# *Semiconductors 1853-1919: an historical study of selenium and some related materials*

Hempstead, Colin Antony

Hempstead, Colin Antony (1977) *Semiconductors 1853-1919: an historical study of selenium and some related materials*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/8205/

# SEMICONDUCTORS 1833-1919: AN HISTORICAL STUDY OF SELENIUM AND SOME RELATED MATERIALS.

BY

COLIN ANTONY HEMPSTEAD.

DEGREE: DOCTOR OF PHILOSOPHY.

INSTITUTION: UNIVERSITY OF DURHAM.

DEPARTMENT: PHILOSOPHY.

YEAR OF SUBMISSION: 1977.

No part of this thesis has previously been submitted for a degree in any University.

The copyright of this thesis rests with the author. No quotation from it should be published without his prior written consent and information derived from it should be acknowledged.

# CONTENTS.

## ACKNOWLEDGEMENTS.

My thanks are first offered to my Supervisor, Dr. David Knight of Durham, whose encouragement, help and gentlemanly pressure ensured the production of this thesis. Teesside Polytechnic offered me time and facilities in order that the path of my research should be as smooth as possible; and to the Librarians of that Institution I owe a particular debt of gratitude. Finally to my family my acknowledgement is extended; their encouragement was ever present and their occasional help with some of the more tedious aspects of historical research and writing was always gratefully received.

# SEMICONDUCTORS 1833-1919: AN HISTORICAL STUDY OF SELENIUM and SOME RELATED MATERIALS.

Abstract by C.A. Hempstead, (1977).

The history of semiconductors began in 1833 when Faraday noted that the conductivity of silver sulphide increased with temperature. This study ends in 1919 when Pohl went to Göttingen. Five periods are identified: 1833-1895; 1895-1919; 1919-1931; 1931-1948; 1948-present. Only towards the close of the second period was the semiconductor 'class' recognised; until then researches on selenium did not interact with those on other materials.

Faraday's discovery excited little interest, but photoconductivity in selenium, 1873, engendered considerable activity during which rectification and photovoltaicity were noted. Allotropic and electrolytic theories were suggested, (by 1877), with the latter being extensively developed. Theories of electricity were insufficiently agreed to form other than a qualitative base for conduction in solids; until the electron theory and Arrhenius's picture, electrolysis was not an unsatisfactory basis on which to construct an account of the properties of selenium.

The understanding of electrolysis and the electron theory made an alternative description of the action of selenium desirable and attractive. Initially, to c1912, an allotropic theory was developed to be replaced, by 1914, by an electron theory for there was no <u>direct</u> empirical evidence in support of the former. With the adoption of an electron theory selenium was no longer unique and its properties were compared with those of other non-metallic, non-electrolytic conductors, (c1915). With the electron at the root of all electrical properties a new class of materials was defined, the <u>halbleiter</u>, but at the same time the shortcomings of the 'electron gas' theory were highlighted.

By 1919 work on polycrystalline selenium and naturally occurring materials had extended electrical knowledge; but Pohl's work on single crystals and the development of the quantum theory paved the way for the modern understanding; an understanding whose theoretical beginning was Wilson's theory of 1931.

# CHAPTER 1. Introduction and Outline of Research.

## 1. The Present Significance of Semiconductors.

It is not inappropriate to begin this historical study with a brief consideration of the present situation, although, as much work is being actively pursued, it is impossible to include more than a sketchy and more or less outdated picture of modern developments. The study of semiconductors forms part of the much wider field of the solid state where the study of crystalline materials has been enlarged to include investigations into the properties of glassy materials[1] and began to become part of the 'establishment' of science in the 1950's.[2] The interests of commercial concerns showed a similar pattern in the period[3] with the spread of transistor technology and the establishment and enlargement of research and development laboratories.[4] One major source of impetus to the development of effective semiconductor devices was the demands of the military, placing very difficult problems before engineers and scientists, particularly those working in the areas of guided weapons and space technology. The expenditure of government money greatly encouraged the development of solid state devices and led, eventually, to their spread into the civil field.[5] (Investigations at present being undertaken by a group at the University of Aston may throw some light on the determinants of innovation in the semiconductor industry. In particular they are examining the relationship between expectations and achievements in the semiconductor industry since the introduction of the transistor.[6] The particular problems of missile technology, for example shortage of power, lack of space and the need for complex electronics for the purposes of information processing coupled with stringent requirements for robustness, were inadequately met by the miniaturised valves of the early 1950's. These difficulties were dramatically eased by the introduction of the transistor, and particularly by the silicon transistor in the late 1950's. The advantages were so marked that, in the case of one British firm at least, considerable trouble and expense was undertaken to ensure the supply of suitable devices for incorporation into their guided missile.[7]

Under the aegis of government spending[8] the transistor rapidly evolved from its original role as a single component, to be compared with a valve in the same situation, to just one member of a complete 'solid' circuit. New production techniques allowed and encouraged the introduction of integrated circuits with concomitant decreases in size and increases in reliability. In recent years much has been written on the evolution of solid state technology; and the technology changes so rapidly that it is difficult to be completely up to date. Typical of many writings and opinions are the thoughts expressed in a recent article published in Scientific American[9], in which the following passages appear.

