads to excessive dV/dt in the interrupted circuit. Metals such as a copper were also tried, but proved to be too gassy even after being vacuum melted in graphite crucibles. The epiphany occurred when James D. Cobine, following suggestions from Malcolm H. Hebb, tried single crystal copper and zone refined copper. Single crystal copper proved to be very gas free upon repeated operations of the vacuum interrupter, but it was not economically feasible due to cost. Luckily, the zone refined copper showed itself to be reliably gas free and inexpensive. Note,

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[547] R.A. Millikan, B.E. Shackelford; On the Possibility of Pulling Electrons from Metals by Powerful Electric Fields.; Physical Review; Vol. 15 (2nd Series); 1920; pp. 239-240.

R.A. Millikan, C.F. Eyring; Laws Governing the Pulling of Electrons out of Metals by Intense Electric Fields; Physical Review; Vol. 27; January 1926; pp. 51-67.

[548] J.M. Lafferty (Ed.); Vacuum Arcs, Theory and Application; John Wiley & Sons; 1980; pp. v-xiv.

copper, even after zone refining, was still not the best electrode material, but at least it was a start.

Today, vacuum breaker technology has progressed to the point that modern research units can stand up to 120 kV; commercial vacuum breakers have the following ranges 3.6-36 kV @ 8-63 kA. [549] Besides better vacuum techniques, the metal contacts are essentially gas free, not just at their surface but also in their bulk, due to the use of zone refining and other material preparation processes.

Although, 'vacuum arcs' are being used commercially, one should still not lose sight of the fact that applications of this phenomenon/phenomena, no matter how successful, are still more of an art than a science. And as with most technological innovations, their widespread use may eventually confer understanding, but they will be used regardless of whether or not they are understood.

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[549] Kunio Nakanishi (Ed.); Switching Phenomena in High-Voltage Circuit Breakers; Marcel Dekker, Inc.; 1991; p. 145.

APPENDIX G - THE COPPER OXIDE RECTIFIER

"Luck sometimes visits a fool, but never sits down with him."
- German Proverb

To put the copper oxide rectifier in the proper context, a little history is essential. The point contact diode, while well suited to the detection of radio signals, was not able to handle high voltages or high currents. Hard vacuum tube rectifiers (thermionic diodes), while superbly able to handle high voltages, could not easily work at high currents [and low voltages] due to their very high internal resistance. [550] In addition, vacuum tubes suffered from excess baggage due to the necessity of having to have a filament power supply. The so-called wet type rectifiers could handle high currents [at low voltages] but not high voltages; they were also restricted to rectifying low frequencies, although, it appears that this caveat was only true where large currents were concerned. Because wet type rectifiers are no longer part of the modern technologist's repertoire, a brief description of their construction and mode of operation is in order.

At its simplest, a wet type rectifier consisted of, for example an electrolytic cell composed of an aluminum plate and a lead plate dipped into a solution of water and borax. If an alternating voltage was applied across these two electrodes, the lead electrode was indifferent to its polarity, but not so for the aluminum electrode. When the aluminum electrode was positive (anode), oxygen was evolved at its surface producing a thickening of the alumina (Al_2O_3) passivation layer, which due to its insulating nature would prevent any current from flowing; the passivation layer rapidly dissolved when the aluminum electrode was negative (cathode), thus allowing the current to pass unimpeded through the cell. It was this growth and dissolution of the insulating alumina layer which gave rise to rectification in the wet type rectifiers. Though wet type rectifiers are long gone, their direct descendants are still with us: aluminum electrolytic capacitors, which depend for their proper functioning on the electrolytically 'formed' insulating layer of alumina on their plates. These capacitors are, of course, polarity sensitive, if put in the circuit backwards the

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[550] Mercury-vapor rectifiers and ignitrons did <u>not</u> have the high internal resistance of hard vacuum tubes and so could provide high currents. In fact, the voltage drop across these devices was almost independent of the current. Early automobile battery chargers used an offshoot of the mercury-vapor rectifier called the Tungar® rectifier (circa 1915), which substituted high pressure argon in place of mercury. The advantage of argon over mercury was that the filament and plate voltages could be applied simultaneously since the argon was already in the gaseous state. In the mercury-vapor rectifier, the filament had to be turned on <u>first</u> and allowed to warm up the globule of mercury, and so increase the pressure of the mercury vapor, before applying the plate voltage. Turning on both the filament and plate voltage together would result in a large voltage drop across the tube, specifically in the cathode fall of the gas discharge, resulting in the cathode being bombarded by very high energy positive mercury ions accelerated through the abnormally large cathode fall, with the result being the eventual destruction of the cathode. The potential drop along the length of a gas discharge was not uniform, almost all of the drop occured close to the cathode, hence, the term 'cathode fall'.

alumina film will dissolve resulting in the shorting out and possible destruction of the capacitor, due to overheating as a direct result of increased current flow. [551] Tantalum capacitors also work because of the presence of an electrolytically 'formed' insulating film, but they have a higher capacitive density (microfarads/volume) due to the sintered nature of their electrodes with their concomitantly larger surface areas.

Electrolytic detectors for wireless telegraphy were also in vogue in the time period 1900-1910 (see APPENDIX B).

Wet type rectifiers initially served in battery chargers working off of the normal 60 Hz 110 VAC found in most households, but they were prone to leaking their electrolyte to name just one of their problems. In short, a new rectifier was needed, preferably of the dry type. One promising candidate was the copper oxide rectifier or varistor as it was sometimes called [552] ; another up and coming contender was the selenium rectifier. [553] Coincidentally, the rectifying properties

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[551] C.I. Zimmerman; The Aluminum Electrolytic Condenser; Transactions of the American Electrochemical Society; Vol. 5; 1904; pp. 147-170.

Harold P. Manly, L.O. Gorder; <u>Drake's Cyclopedia of Radio and Electronics</u>; Frederick J. Drake & Co.; 1951; see RECTIFIER, ELECTROLYTIC. [Most electrolytic rectifiers used lead for the inactive electrode; the active electrode was usually made of tantalum (in sulfuric acid), aluminum (in a saturated solution of ammonium sulfate or ammonium phosphate) or magnesium (in a solution of sodium fluoride).]