> 'It is now about 15 years since the electronics industry learned how to make miniature electronic circuits on a "chip" of silicon substrate by alternating processes of masked etching and diffusion.[10] In the early 1960's the commercially available integrated circuits incorporated at most a score of components such as diodes, transistors and resistors. Production yields (the fraction of circuits that worked) were low, and packaging technology did not allow the realisation of practical devices with more than a dozen leads, or connections. The basic technology, however, was so amenable to improvement and the rivalry among manufacturers was so keen that every year since then the number of components that could be economically placed on a single chip has been doubled. Today chips less than a quarter of an inch on an edge can incorporate well over 20,000 components. As a result the cost per component has in 10 years dropped by a factor of more than 100, from about 20 cents to a small fraction of a cent. The steady increase in component density, combined with a parallel advance in circuit organisation has led to the microcomputer, a full fledged general purpose machine whose logic and memory circuits can be mounted on a single plastic card that could fit comfortably into a cigar box. Where space is at a premium the complete microcircuit can be squeezed onto a substrate two inches square.'

The article ends:-

> 'Any attempt to speculate on the potential applications of a new device as powerful and versatile as the microcomputer is bound to appear

> naive within a very few years. The early user of a new technology is constrained by his past experiences to direct his thinking along familiar channels. Moving beyond its currently obvious applications (such as traffic control systems), the microcomputer will soon be in the hands of a new generation of designers who will be trained to regard it as a simple device, much as today's engineers look at the transistor or even moderately complex integrated circuits.'

These passages are interesting for several reasons. The first extract encapsulates the very recent history of semiconductor devices, highlighting the cost and size advantages of transistors, particularly as diffusion and masked etching techniques became available. The author of the article points out that the basic technology was 'amenable to improvement' but does not indicate the factors that made this possible. A significant feature in this improvement was that economic factors were not the only determinants; the fact that a well understood theory existed enabled the development of semiconductor devices to be undertaken with a greater degree of certainty than appears to have been possible in the case of vacuum tubes. Developments in semiconductors could be guided theoretically, while valve design owed much to 'ad hoc' experimentation.

The second extract suggests that further potentialities exist in the devices he describes but that a 'new generation of designers' will be needed to make the best use of them. This raises the general question, 'Do new devices or ideas need new men to put them into action?' The introduction of transistors seemed to catch the imagination of designers but found them caught in their 'valve training' and this presented them with design problems that in retrospect seem more imagined than real; the insistence that valves were voltage operated while transistors were current operated and the fascination with the power gain given by a common base circuit are perhaps symptomatic of this trouble.[11] In a sense the unfamiliar, or unfashionable, has been a continuous problem in the study and application of semiconductors until recent times, although the problem area shifted from an academic to an industrial environment as the solid state gained respectability in physics departments of universities, commercial prospects in industry and usefulness in defence systems.

Summarising this section it can be rightly claimed that in the last 30 years the subjects of the solid state in general and semiconductors in particular have witnessed a rapid growth of interest. For example in Physics Abstracts[12] of 1944 there first appeared a separate section for semiconductors, and there were just three papers cited under that heading. A measure of the increase of activity is that the proportion of papers cited in the Abstracts under 'semiconductors' has increased with a doubling period of about three years up to 1960. There has since been a change in the classification of papers that makes a continuing comparison difficult. Indeed, there is really little point in attempting to quantify a growth that is readily apparent. It is interesting to note that the increasing interest of scientists in semiconductors as indicated by citations is paralleled by the interest demonstrated by engineers, for an examination of Engineering Abstracts indicates a like pattern.

The growth of interest followed the invention and exploitation of the transistor, this itself being one of the technological outcomes of the Second World War. The tremendous quantity of work since has rested on considerable commercial interest and the possession of an adequate theory; the commercial interest is considered elsewhere[13], this thesis will include a very brief examination of the genesis and development of the theory, which was published in 1931.[14]

## 2. Historical Outline.

Although the vast majority of the work contributing to our understanding of semiconductors is of comparatively recent origin, the history of the discoveries and interest in the materials is of respectable length. The early years saw the discovery of many of the properties of semiconductors, although a clear definition of the materials and their naming was not possible until the theory of Wilson. It would be anachronistic to apply the modern sense of the term 'semiconductor' before about 1931 but since with hindsight we can see that many of these materials were the subjects of experimental and theoretical investigation the term will be applied, where appropriate, for its value as an exact definition. When analysing the work carried out before 1931, and the attempts made to link the results of experiments with the existing theories it is useful to have in mind the modern accounts of the various properties of semiconductors.[15]

The semiconductor story, as normally told, is one of irregular progression, sometimes awaiting experimental clarification, sometimes a theoretical insight; sometimes resting while interest was generated. Many 'pioneers' in the field of solid state physics have committed to paper their versions of the history of semiconductors and it is this history that is commonly known and accepted. While this thesis is primarily concerned with the history of selenium between 1873 and 1919 it is important to appreciate the broader context.

Discussing the chronology of the discoveries in a short historical paper published in 1955 Pearson and Brattain wrote[16]

> 'Thus by 1885 four of the fundamental properties of semiconductors - (1) negative temperature coefficient of resistance, (2) rectification,

> (3) photo-conductivity and (4) photo-electromotive force - had been observed, although not in the same material.'

And in a similar vein Wilson in his Presidential address to the Institute of Physics in 1963 stated that[17]

> 'By the middle of the 1920's the electrical and thermal conductivity of metals were to a certain extent understood on the basis of the Drude-Lorentz theory which dated back to the turn of the century and which was one of the minor (minor because only partially successful) triumphs of the classical kinetic theory. Considerable progress had also been made by Born and others in investigating the cohesive properties of insulators. The advent of the new quantum theory in 1925 led to the recognition that, if free electrons were present in metals their density would be so high that they must be described by Firmi-Dirac statistics....... Progress in the five years 1928-33 was extremely rapid, and by the end of this period it can be said that, with the exception of superconductivity, all the basic principles concerning the solid state had been established.'

Pearson and Brattain suggest that in the early years there existed some commercial possibilities in the properties of semiconductors. They suggest that:-[18]

> 'The demonstration of the existence of radio waves by H. Hertz in 1888 created a demand for a suitable detector, but it was not realised until 1904 that semiconductor rectifiers were well suited for this purpose.'