[552] The inventor of the copper oxide rectifier appears to have been a Mr. Lars Olai Grondahl who was working at the time for the Union Switch and Signal Co. see,

L.O. Grondahl; A new type of contact rectifier; Physical Review; Vol. 27 (2nd Series); January-June 1926; p. 813.

Idem; Theories of a New Solid Junction Rectifier; Science; Vol. 64; No. 1656; 1926; pp. 306-308.

Lars O. Grondahl also claimed that he and a coworker (Paul H. Geiger) were the first ones to observe the photoelectric effect at a copper-cuprous oxide interface. It is important to note, as Grondahl does, that what he and Geiger observed was an <u>external</u> photoelectric effect; A.H. Pfund had already observed the <u>internal</u> photoelectric effect in cuprous oxide, which gave rise to the photoconductive effect. The photoconductive effect was a passive effect in that it would only be observed by applying an external source of EMF (ElectroMotive Force) across the oxide, while the external photoelectric effect caused the copper oxide rectifier to <u>become</u> a source of EMF, itself, i.e., it could act as a solar cell.

L.O. Grondahl; Note on the Discovery of the Photoelectric Effect in a Copper-Oxide Rectifier; Physical Review; Vol. 40 (2nd Series); April-June 1932; pp. 635-636.

For more information on the internal photoelectric effect in cuprous oxide see,

A.H. Pfund; The Light Sensitiveness of Copper Oxide; Physical Review; Vol. 7 (2nd Series); No. 3; 1916; pp. 289-301.

[553] The copper oxide rectifier was replaced eventually by the selenium rectifier, which had been invented around 1925 by E. Presser. However, copper oxide rectifiers still had a large market share even as late as 1948. The following are references to the discovery of rectification in selenium,

E. Presser; Selen als Gleichrichtermaterial [Selenium as a Rectifier Material]; Funkbastler [Radio Amateur]; Vol. 44; January 1925; pp. 558-559. [**Warning**, there is an error in Fig. 1. The right hand 'e', which is pointing at the metal foil layer, should be a 'c' to be in accordance with the text, and not cause confusion with the left hand 'e' which is pointing at the layer of selenium under the foil.]

of the copper oxide and selenium rectifiers were discovered in the same way. Both cuprous oxide and selenium had been known to exhibit photoconductivity and so they were configured as photoconductive cells for use in light meters; in addition, both cuprous oxide and selenium exhibited photovoltaic effects and were, in fact, the earliest solar cells. [554] Grondahl and Presser discovered the asymmetrical I-V characteristics of copper oxide and selenium cells, respectively, by examining their own versions of these photoconductive cells. This led to the construction of copper oxide structures solely for the purpose of rectification.

Idem; Der Selengleichrichter [Selenium Rectifier]; Elektrotechnische Zeitschrift [Electrical Engineering Journal]; Vol. 53; April 7,1932; pp. 339-341.

[554] The first photovoltaic cell was constructed around 1839 by Edmond Becquerel,

E. Becquerel; Mémoire sur les effets produits sous l'influence des rayons solaires [Memoirs on the effects produced by the influence of sunlight]; Comptes Rendus Hebdomadaries des Seances de l'Academie des Sciences (Paris); Vol. 9; 1839; pp. 561-567.
Among the many photovoltaic cells he constructed, one of the first was an electrolytic cell composed of a shiny brass electrode and an oxidized brass electrode (cuprous oxide) dipped in a dilute nitric acid solution.

During their researches in 1876 on the electrical effects of light on selenium, W.G. Adams and R.E. Day noticed that the increase in the conductivity of selenium (internal photoelectric effect) upon exposure to light depended on the polarity on the Wheatstone bridge used to measure its resistance, i.e., the conductivity was a function of the direction of the DC current through the selenium sample. They wondered if this asymmetrical behavior was due to an electrical current created in the selenium by the light. If such was the case, then they reasoned that it might be possible that this current could be made to flow in a closed circuit. To test this hypothesis, they connected a sample of selenium up to a galvanometer and observed a deflection only in the presence of light, confirming their hypothesis. Adams and Day showed great physical intuition in their researches. They correctly surmised that the photovoltaic effect was not a thermal effect because its time constant was so short, i.e., the light induced current started immediately upon the application of the light and ceased without delay after the light was removed. And they appreciated that different samples of selenium from the same lot, while possessing the same qualitative behavior, had vastly different quantitative behavior - a problem that was to plague semiconductor researchers until the 1920s & 30s when Robert Pohl showed that it was due to heterogeneous distributions of impurities. For more information see,

W.G. Adams, R.E. Day; The Action of Light on Selenium; Proceedings of the Royal Society (London); Vol. 25; 1876-77; pp. 113-117.

Further improvements in the construction of the selenium photocell followed the ground breaking work of Adams and Day. See, for example,

C.E. Fritts; On a New Form of Selenium Cell, and some Electrical Discoveries made by its use; American Journal of Science; Vol. 26 (3rd Series); Nos. 151-156; July-December 1883; pp. 465-472.

To realize a copper oxide rectifier, one took a copper disk; heated it up in an air or an oxygen oven until the resulting reddish cuprous oxide layer achieved the desired thickness; after cooling down, the oxide layer was removed from one side of the disk; the oxide layer on the opposite face was treated to remove the overlayer of black cupric oxide (CuO); [555] finally, a counterelectrode was deposited on this cuprous oxide layer. [556] The counterelectrode could be either a metal film sputtered or evaporated over top of the oxide, or it could be that colloidal graphite, a.k.a. Aquadag®, [557] was painted on the oxide and then a flat piece of tinned lead was firmly pressed against the Aquadag®-oxide-copper combination. The electrically conducting Aquadag® filled any spaces between the free surface of the cuprous oxide and the lead counterelectrode, while the tin coating on the lead prevented a chemical reaction from occurring between the lead and the cuprous oxide at those points where these substances came into direct contact. Unlike the semiconductor rectifiers, which would later replace it, the copper oxide rectifier's active layer - the cuprous oxide - was polycrystalline. The polycrystalline nature of the cuprous oxide layer of the copper oxide rectifier was what made analysis of its behavior by standard solid state physics techniques difficult. The sensitivity of this rectifier to variations in the stoichiometry of the cuprous oxide layer, in particular, to excess oxygen, which seemed to increase its conductivity, was suggestive of doping to produce an extrinsic semiconductor. [558] It should also be noted that the electrical properties

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[555] Initially this layer was removed mechanically via abrasion with an emery wheel, nitric acid was also tried, but in the end the production units had their cupric oxide layers removed chemically using a solution of sodium cyanide. See,

L.O. Grondahl; The Copper-Cuprous-Oxide Rectifier and Photoelectric Cell; Reviews of Modern Physics; Vol. 5; April 1933; pp. 141-168.

[556] The trick to making these devices was in the intimate nature of the junction achieved by growing the cuprous oxide directly out of the copper electrode and insuring that the oxide was formed with excess oxygen. Joseph A. Slepian - a very well known electrical engineer/designer at the Westinghouse Electric & Manufacturing Co. - admitted as to how he had failed in his attempts to build a copper oxide rectifier due to not growing the oxide properly; the tricks were not obvious even to someone as clever as Slepian. See,

L.O. Grondahl, P.H. Geiger; A New Electronic Rectifier; Transactions of the American Institute of Electrical Engineers; Vol. 46; February 1927; pp. 357-366.

[557] According to the H. Bennett; Concise Chemical and Technical Dictionary; Chemical Publishing Co.; 1986; p. 123; Aquadag® is a "…colloidal solution of deflocculated Acheson graphite in water…". Aquadag® was invented by Edward Goodrich Acheson who was also the discoverer of the industrial process for making Carborundum® (SiC); silicon carbide had been, like aluminum, a laboratory curiosity for many years. He also invented the process for making artificial graphite. Natural graphite was mined in Ceylon (now called Sri Lanka) and Canada for many years, but its lack of purity would prevent it from being used in such critical applications as moderator material in nuclear reactors. Aquadag® is still used by the electronics industry as an opaque, electrically conductive layer inside TV picture tubes and oscilloscope tubes, it forms the anode in these types of vacuum tubes.

[558] Eberhard Spenke; Electronic Semiconductors; McGraw-Hill; 1958; pp. 39-40, 56-57. [According to Spenke, when cuprous oxide with excess oxygen was examined via the Hall effect, the result indicated the presence of positive charge carriers. And since ionic conduction could be ruled out for various reasons, this result implied that holes were the culprits. Thus, cuprous oxide

of these rectifiers were a strong function of heat treatment history of the cuprous oxide layer: slow cooling of the cuprous oxide-copper combination in air yielded rectifiers with high reverse breakdown voltages, while rapid cooling - water quenching - produced rectifiers with low forward and reverse resistances, which were not able to support as large a reverse voltage as the slow cooled, high resistance, rectifiers, but could tolerate higher currents. [559] One thing that was not explicitly mentioned about the processing of the rectifier was whether or not the copper, on which eventually was grown the oxide, was pretreated in some way, e.g., polished. My feeling is that for all of Mr. Grondahl's candor in his description of how these devices were made, there were probably some proprietary steps in the manufacture of these rectifiers which he was not willing to divulge.

In addition, while a pure cuprous oxide layer will work, it was not optimal. The presence of impurities could produce higher rectification ratios and smaller reverse leakage currents. In particular, the impurities inherent in Chilean copper had been found to yield the best rectifiers. [560] The exact nature of these impurities and the history of how Chilean copper was discovered to make the best rectifiers does not <u>seem</u> to have made it into the open electrical engineering literature. [561] In fact, in an earlier review article L. O. Grondahl stated <u>almost</u>

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with excess oxygen was an acceptor or P-type semiconductor created by defects, i.e., the absence of Cu atoms; acceptor or P-type semiconductors could also be created by adding acceptor substitutional impurities, i.e., substituting aluminum for silicon atoms.

Note, the absence (defect) of a Cu atom left the attendant oxygen atoms unfulfilled as far as their outer orbitals were concerned. If the temperature was high enough, an electron from the filled valance band could hop into the unsatisfied oxygen orbital associated with the defect position, leaving a positive electron or hole free to migrate (conduct) in the valence band; the defect position, upon picking up the extra electron, became negatively charged and was spoken of as being ionized.]

[559] L.O. Grondahl; The Copper-Cuprous-Oxide Rectifier and Photoelectric Cell; Reviews of Modern Physics; Vol. 5; April 1933; pp. 141-168.

[560] W.H. Brattain; The Copper Oxide Varistor; Bell Laboratories Record; Vol. 19; September 1940 - August 1941; pp. 153-159. See also,

Idem; Specific Resistance of Cuprous Oxide; Physical Review; Vol. 45 (2nd Series); January-June 1934; p. 745.

[561] A good source of information on the subject of copper oxide rectifiers is: The Archives Coordinator; AT&T Bell Labs; Rm. 1D-423; 101 JFK Parkway; Short Hills, NJ 07078. The Archives Coordinator provided me with an exhaustive bibliography on this subject at no charge - I wish to thank Edward Eckert of AT&T Archives for responding to my request for information in such an efficacious manner.

With regards to the term 'Chilean copper', the only other place I have seen it mentioned - besides the two articles by Brattain - was in an article on the history of the point contact transistor,

L. Hoddeson; The discovery of the point-contact transistor.; Historical Studies in the Physical Sciences; Vol. 12; Part 1; 1981; pp. 41-76.