Yet, as they point out later, the potential was not realised and they suggest a reason.

> 'The next period, beginning in the 1920's, saw the development of barrier layer rectifiers and photo-cells as commercial devices. Some good science and a large amount of art was involved.......... The real understanding had to await the help of quantum mechanics and its application to the understanding of solids.'

Whether there was 'some good science and a large amount of art' is a matter of opinion. For the moment it is sufficient to note that Wilson does not totally share this opinion, for in the address cited earlier he says[19]

> 'The insight into the behaviour of metals and more particularly of semiconductors ought to have stimulated a large increase in experimental work, but it did not, and no new lines of work were opened up except in the study of superconductivity. The reasons for this are complex, but one stultifying influence was the existence of two papers by H.J. Seeman in the Physikalische Zeitschrift in 1928. ......... Seeman had purported to demonstrate that pure silicon was a metallic conductor, and that impure silicon, like impure titanium, owed its semiconducting properties to the existence of oxide films. When pleas were made in Cambridge for work to be carried out on pure germanium it was always pointed out that, since pure silicon, was known to be a metal, what possible interest could there be in germanium?'

Wilson is perhaps being less than fair. For as will be discussed later many formidable problems existed for the early experimentalists, not the least being the lack of interest evinced by the theoreticians. Wilson expresses himself on the subject of the interrelationship between theoreticians and experimenters:-[20]

> 'This unfortunate set of circumstances put back the work on semiconductors by about a decade, and, as you all know, the situation was only radically changed by the interest aroused during the war in semiconductor devices, which eventually culminated in the invention of the transistor in 1948. It is, of course, the industrial importance of solid state devices which has led to the great technological advances which in their train have given such a great impetus to the basic physics of the solid state.'

Wilson's comments and opinions in this paragraph give rise to three questions that are worthy of attention for they impinge upon some of the more obscure features of science. First is it possible to attach any meaning to the claim that the work on semiconductors was put back about a decade? The second world war has been suggested as the cause of many scientific and technological advances, is this also true of semiconductors? Thirdly Wilson argues that industry's interest in devices stimulated both technological and scientific progress leading to the question how important was industry's influence and how was its interest communicated to research workers?

These questions suggested by Wilson's address although important will not form part of this study; the Aston University group is concerned with these externalities.[21] It is the development of the theoretical understanding of semiconductors to which this study will be primarily directed; and then to a small part only. The glosses of the pioneers and the researches carried out for this history indicate that within the story of semiconductors four important factors determining the growth of understanding can be identified. First that the appearance of a satisfactory theory was essential to the prosecution of successful empirical understanding. Second that both theoreticians and experimentalists had to become interested together before real and effective progress could be made. Third that the involvement of eminent scientists was vital to the subject. For, in this history at least, it appears that however important discoveries may be or may prove to be and however well work based on the discoveries is done they stand little chance of being accepted into the 'establishment' of science if first rate scientists give little support. Fourth that a research interest outside the 'mainstream' activity will falter and perhaps disappear unless the previous three factors conspire to reawaken interest and to bring the 'new' subject into the orbit of 'mainstream' interest.

The behaviour of semiconductors was peculiar, the name itself implying some intermediate state between metals and insulators. Beneath an apparently simple behaviour there is a complexity of phenomena that were almost totally puzzling before the early 1930's.[22] Indeed review papers written as late as 1934[23] underline the difficulties being encountered by the physicists who were struggling with problems of understanding and definition. Errors such as Wilson found in Seeman's researches[24] were by no means uncommon. Only when Wilson's theory became known and comprehended could a clear definition of semiconductors be given. Nevertheless much experimental work, particularly during the 1920's, greatly clarified the view and allowed some determining parameters of semiconductors to be defined. For example it was shown, before the theoretical insight given by Wilson, that for reliable and repeatable results a high degree of chemical and physical purity was required. It is claimed by most writers that the advent of quantum theory and statistical mechanics was necessary before the properties of semiconductors could be understood. However from the beginnings in 1873 serious attempts were made to apply the theoretical pictures of electrical conduction to the phenomena in semiconductors. Thus successively we find appeal being made to electrolysis, to variable chemical reaction rates, to electron theory, to the photoelectric effect, and so on. The aim was always to bring the theory of electrical conduction in solids, and particularly in semiconductors, to the same level of understanding as for liquids and gases. Rarely do we find the properties of semiconductors being studied as phenomena in their own right without being conjoined to the properties of other materials be they solid, liquid or gaseous. One exception to this is found in the work of Baedeker[25] [26] who in a series of papers published in the first decade of this century uncovered many of the facts of semiconduction. He suggested mechanisms that might have led to an earlier understanding if more interest had been aroused. However that was not to be, for until the thirties no theory was found that was capable of providing a satisfactory explanation or of providing the means for further progress as the detailed discussions in Chapters 2 to 5 will indicate in the case of selenium.

The interest in semiconductors was limited in extent. For example, J.J. Thomson in his Electricity and Magnetism[27] gives very little attention to the known properties of materials such as selenium and other writers, Lodge for instance[28], also seemed not to be fully aware of these materials. Both Lodge and Thomson were concerned with the 'mainstream' and 'important' topics of electromagnetism and electrolysis. Research into the properties of semiconductors seems to have been carried out, in the main, by men of the second rank. Thus we find work being done by Fournier d'Albe in Birmingham, Frances Wick[30] in the United States and by Pohl in Göttingen. Interestingly enough Pohl's account of his work at Göttingen[31] serves to underline the claim that theoretical physicists took very little interest in the electrical properties of semiconductors, in spite of, or perhaps because, there were some first rate thoeoretical physicists at Göttingen.[32] In Cambridge and Oxford in England few men were concerned with the special problems of solid state physics until the 30's and even less were putting their minds to a consideration of the narrower field of semiconductors. Thus although there was some interaction between theories and results up to 1930, there was little discussion between theoreticians and experimentalists. Conversely after Wilson had published his papers[33] there then existed a sound theoretical foundation for the study of semiconductors but experimentalists in Cambridge could not, according to Wilson[34] be interested in studying the properties of the materials in the detail and with the understanding that was made possible by his insights.

One problem, therefore, was the construction of lines of communication between scientists and the generation of interest; here the role of the scientific 'establishment' is important. This is not easy to define but the acceptance of a field of study as a worthwhile research theme for students and professors rests heavily on the attitudes of those who direct research and obtain funds for equipment and personnel. It will be argued later in this thesis that research into the properties of semiconductors did not conform to the generally accepted 'frontier of knowledge! Thus in the early period, to c 1880, we find that the conduction of electricity through gases and the extension of Maxwell's field theory dominated the work in electricity. From here research led through atomic phenomena to quantum theory, matrix and wave mechanics. With these theories the solid state could be understood, but by then the interest of physicists had shifted to the nucleus and studies in the solid state must have waned. Indeed it has been argued that had it not been for some commercial interest and the problem posed during warfare investigations into the solid state in general and semiconductors in particular would never have captured the minds of first rate scientists.[35]

The study of semiconductors did not, of course, disappear. A series of 'chances' intervened to awaken and increase interest. The appointment of Mott to the Chair of Physics at Bristol University;[36] the Second World War; Bell Telephone Company's desire to develop a solid state analogue of the triode valve; the realisation that a study of the solid state could give information about intermolecular interactions; all contributed to the present large scale academic and commercial exploitation of solid state physics.

## 3. Periods in the History of Semiconductors.

The history of semiconductors can be divided into five periods. The divisions are determined partly by general 'internal' considerations and partly by the history of selenium to which this thesis is, of course, mainly devoted.

a). From 1833 to 1895:- selenium and semiconductors before the electron theory.

b). From 1895 to 1919:- Introduction of the electron theory into theories of conduction in non-metallic solids.

c). From 1919 to 1931:- the work of the Göttingen school under the leadership of Robert Pohl.

d). From 1931 to 1948:- consolidation of the band theory, and technique before the transistor.

e). From 1948 to present:- the modern history.

This thesis concentrates on the history of selenium during the first two periods. For while modern review articles and commonly known histories indicate correctly that the majority of publications concerned with semiconductors have appeared since 1931, they convey a false impression of the quantity of work before then. While Faraday's discovery, in 1833, of the positive temperature coefficient of conductivity of silver sulphide[37] was not followed up immediately, the discovery of the photoconductivity of selenium[38] generated great interest that continued until at least the 1920's. The properties of other non-metallic substances were studied in increasing detail from about 1873, but were investigated largely separated from work on selenium. Thus while the sheer volume of source material available in the period up to 1919 precludes a detailed study of all the work on semiconductors the history of selenium can and has been investigated separately. By 1919 it was realised that the properties of selenium, of silicon, copper iodide and so on possessed enough similarities to define a new class of materials; the class we call semiconductors. Hence 1919 represents a convenient stopping place in the history and this thesis, with its examination of selenium, represents a first step towards a more general history of semiconductors.

## 4. Historiography.

The main body of material leading to the production of this thesis has been drawn from the work published in journals, a full list being given in the bibliography. Crudely two broad classes can be defined. First the 'learned' journals such as those published by National Academies and Societies, for example *Philosophical Transactions* of The Royal Society and *Comptes Rendus* of the Academie des Sciences. Second the 'semi-learned' journals a much more amorphous collection including, for example, *Scientific American*, *Nature*, *The Electrician*[39] and so on.

Without being too categoric the two types have served different ends in the research. 'Learned' journals carry up to date research with little or no editorial comment and reflect the interests in academic circles. 'Semi-learned' while reporting and publishing contemporary research interests have been found useful for two broader reasons. First they give some indication of how widely the discoveries of scientists were disseminated, and accepted, outside academic circles; for many of these journals saw themselves as fulfilling an educative and an informative role. Thus we find that Fournier d'Albe contributed a series of articles in The Electrician entitled Contemporary Electrical Science in an almost unbroken run for nine years. Thus while 'learned' journals are the primary sources for this thesis, 'semi-learned' journals are secondary sources for the historical facts concerning fundamental research but primary sources, in many cases, for the results of the applications of the outcomes of such research.

Contemporary textbooks have proved to be valuable in giving an understanding of electrical theories that were being taught from time to time throughout the period 1870 - 1919. The work on selenium appears to have been carried out by workers who, although often very good experimentalists, were not in the forefront of theoretical physics and did not contribute very much to the theories of conduction. The theories they used were, essentially, those that appeared in textbooks. Conversely textbooks also contain what the writer thought was important; and hence we may assess the value given to discoveries associated with semiconductors.

The early history of semiconductors is marred by the complete absence of notebooks and letters that have any import. These are often a rich source of comment and information both on the 'internal' history of a subject and on the 'external' factors, such as financial and establishment support, that may have affected the development of research. Now, on the whole, the work on selenium was performed by scientists who were not particularly eminent then and who did not become eminent in their later years.[40] Only eminent scientists are honoured by collections of all their works while the unpublished work of lesser men disappears. This, then, is a problem. It would have been desirable if the analysis of the history of selenium could have drawn on the unpublished works of the major workers; but this has proved to be impossible. However an interview with Professor Robert Pohl[41] and another with Sir Alan Wilson[42] provided some valuable information concerning the internal and unpublished influences on semiconductor experiment and theory.