According to Hoddeson, when Joseph Becker and Walter Brattain began investigating the properties of copper oxide rectifiers, one of the many questions they had to answer was the following. "And why do certain samples of Chilean copper not work in rectifiers?" This quote, which came from p. 46 of Hoddeson's article, was annotated with a footnote referring to some "Case reports (BLC) [Bell Telephone Laboratories, Private Collection]". In an effort to learn more unequivocally that of all the impurities, that he had occasion to try, none improved the performance of the rectifiers. He did admit, when questioned, that he knew of something - he called it a "…condition…" - that appeared to improve the characteristics of the rectifiers, but then he added, rather cryptically, that "…I am not prepared to talk about that." [562]

The properties of Chilean copper - whatever they were - should have been well known given the fact that Sir Charles Tilston Bright's 1898 tome on the subject of submarine telegraph cables made mention of the desirable qualities of copper ore from, among other places, Chile. Specifically, he cited four geographical regions which yielded, at that time, the world's supply of copper for electrical signaling use: U.S./Canada (Lake Superior), Australia (Burra-Burra), Chile and Japan. While most of the copper was found in the form of ores, e.g., copper pyrites, the lone exception was the Lake Superior source where copper was found naturally in the uncombined state, and so was very inexpensive to process because fewer smelting and refining steps were required. Bright indicated that of those sources of copper ore, Chile provided one of the best ores in the sense of being <u>free</u> from objectionable impurities; an example of an objectionable impurity was arsenic, small quantities of which can reduce the electrical conductivity tremendously and removing it completely was very difficult. [563] This last statement appears to indicate that it was the relative freedom from impurities which made Chilean copper desirable. I do not know whether I will ever be able to figure out the mystery behind Chilean copper - if, in fact, there ever was one.

It should be mentioned that commercial production of copper from Chile can in fact be traced as far back as 1800, [564] while copper production for internal use, i.e., as religious, political and cultural artifacts, by the indigenous people of this region has been recently verified by archeologists and shown to date back as far as 500 A.D. [565]

Just before putting the final touches on this thesis, I stumbled - as I have done so often and so fruitfully in the past - upon an article devoted to the subject

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about the use of Chilean copper by Bell Labs, I wrote, again, to the AT&T Archives Coordinator asking if he or she could find these case reports? Edward Eckert wrote back to inform me that he could find <u>no</u> such case reports based on the information I had provided. I then decided to ask Hoddeson if she either had copies of these reports or knew where they were located? Her address is: University of Illinois at Urbana-Champaign, Department of Physics 1110 West Green St., Urbana, Illinois 61801-3080. I have yet to receive a response.

[562] L.O. Grondahl; Copper Oxide Rectifiers; Transactions of the Electrochemical Society; Vol. 72; 1937; pp. 225-245.

[563] Charles Bright; <u>Submarine Telegraphs, Their History, Construction and Working</u>; C. Lockwood; 1898; Part II, Chapter 1, The Conductor [Reprinted in 1974 by Arno].

[564] Joseph Newton, Curtis L. Wilson; <u>Metallurgy of Copper</u>; John Wiley & Sons; 1942; pp. 450-452.

[565] I. Shimada, J.F. Merkel; Copper-Alloy Metallurgy in Ancient Peru; Scientific American; Vol. 265; No. 1; July 1991; pp. 80-86.

of Chilean copper. [566] This article was doubly unusual: first, because it confined itself to the subject of Chilean copper and its use in copper oxide rectifiers, and second, because it used the term 'Chilean copper' in its title. Before delving into the gist of this paper, I am going to review the contents of the first article referenced by Hein and Hickam, a relatively unknown article by Lars O. Grondahl. [567] This particular article by Grondahl, which appeared almost 25 years after the paper in which he first announced the discovery of the copper oxide rectifier, gave a firsthand account what really happened as far as the history of the copper oxide rectifier was concerned including information on the use of "…Chile copper…".

Grondahl revealed important details about the history of the copper oxide rectifiers which appeared in print nowhere else. For example, the first paragraph of his paper disclosed that the copper oxide rectifier was invented in November 1920 and that by 1924 these devices were in commercial service - specifically, as he discussed later, in train control equipment on the Delaware, Lackawanna and Western railroads. So that by the time of his announcement in the 1926 edition of the *Physical Review*, it was already a *fait accompli*. I assume that Grondahl's employer, Union Switch and Signal Company, Swissvale, Pennsylvania, prevented any earlier revelations due to concerns about patent rights. That the company's caution was well founded was adequately demonstrated by Grondahl's detailing how Westinghouse Electric Corporation began manufacturing the rectifiers in the fall of 1926 - probably by a licensing agreement with Union Switch and Signal, although Grondahl was noncommittal on this point - to be used in an 'A battery' charger;[568] according to Grondahl, in the "…latter part of 1926 this production rose to 6,000 'A battery' chargers a day [Emphasis added]." Clearly there was an enormous amount of money to be made in exploiting the copper oxide rectifier. The main reason was that the competing rectifiers had a rectifying efficiency of no better 20% and, to add insult

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[566] C.C. Hein, W.M. Hickam; Carbon, Oxygen, and Sulphur Content of Chilean Coppers as related to Cuprous-Oxide Rectifiers; Journal of Applied Physics; Vol. 22; September 1951; pp. 1192-1195. [I found this article while perusing the subject indexes of the various abstracting services concerned exclusively with metals such as the ASM Review of Metal Literature, Review of Metal Literature, and Metal Abstracts. Specifically, the Hein and Hickam piece was found abstracted in the Review of Metal Literature; Vol. 8; 1951; p. 59, abs. no. 118-C.

The ASM Review of Metal Literature was published by: American Society for Metals, Cleveland 3, Ohio.

The Review of Metal Literature was published by: American Society for Metals, Cleveland 3, Ohio.

The Metal Abstracts is published by: The American Society for Metals and The Metals Society.]

[567] L.O. Grondahl; Twenty-Five Years of Copper-Copper Oxide Rectifiers; Transactions of the American Institute of Electrical Engineers (AIEE); Vol. 67 (Part I); 1948; pp. 403-410.

[568] The terminology 'A battery', 'B battery' and 'C battery' were associated with vacuum tubes. The 'A battery' was the low voltage, high current battery used the heat the filament, while the 'B battery' and 'C battery' were the high voltage, low current batteries used for the plate and control grid, respectively, of the vacuum tube. See,

Stuart Ballantine; Radio Telephony for Amateurs; David McKay Company; 1922; pp. 46-48.

to injury, a very short lifespan. Towards the end of the article, Grondahl finally acknowledged that a "…Chile copper prepared for rectification production by special rolling processes was used universally because it produced the most consistently satisfactory results." Why was Chilean copper better than say OFHC (Oxygen Free High Conductivity) copper? Grondahl could only point to the fact that the best rectifiers were produced from copper which contained approximately 0.03% oxygen, which Chilean coppers did. According to a 1941 article by Williams and Thompson, the 0.03% oxygen was necessary to assure good adhesion between the mother copper and its thermally grown oxide layer; OFHC had been tried, but the copper-copper oxide interface was found not to have satisfactory adhesion. [569] Grondahl apparently did not know if there were any other beneficial impurities present in Chilean coppers; the purity of this copper was 99.95% Cu, ~0.035% O_2 [N.B., I am <u>not</u> assuming that the oxygen existed in the copper existed in its diatomic form. I used the symbol O_2 simply out of convention.], and the remaining 0.02% composed of other elements. The confusion about what 'really' constituted a good copper, out of which to construct copper oxide rectifiers, can be illustrated by the following quote from the discussion following the paper by Williams and Thompson (1941),

> Dr. R. E. Blakey: …
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> … My experiments indicate that it is possible for the copper to be too pure, and as a result of prolonged experiment I find that for our own process a figure of 99.96% is the most suitable. This does not imply that any copper of such purity will perforce produce satisfactory rectifiers. Indeed, this is far from being the case. [570]

Carl C. Hein and W. M. Hickam, were employees of the Westinghouse Research Laboratories, which was a part of the Westinghouse Electric and Manufacturing Company. Their paper focused on examining the carbon, oxygen and sulfur content of lots of Chilean copper that had been employed in the manufacture of commercial rectifiers over a period of ten years (~1940 to 1950). They also attempted to correlate the amounts of these impurities with the electrical performance of the rectifiers (specifically, the reverse leakage currents) in a bid to determine which of these impurities gave Chilean copper its advantage. The results indicated that only oxygen and sulfur correlated with the rectifier electrical characteristics, and that these substances worked best only in small amounts on the order of 220 and 5 ppm (parts per million), [571] respectively.

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[569] A.L. Williams, L.E. Thompson; Metal Rectifiers; Journal of the Institution of Electrical Engineers; Vol. 88 (Part I); No. 10; October 1941; pp. 353-383. [See, in particular, p. 358.]

[570] Ibid.; p. 372.

[571] To calculate the ppms of O_2 in a sample of Cu, the following formula is used,

$$\text{ppm } O_2 = (\text{weight } O_2 \text{ in the Cu sample/total weight of Cu sample})10^6.$$

Note, % O_2 = pph O_2, i.e., the percentage of O_2 (by weight) in a Cu sample is equivalent to parts per <u>hundred</u> of O_2 in the same sample. According to Hein and Hickam, an oxygen content of

That the use of Chilean copper in the manufacture of copper oxide rectifiers was a closely guarded secret can be supported by two pieces of evidence. First, in all the articles and patents he wrote or coauthored, Grondahl never mentioned anything about Chilean copper. Only in his last paper on the subject, in 1948, when the copper oxide rectifier was about to be eclipsed by its old rival the selenium rectifier, and the selenium rectifier was itself about to be usurped by the germanium and then silicon rectifiers, did he finally mention the fact that Chilean copper "…was used universally…" in the production of copper oxide rectifier units. And we know that Chilean copper was used as far back as 1940 from the article by Hein and Hickam. In addition, Grondahl admitted that several years after the start of commercial manufacturing of rectifiers began Chilean copper became the *sine qua non* for the process. Second, Heinz K. Henisch's 1949 book, <u>Metal Rectifiers</u>, which was an exhaustive compendium of all available knowledge on copper oxide, selenium and other metal rectifiers, made <u>no</u> mention of Chilean copper, even though Henisch did spend a considerable amount of time on other esoterica related to the rectifier manufacturing process. Henisch's thorough bibliography, which was organized by year, did <u>not</u> contain a citation to Grondahl's last article in the 1948 section nor did it cite the 1941 *Bell Laboratories Record* article by Walter Brattain which appeared to be the first public mention of the term 'Chilean copper'.

One mystery which still remains has to do with how Walter Brattain knew about the Chilean copper? He wrote about how Chilean copper was the material of choice for the manufacture of copper oxide rectifiers in an article in the 1940/41 volume of the *Bell Laboratories Record*. Since he worked for the Bell Telephone Company and <u>not</u> for either Westinghouse Electric and Manufacturing Company or Union Switch and Signal Company, it was not obvious how he came by this knowledge. As already mentioned, this paper was absent from the bibliography in Henisch's book. Brattain was supervised during his initial work on the copper oxide rectifier by Joseph Adam Becker. It is possible that Becker was the actual source of information regarding Chilean copper, and that Brattain was simply the messenger. The best evidence for this hypothesis comes from the fact that Joseph Adam Becker, before he began to work at Bell Labs in 1924 as a Research Engineer, had previously been employed by the Westinghouse Electric and Manufacturing Company as a Research Assistant from 1919 to 1924.[572] Thus, Becker was present at Westinghouse during the very years when Grondahl first discovered the copper oxide rectifier and when it was initially put into production.

~220 ppm yielded copper oxide rectifiers with good electrical characteristics. Since there are 10^4 ppm in each pph (%): 220 ppm O_2 = 0.0220 pph O_2 = 0.0220 % O_2, which is close to the value of 0.03 % O_2 championed by Grondahl.

[572] Winfield Scott Downs (Ed.); <u>Who's Who in Engineering, A Biographical Dictionary of the Engineering Profession, 1948</u>; Lewis Historical Publishing Company, Inc.; 1948; p. 129.