The study of review papers and articles has formed part of the methods of research; as in the case of journals and textbooks the uses to which review articles have been put depend on when they were written and on the audience for whom they were intended. There has been a considerable number of reviews published, particularly in recent years, and a full list is included in the bibliography. Early reviews can be considered as primary sources, later writings as secondary sources, very often including some historical material. Academically they can be divided into three fairly distinct classes. A small, but very important group, explore the limits of known knowledge; indicating what had been achieved; what problems were important and possibly seminal for further progress; these reviews were intended for an active and highly informed readership. (For excellent examples of reviews of this type see those by Gudden[43] and Lark-Horovitz[44]). A second group of review papers are directed at a readership which although fairly well informed in the basic science of the solid state or semiconductors does not necessarily possess the deep understanding or interest of research workers in the field. They often take the form of reminiscences by a pioneer of solid state physics, and sometimes appear when the worker is being honoured in some way or another. (Wilson's presidential address to the Institute of Physics is a fine example of this type of article.[45]) Finally there exist many writings of the 'semi-popular' type, intended for those who wish to be informed of the state of the semiconductor 'art' yet probably would not comprehend the theories. Articles which fall into this category frequently appear in publications like Wireless World and sometimes as general interest papers in more learned journals. (For example the article by Pearson and Brattain formed part of the Proceedings of the Institution of Radio Engineers December 1955.) Various 'anniversaries' of the transistor have been 'celebrated' in the United States by the publication of these 'semi-popular' reviews and potted histories. The authors of these are both famous and unknown, but regardless of authorship they merely mark the passage of time from the invention of the transistor and add little new to historical documentation or interpretation.

Of great use have been those reviews which in attempting to provide an accurate picture have included some historical discussion. As was pointed out above the date of publication is very important while of lesser significance is the author. Substantial reviews of the quality of that written by Lark-Horovitz[47] have been of inestimable value; their extensive references, their historical framework and the knowledge of the writers provided both the starting point and part of the structure of the research reported in this thesis.

## CHAPTER 2. Semiconductors before the Electron Theory.

Viewed with the perspective of hindsight the judgement can be made that the experimental investigations into the electrical properties of solids possessed a 'Baconian' character in that the work progressed by the accumulation of data rather than under the guidance of a suitable theory. It is important to realise that this is a modern gloss, the workers themselves making no such claim; indeed many of them attempted to show that the experimental results accorded with the theoretical pictures of the mechanisms of current flow and of electro-magnetism in favour during this period.[1] However, as we know, 19th century theories are inadequate for the representation of the electrical behaviour of solids. In a sense then, as will be argued later, the application of theories of electricity to the solid state required a stretch of the imagination that gives them an 'ad hoc' appearance.

In most discussions of the history of physics during the past century an obvious and realistic separation between 'classical' and 'modern' is marked by a clutch of discoveries at the end of the 19th century. For example the discovery of X-Rays by Röntgen (1895); radioactivity by A.H. Becquerel (1896); the electron by J.J. Thomson (1897) can all be seen as marking the end of one era and the beginning of another. Indeed, as far as atomic and nuclear physics is concerned, this is so. In the case of the electrical properties of solids, and of semiconductor materials in particular, although there was a slight change in emphasis the main effect of the 'New Physics' was not to be felt until the 1920's. Hence this chapter will consider experimental work up to about 1900. For although with the electron theory, accurate quantative accounts of electrical conduction in metals and semiconductors were still impossible, pictorial representations were now clearer.

## 1. The Work of Faraday.

In 1833 Faraday published the following remarks.[2]

> 'The effect of heat in increasing the conducting power of many substances, especially for electricity of high tension, is well known.
> I have lately met with an extraordinary case of this kind, for electricity of low tension, or that of the voltaic pile, and which is in direct contrast with the influence of heat upon metallic bodies, as observed and described by Sir Humphry Davy.
> The substance presenting this effect is sulphuret of silver.'

As usual Faraday gave a description of the method of preparation of the substance and the experimental arrangement he used to obtain his results. His account of his observations was:-[3]

> 'On applying the lamp under the sulphuret between the poles, [of the voltaic battery], the conducting power rose rapidly with the heat, and at last the galvanometer needle jumped into a fixed position, and the sulphuret was found conducting in the manner of a metal. On removing the lamp and allowing the heat to fall, the effects were reversed. . . [the needle] then gradually left its transverse direction, and at last returned to a position very nearly that which it would take when no current was passing through the galvanometer.'

Faraday noted that occasionally the heat generated by the current itself was sufficient to produce the increase in conduction.[4] Later he made an intriguing remark.[5]

> 'Occasionally, also, the effects would sink of themselves and could not be renewed until a fresh surface of the sulphuret had been applied to the positive pole. <u>This was in consequence of peculiar results of decomposition, to which I shall have occasion to revert in the section on Electro-chemical Decomposition,</u>*....'

At that time (1833) Faraday knew of no other substances that behaved in that fashion[6] but by 1838 he had added one more compound to the class, fluoride of lead.[7] His report of the properties of lead fluoride in respect of its electrical conduction was similar to that referring to silver sulphide; but here he added some remarks on the possibility of electrolytic action.[8]

---

* My emphasis.

> 'During all the time, [that is during the passage of current], there was scarcely a trace of decomposing action on the fluoride, and what did occur, seemed referable to the air and moisture of the atmosphere, and not to electrolytic action.'

Faraday also suggested that periodide of mercury, corrosive sublimate and possibly protoxide of antimony possessed similar properties.[9]

He had no intention then of examining the particular relation of heat and electricity but he wrote[10]

> '...... we may hope hereafter to discover by experiment the law which probably holds all the above effects with those of the evolution and the disappearance of heat by the current, and the striking and beautiful results of thermo-electricity, in one common bond.'