As a postscript to the mystery of Chilean copper, it should be noted that the annals of the history of selenium rectifiers were haunted by a *Dopplelgänger* to Chilean copper known as the "…thallium catastrophe…". [573] According to Eberhard Spenke, the production of selenium restifiers for the German war effort came to a standstill in 1942 when the electrical characteristics of these devices suddenly and inexplicably changed. Specifically, the electrical characteristics which degraded were associated with the forward bias region of the current-voltage curve; no degradation was observed in the reverse bias region, in fact, the characteristics in this region actually experienced a dramatic improvement, even as those in the forward region were denigrated. During the ensuing scramble to uncover what had changed in the manufacturing process, someone noticed that one of the things that had changed was that the solder used to attach electrical leads to the devices came from a different manufacturer than the solder used previous to the catastrophe. A chemical analysis of the 'new' solder revealed the presence of thallium in amounts higher than in the 'old' solder. The inference was drawn, and apparently verified by experiment, that the thallium was indeed the culprit. Changing the solder brought the manufacturing process back into line with no one the wiser, especially about why thallium had such a strong influence? The preceding tale came from an unpublished report authored by Spenke and reviewed by Ernest Braun. [574]

Further corroborative evidence for the disproportionate influence of thallium on the electrical characteristics of selenium rectifiers can be found in the book by Heinz K. Henisch. [575] Henisch stated that small amounts of thallium

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[573] Ernest Braun; Selected Topics from the History of Semiconductor Physics and Its Applications; in Lillian Hoddeson, Ernest Braun, Jürgen Teichmann, Spencer Weart (Eds.); Out of the Crystal Maze, Chapters from the History of Solid-State Physics; Oxford University Press; 1992; p. 445. [**Note**, it was odd that this tome made no mention of the Chilean copper episode. This was doubly curious given that one its editors/contributors, Lillian Hoddeson, had explicitly brought up the subject in an earlier article,

L. Hoddeson; The discovery of the point-contact transistor.; Historical Studies in the Physical Sciences; Vol. 12; Part 1; 1981; pp. 41-76.]

[574] E. Spenke; Beitrag zur Frühgeschichte der Halbleiter-Elektronik und der Kupferoxydul und selen-Gleichrichterentwicklung vornehmlich im Hause Siemens [Contributions to the early history of semiconductor electronics and of the copper oxide and selenium rectifier development with emphasis on the work at Siemens]; unpublished report. [As part of its commitment to the International Project on the History of Solid State Physics, the AIP (American Institute of Physics) has published an index to source material relating to the history of condensed matter physics,

Joan Warnow-Blewett, Jürgen Teichmann; Guide to Sources in the History of Solid State Physics; American Institute of Physics; 1992; ISBN 156-396-0680.

According to the author index of this guide, Spenke's unpublished report can be found at the Deutsches Museum of Munich, Department of Sciences.

The Guide to Sources… itself can be purchased for $21.50 ($19.00 + $2.50, shipping and handling; make out the check to the American Institute of Physics) from: AIDC (American International Distribution Corporation), 64 Depot Rd., Colchester, Vermont 05446, (800)488-2665.]

[575] Heinz K. Henisch; Metal Rectifiers; Oxford University Press; 1949; pp. 11-12. [Henisch indicated that he obtained some of his information about the influence of thallium on the electrical characteristics of selenium rectifiers from the following reference,

alloyed with the metal used to form the counter electrode improved the reverse voltage characteristics of the rectifier, but that excessive amounts of thallium adversely affected its ageing characteristics (especially the forward bias resistance). The junction between the counter electrode and the selenium was the site of the rectification action.

So while the ability of impurities to enhance its electrical behavior was something copper oxide rectifiers had in common with present day silicon rectifiers, their polycrystalline morphology was something not shared with modern semiconductor devices, with the exception of perhaps the early 1N2X point contact diodes which also initially employed a polycrystalline piece of semiconductor. Nevertheless, cuprous oxide rectifiers worked because cuprous oxide was a semiconductor. Note, a competing but erroneous theory of why copper oxide rectifiers work was the thermoelectric theory, [576] which also saw service in trying to explain why the galena point contact diodes and other crystal detectors functioned, until George Washington Pierce *et al.* debunked this claim. The thermoelectric scenario attempted to explain the asymmetrical I-V characteristic in the following manner. When current flowed across the copper-cuprous oxide junction, the resulting I^2R heating induced a thermoelectric voltage at the dissimilar materials junction. The sense (direction) of this thermoelectric voltage aided current flow in one direction while opposing its flow in the other and so yielded an asymmetrical I-V curve. Among the many reasons for disavowing this mechanism of action were: the sense of the thermoelectric voltage in the case of copper-cuprous oxide was the opposite of what it should be to account for the observed current asymmetry; and slight amounts of flexing of the copper-cuprous oxide junction irreversibly reduced the rectification ratio, due to its degrading the required intimate association between the base metal and its oxide, but <u>without</u> affecting the corresponding thermoelectric voltage.[577] In a similar vein, it was shown recently that two dissimilar metals could form a

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A.L. Williams, L.E. Thompson; Metal Rectifiers; Journal of the Institution of Electrical Engineers (JIEE); Vol. 88 (Part I); No. 10; October 1941; pp. 353-383.

Note, Henisch's book contained a very extensive and invaluable bibliography containing many references to both copper oxide and selenium rectifiers. **Warning**, Henisch's bibliography contains a significant number of errors including misspellings of the last name of the author(s), incorrect volume numbers, improper journal titles, etc.]

[576] S.P. Chakravarti, S.R. Kantebet; Current Rectification at Metal Contacts; Proceedings of the IRE; Vol. 20; No. 9; September 1932; pp. 1519-1534.

[577] L.O. Grondahl; The Copper-Cuprous-Oxide Rectifier and Photoelectric Cell; Reviews of Modern Physics; Vol. 5; April 1933; pp. 141-168, see p. 157. [For Grondahl, the reduction in the rectification ratio brought about by flexing the copper-cuprous oxide interface was an undesirable effect since he was interested in rectification. However, the nonlinear but almost symmetrical I-V curves that resulted from flexing were ideal for modulation. On the other hand, a normal copper oxide rectifier could only modulate in the forward direction, since it passed almost no current in the reverse direction. Joseph A. Becker of Bell Laboratories got the bright idea of using deliberately flexed copper oxide rectifiers as modulators in the phone system,

J.A. Becker, Bell Telephone Laboratories,Inc.; Unidirectional Current Passing Device; U.S. Patent No. 1,980,176; November 13, 1934.