Faraday was, of course, speaking hopefully and prophetically;  the solution was not to come for many years.  Faraday, himself, did not devote much time to these phenomena and after all, his researches into the fundamentals of electrolysis and electromagnetism provided most of the material for the rest of the century.  Faraday's researches impress us for many reasons, one being the highly organised and systematic structure they display. Faraday always seemed to be following lines of investigation stretching across a number of years. His Experimental Researches in Electricity show that whatever Faraday did, what he did not do was to collect facts in a random way. As far as electrical conduction was concerned Faraday's aim was to understand the means whereby electricity moved through electrolytes; he rarely paid any attention to metals, (or isolated elements for that matter). It is interesting, and admittedly a-historical, to speculate on the outcome of his having been interested in the solid state: would he, for example, have disclosed the properties of selenium, the first elemental semiconductor to be studied? Later discoverers and investigators lacked Faraday's supreme experimental skill and interpretive genius for their exploitation.

## 2. Photoconductivity, Rectification, Photovoltaic Effects.

In Lodge's book Electrons,[11] written for an educated general public, the following passage is of interest.[12]

> 'In Maxwell's Electricity[13] published in 1873, section 57, the following sentence occurs in connection with the discharge of electricity through gases, especially rarefied gases:
>
> > "These and many other phenomena of electrical discharge are exceedingly important, and when they are better understood they will probably throw great light on the nature of electricity as well as on the nature of gases and of the medium pervading space."
>
> This prediction has been amply justified by the progress of science, and, no doubt, still further possibilities of advance lie in the

> same direction. The study of conduction through liquids, first, and the study of conduction through gases, next, combined with a study of the processes involved in radiation, have resulted in an immense addition to our knowledge of late years, and have opened a new chapter, indeed a new volume, of physics.'

Lodge's gloss written in 1906 is a fair one. Faraday's investigations and conclusions with regard to the conduction of electricity in liquids spawned a considerable effort: and Maxwell's treatment of the phenomena of electro-magnetism provided the impulse and starting point for some highly original developments in the 19th century.[14] Maxwell's remark concerning the studies of gases was prophetic for this line of investigation provided one route into modern quantum theory; the other stemming from the problems raised by the radiation emitted by a hot solid.[15] Yet Lodge's remarks quoted above underline, by omission, the lack of interest in the problems of conduction in the solid state. Yet by a strange irony in the very year that Maxwell's Treatise was published there appeared in the Journal of the Society of Telegraph Engineers a report of the action of light on selenium.[16] This, together with the discovery of rectification (1874)[17] and the photovoltaic effect (1876)[18] provided a trio of problems that Maxwell's theory was powerless to solve.

## 3. The Discovery of Photoconductivity.

Willoughby Smith's announcement of the discovery of photoconductivity was unremarkable yet not unremarked. The report was contained in a letter read to the Society of Telegraph Engineers on the 4th February 1873[19]. Smith's letter begins:-

> 'My Dear Latimer Clark, - Being desirous of obtaining a more suitable resistance for use at the shore station in connection with my system of testing and signalling during the submersion of long submarine cables, I was induced to experiment with bars of selenium - <u>a known metal of very high resistance.</u>*[20]........ The early experiments did not place selenium in a very favourable light for the purpose required, for although the resistance was all that could be desired ........ seldom did different operators obtain the same result. While investigating the cause of such great differences in the resistances of the bars, it was found that the resistance altered materially according to the intensity of light to which they were subjected.'

Thus was the announcement of a new effect made. While searching for a suitable resistance material Smith had shown that light could directly affect the conducting power of a material, without, apparently, there being any physical or chemical change in the sensitive substance. He finished his letter with a promise in these words:-

> 'I hope before the close of the session that I shall have the opportunity of bringing the subject more fully before the Society in the shape of a paper, when I shall be better able to give them full particulars of the results of the experiments which we have made during the last nine months.'

---

*My emphasis

Apart from a paper published in 1877[21] enlarging upon his discoveries Smith made no substantial contribution to the study of selenium and the effect of light upon it; the story was taken up with enthusiasm by others. It is worth recording the remarks of the chairman of this February meeting.[22]

> 'The Chairman remarked that he thought this was a very interesting scientific discovery, and one on which it was probable they would hear a good deal in future. . . . . Its [selenium's] sensitivity to light was extraordinary, that of a mere lucifer match being sufficient to effect its conducting powers. For the experiments that would be carried on in future, selenium, sulphur, and phosphorus, which belonged to the same group,[23] would be experimented upon, as also, he believed, tellurium. He had heard of one instance in which plumbago had shown similar effects.[24] Selenium, he said, existed in two forms, like sulphur and phosphorus.[25]........ Mr. Smith showed him some experiments, in which he placed pieces of rock salt, alum, and other substances before the selenium, which might have intercepted the rays of heat;[26] but the effect was as powerful through these as through the ordinary air . . . . It seemed to him [the chairman] to afford a most reliable means of measuring the intensity of light, and to constitute a perfect photometer.'

There is evidence in this paragraph of confusion - the word is used from a modern point of view - as to the place of selenium in its group and, more significantly, whether the observed effect was a result of heat or light. The distinction to be made here is between the effect of direct temperature changes and the response to light or heat rays. Without doubt direct heat would modify the conductivity of selenium; the problem seemed to be whether light, heat or actinic radiation produced the observed effects. The existence of the problem implies that the identity of light, heat and actinic rays was not recognised at that time by those taking part in the Society of Telegraph Engineers meeting. This is hard to credit, for eight years earlier Maxwell had written:[27]

> 'The general equations are next applied to the case of a magnetic disturbance propagated through a non-conducting field, and it is shown that the only disturbances which can be so propagated are those which are transverse to the direction of propagation, and that the velocity of propagation is the velocity 'v', found from experiments such as those of Weber, which expresses the number of electrostatic units of electricity which are contained in one electromagnetic unit.
> This velocity is so nearly that of light, that it seems we have strong reason to conclude that light itself (including radiant heat, and other radiations if any) is an electromagnetic disturbance in the form of waves propagated through the electromagnetic field according to the electromagnetic laws.'

To-day this is a non-problem. The formal identity of the various electro-magnetic radiations is fully accepted; so much so that we occasionally qualify the noun 'light' with the adjective 'visible'. Had Maxwell's theory been the only indication of the identity of light and heat it is possible to understand the difficulty; but this was not the case. The relationship between light and radiant heat was considered by Tyndall in a Royal Institution discourse given in 1872.[28] That he should have discussed the subject in such a forum, typically devoted to "frontier" issues, indicates that even he was not fully convinced of the identity of radiant heat and light. He said:-[29]

> 'It is not so very long since the late Principal Forbes was eagerly engaged in establishing the important point that radiant heat, like light, is capable of being polarised. Since that time Knoblauch, Foucalt, Fizeau and Seebeck have applied their refined experimental skill to this question of identity; and those excellent investigators De la Provostaye and Desains, pushed the analogy between light and heat so far as to prove that the magnetisation of a ray of light, in Faraday's sense of the term has its parallel in the magnetisation of a ray of heat.
>
> . . . . .
>
> Recent discoveries will, I trust, enable me to make evident to you tonight, effects which have been hitherto confined to far more limited circles; . . . . . And if those accidents that often hold sway over lecture-experiments of a delicate character should prove favourable, we may be able to push the subject a hair's breadth beyond the limits which observation has hitherto assigned to it.'

Tyndall's discourse continued with a repetition of the experiments that demonstrated the analogies that existed between light and heat; but the published version of his talk contains no conclusion. No doubt the listeners were expected to draw their own. But diffidence can be detected and if Tyndall felt so it is not altogether surprising that other, and perhaps lesser, scientists should be less confident; (the observations could have been interpreted as another piece of evidence <u>in favour</u> of the identity of heat and light for example.)

There was thus promise of a small controversy. It could be no more than that for it died away when the identity of the various forms of electromagnetic radiation was accepted.[30] The work of Sale[31] and the Earl of Rosse[32] (brother of C. Parsons) were directed to defining the type of 'rays' that produced the variation in conductivity; but their different results can be seen as the effect of instrumental errors. Sale's conclusions were.[33]

> '(1) That the resistance of selenium is largely affected by exposure to light.
> (2) That the effect is not produced by the actinic rays, but is at a maximum at, or just outside the red rays, at a place nearly coincident with the locus of the maximum of the heat rays.
> (3) That the effect of varying resistances is certainly not due to any change in temperature in the bar of selenium.
> (4) That the effect produced on exposure to light is sensibly instantaneous, but that, on cutting off the light, the return to the normal resistance is not so rapid.

> It would seem that there exists a power in rays nearly coincident with the heat rays of high intensity, of altering instantaneously and without change of temperature the molecular condition of this particular element.'

Thus were announced to the Royal Society the most important results pertaining to the photoconductivity of selenium; the first example of its kind. The Earl of Rosse attempted to clarify the identity of the active rays; presenting the results of his experiments in March 1874. Quite rightly he pointed out that Sale's work was subject to the objection that no precautions had been taken to calibrate the intensities of the spectral sources he had used. The Earl did not agree with Sale on this one point believing that he had shown selenium to be mainly sensitive to light. He was satisfied 'as to the comparative, if not absolute insensibility of a bar of selenium to radiant heat of low refrangibility.'[34] Neither Sale nor the Earl gave any theoretical explanation of photoconductivity. They do not appear to have re-entered the arena.

## 4. Siemens' Theory.

The direction from which a theoretical understanding of photoconductivity could be expected was indicated by William Siemens in February 1876. His Friday discourse at the Royal Institution was directed towards The Action of Light on Selenium,[35] and contained, besides some romantic imagery concerning the nature of light,[36] a description of a sensitive cell constructed by his brother and an outline of three theories decribing the light/selenium interaction. One due to Werner Siemens was summarised by William Siemens in the following words.[37]

> 'My brother arrives at the conclusion that the influence of light upon selenium may be explained by a change of its molecular condition near the surface from the first or electrolytic into the second or metallic modification,* or in other words by a liberation of specific heat upon the illuminated surface of crystalline selenium,* which liberated heat is reabsorbed when the liberating cause has ceased to act.'

In 'opposition' to this Adams[38] had suggested two alternatives; that the effect of light may be to produce an electromotive force acting in the same direction as that due to the battery, opposite to polarisation; or that the light produced a change on the surface of the selenium 'akin to the change it produces on the surface of a phosphorescent body'[39] this change being supposed to allow the easier passage of an electric current. Siemens could not commit himself to a decision between the competing views, but he had, he thought, adequate evidence in support of his own, or rather his brother's, interpretation.

Siemens' theory, certainly one of the first to be propounded, was to return in modified form, on and off for some fifty years. (A few lines were given to an 'Allotropic Theory' in the 1925 edition of

---

*My emphasis

Photo-Electricity by H.S. Allen[40].) The validity of Siemens' theory rested on three empirical discoveries; that there were at least two types of selenium, (in fact there were three); that at least one type of selenium had a good conductivity; and that a release of 'specific heat' occurred when a type of low conductivity changed into one of high conductivity. The acceptability of the theory depended on the assumption that the effect of light was to release the 'specific heat' thus allowing the allotropic modification to occur.