Anon.; Varistors as Modulators; Bell Laboratories Record; Vol. 20; December 1941; p. 105.]

thermocouple junction even though they were separated by 5-15 Å. Briefly, this thermocouple was simply an STM (Scanning Tunneling Microscope) with the emission tip made of one metal and the flat counterelectrode made of a different metal with the counterelectrode being heated from underneath via a chopped laser beam. [578]

Given that the thermoelectric theory had been discredited as the mechanism by which the copper oxide diode worked, what was the mechanism? Before Grondahl and other researchers could even pose this question, they had to first determine the exact location of the rectifier action. They knew that the seat of the action was not the cuprous oxide itself since no materials, then or now, exhibited asymmetrical behavior by itself. Because of the planar nature of the copper oxide diode and the relatively thick layer of oxide which was permissible, researchers were able to directly probe the voltage drop across the various layers making up the device, using a sharpened metal tip. When the diode was reverse biased - what they used to call 'blocking' - it was found that all of the voltage drop was across the copper-cuprous oxide interface. By carefully transversely sectioning this interface and also by peeling thinned copper off the immobilized oxide, the presence of what was called a 'reticulum' was demonstrated. This exceedingly thin honeycombed layer appeared to be the site of the rectifying action. It should be noted that while the reverse bias character of the copper oxide diode was mediated by the copper-cuprous oxide interface, the forward bias behavior was a strong function of the counterelectrode material. [579] Having localized the site of the diode action, researchers were eventually able to show that the injection theories of Mott, Schottky and Davydov (see main section entitled THE RESURRECTIONS for references) accounted for a plurality of the observed behavior. This still left much that was not understood about these fascinating devices.

The semiconducting cuprous oxide (Cu_2O) layer was found not to not be homogeneous electrically. As one moved through this oxide from the free surface to closer to the copper base (sometimes called the mother copper), from which the oxide was grown, one observed that the resistivity, ρ, decreased. This effect was shown in 1941 in a paper by Walter H. Brattain. [580] The experimental procedure utilized to secure this observation was as follows. The oxide was initially grown thicker than normal; the resistivity of this initial thick layer of oxide was determined; a few mils (1 mil = 0.001 inch) of the oxide layer were removed - presumably by chemical etching although Brattain does not say; the resistivity of

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[578] J.M.R. Weaver, L.M. Walpita, H.K. Wickramasinghe; Optical absorption microscopy and spectroscopy with nanometre resolution; Nature; Vol. 342; December 14, 1989; pp. 783-785.

[579] Similar investigations were performed on the selenium rectifiers and yielded slightly more complicated results due to the possibility of forming a compound semiconductor during the manufacturing process, i.e., this type of diode resembled the typical PN junction of a modern silicon diode.

[580] W.H. Brattain; The Copper Oxide Varistor; Bell Laboratories Record; Vol. 19; September 1940 - August 1941; pp. 153-159.

the new thinner oxide was evaluated; and the etching and measuring process was then repeated. Thanks to a bibliography on copper oxide research at AT&T provided by AT&T's Archives Department, I was able to find two papers by Brattain *et al.* which detailed some of the work they had done on this resistivity problem before and after the Second World War. [581] Unfortunately, both these informative papers are too massive and complicated to be reviewed in this already overburdened thesis.

The manufacturing processes showed quite an amount of 'artistry' due to the rather incomplete understanding of the underlying mechanisms controlling these devices. A look at some of the relevant patents of the day revealed that while many facts were known, there was little in the way of an overarching theory to tie them together.

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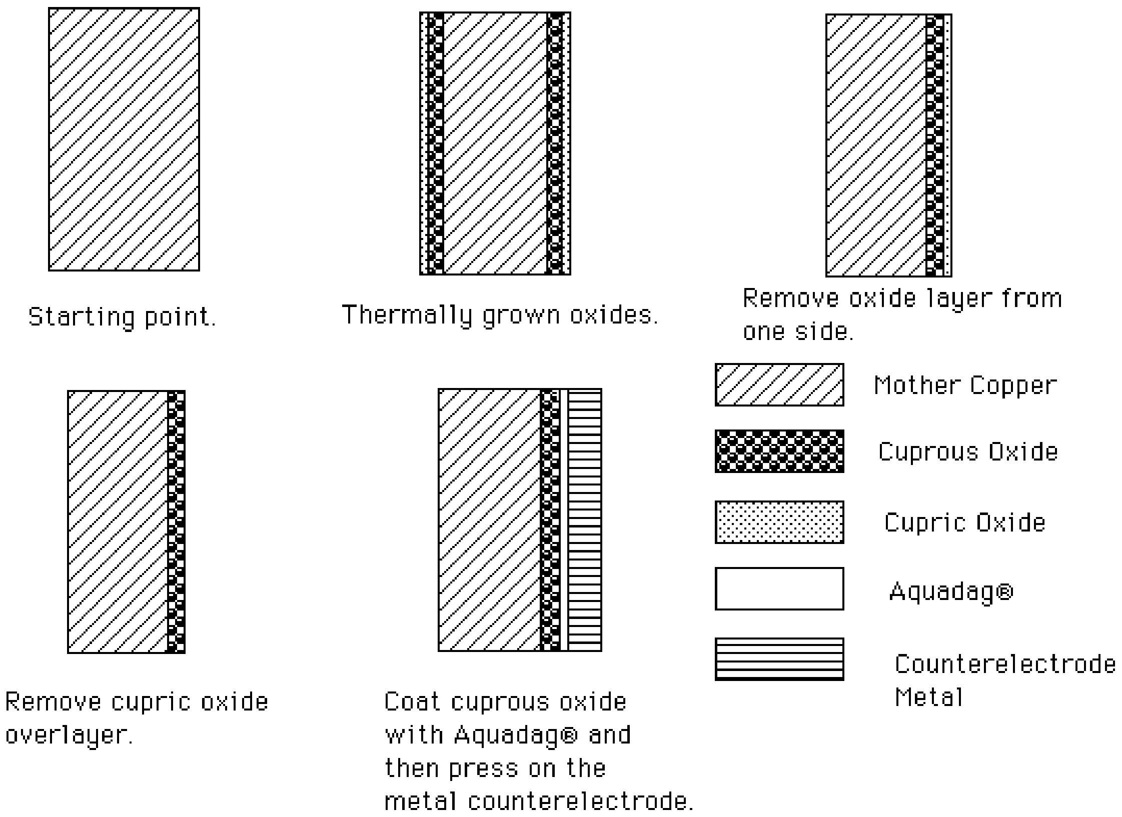
[581] J. Bardeen, W.H. Brattain, W. Shockley; Investigation of Oxidation of Copper by Use of Radioactive Cu Tracer; Journal of Chemical Physics; Vol. 14; No. 12; December 1946; pp. 714-721.

W.H. Brattain; The Copper Oxide Rectifier; Reviews of Modern Physics; Vol. 23; No. 3; July 1951; pp. 203-212. [This paper mentioned the term 'Chilean copper' but offered no historical insight into its origins or commercial uses. The reader interested in learning 'more' about this term was urged by Brattain to consult his 1940 paper in the Bell Laboratories Record. Unfortunately, this advice was not really helpful, since the *Bell Laboratories Record* paper offered only slightly more information regarding the use of Chilean copper.]

FIGURE G1 – Manufacturing a Copper Oxide Rectifier



Starting point.

Thermally grown oxides.

Remove oxide layer from one side.

Remove cupric oxide overlayer.

Coat cuprous oxide with Aquadag® and then press on the metal counterelectrode.

U.S. patent #2,205,263 assigned to Carl C. Hein appeared to indicate that Brattain may not have been the first person to have understood that the cuprous oxide was not electrically homogeneous. [582] Mr. Hein's idea was to increase the maximum permissible reverse voltage of the copper oxide rectifier by growing the oxide layer thicker than necessary and then chemically removing the excess thickness of cuprous oxide, together with the undesired overlayer of cupric oxide, until the proper thickness was achieved. Specifically, if the desired cuprous oxide thickness was 3 mils (1 mil = 0.001 inch), then the oxide was grown to a thickness of say 6 mils, and then the excess thickness of oxide was removed by chemical etching using a solution of 2% sulfuric acid + 0.1% hydrochloric acid @ 80°C. Rectifiers built according to this scheme could take an impressed voltage three times (3X) higher than normally constructed copper oxide rectifiers. Hein's explanation for this enhanced capability was that "…the removal of the excess thickness of oxide also removes certain surface containing impurities of the copper, or it may remove some undesirable boundary condition existing between the black cupric oxide and the red cuprous oxide. I do not desire, however, to be limited to the possible explanation just stated." In other words, he didn't know, but the data on the oxide resistivity presented by Brattain does provide a

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[582] Carl C. Hein, Westinghouse Electric & Manufacturing Co.; Copper Oxide Rectifier; U.S. Patent No. 2,205,263; June 18, 1940.

rationale for his procedure without itself elucidating why the resistivity should change as one approached the copper base.

Another puzzling result of a manufacturing process was to be found in U.S. patent #1,901,563 assigned to George F. Martin. [583] Mr. Martin's idea was to simplify the process of removing the cupric oxide overlayer and then depositing a counterelectrode. Martin's process consolidated these two steps into one. After the oxide layer was thermally grown on the base copper, this structure was transferred to an annealing oven, and from there it was quenched in a specially prepared mineral oil bath. The quenching operation reduced the cupric oxide overlayer to a low resistance copper contact without affecting the rectifying properties of the copper-cuprous oxide interface. The copper counterelectrode produced by this procedure was, surprisingly, an ohmic junction. A fact which does not make a lot of sense given that the copper base-cuprous oxide junction formed by oxidation was rectifying. The cuprous oxide-counterelectrode interface would seem to be as intimate a junction as that formed at the copper base-cuprous oxide rectifying junction. It should be noted that if after removing the cupric oxide overlayer, one deposited a counterelectrode on the oxide, as opposed to growing one out of the cupric oxide layer, this junction was not rectifying, i.e., it was ohmic, as one would expect. In spite of my carping, a non-rectifying counterelectrode, especially a low resistance one, was desirable because an ohmic counterelectrode would not 'buck' the main rectifying junction and cause a reduction in the overall rectification efficiency. In fact, Bell Telephone Laboratories, Inc. had taken out two patents on a process for depositing low resistance, non-rectifying counterelectrodes. [584]

It is my opinion, that someone should revisit the copper oxide rectifier. It may yet surprise and inform us even more than it has already.

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[583] George F. Martin, Westinghouse Electric & Manufacturing Co.; Copper Oxide Rectifier; U.S. Patent No.1,901,563; March 14, 1933.

[584] Joseph A. Becker, Walter H. Brattain, Bell Telephone Laboratories, Inc.; Electrically Conductive Device and the Manufacture Thereof; U.S. Patent No. 2,239,770; April 29, 1941.

Joseph A. Becker, Walter H. Brattain, Bell Telephone Laboratories, Inc.; Electrically Conductive Device and the Manufacture Thereof; U.S. Patent No. 2,239,771; April 29, 1941. [Examination of the Index of Patents for the time period 1926-1941 revealed that Becker was the sole assignor on all the early copper oxide rectifier patents for Bell Telephone Laboratories, Inc., and only in 1941 did he become a coassignor with Brattain. Becker's key *rôle* in Bell's development of the copper oxide rectifier was corroborated by an article he wrote in their in-house technical journal,

J.A. Becker; Varistors: Their Characteristics and Uses; Bell Laboratories Record; Vol. 18; July 1940; pp. 322-327.

Given Becker's prominence in this field, it came as a shock to find that he had written no technical articles in peer reviewed journals on this subject. Perusal of Science Abstracts, Series B (Electrical Engineering) Vol. 29B (1926) - Vol. 44B (1941) showed no papers by Becker, while Science Abstracts, Series A (Physics) Vol. 29A (1926) - Vol. 47A (1944) yielded a large number of papers on thermionic emission, but none on copper oxide rectifiers. Note, Becker's name was mentioned earlier in this thesis with regards to his pioneering investigations into the mechanism of enhancement of electron emission of alkaline oxide coated cathodes.]