Siemens knew that selenium heated to its melting point then rapidly cooled presented an amorphous mass to the observer; an allotrope of very low conductivity. A conducting form of selenium could be persuaded to appear, albeit slowly, by annealing at the temperature of boiling water.[41] This modification of selenium, defined as a crystalline form, showed a positive temperature coefficient of conductivity like that, as Siemens pointed out, of electrolytes. Siemens was able to demonstrate, to his own satisfaction at least, that molten selenium subjected to a slow cooling through to room temperature solidified to a form that had a high sensitivity to light and, like metals, a negative correlation between temperature and conductivity. This led Siemens to his 'electrolytic' and 'metallic' selenium. Unfortunately the published account of Siemens' discourse gave very little experimental details; one cannot, therefore, make a realistic assessment of the precision of his procedures. However, the measurements he made of conductivity variations as a function of temperature seem unequivocal and are reproduced in figure 1 below.

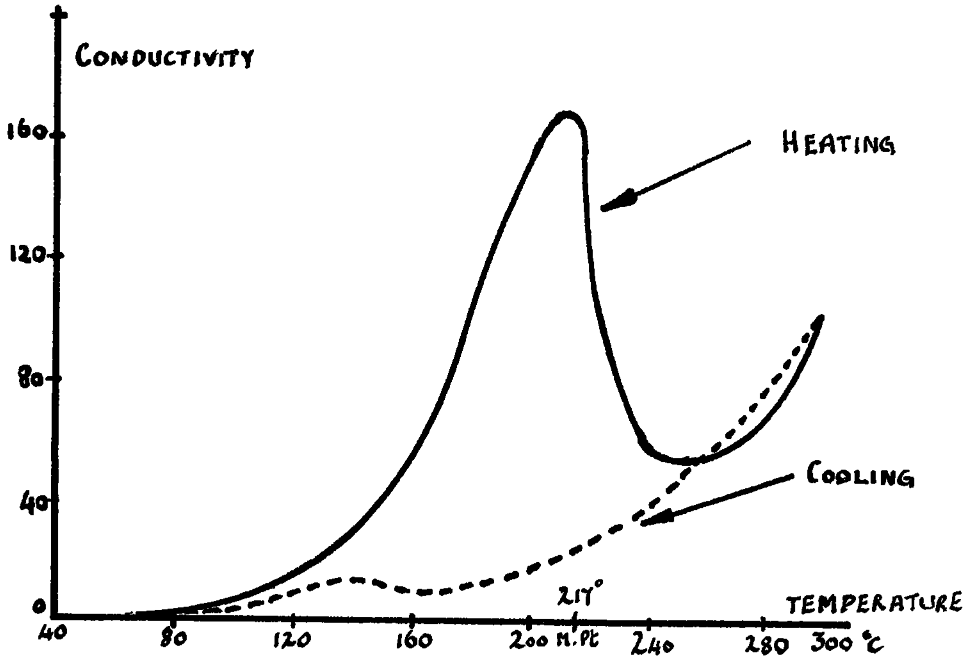


Fig. 1.

Since there is no reason to doubt Siemens' veracity, his claim that a modification of selenium is produced by a slow cooling from the melt and that this is demonstrated by the observed changes in conductivity can be accepted.

Whether the same can be said of his apparent discovery that selenium releases heat energy as it changes from the amorphous variety to the crystalline, or electrolytic, form is more doubtful. Part of Siemens' Fig. 3[42] is reproduced below in figure 2. On this graph rested the interpretation that heat would be evolved on a transformation from one allotrope to another.

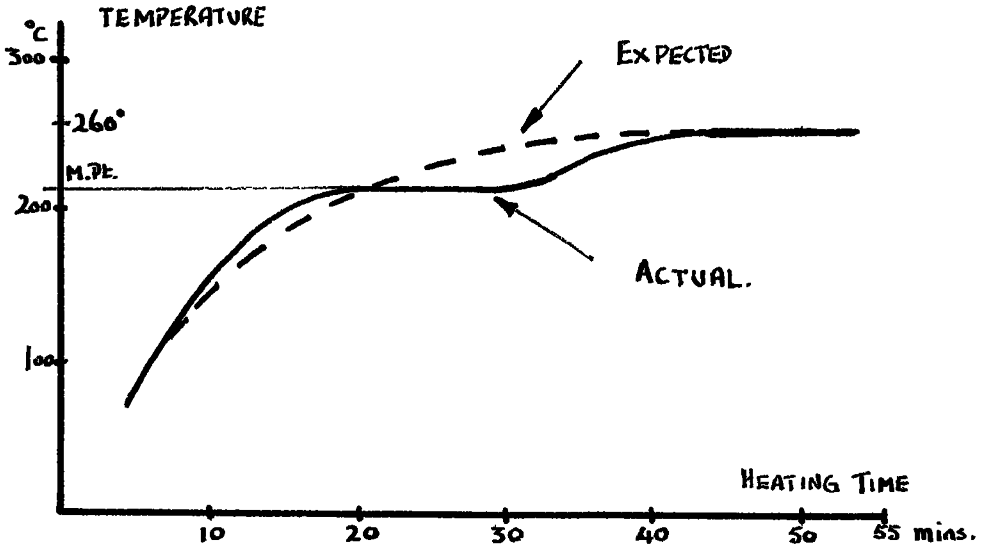


Fig.2.

The effect does not seem particularly marked[43], and, as remarked earlier, too little detail is given of the experiment to allow any assessment to be made of his claim. His results may have been due to instrumental limitations. Nevertheless it would not have been unreasonable to expect such an energy change particularly if the crystalline form was more stable than the amorphous; whether Siemens could really have detected the evolution of the amounts present is impossible to tell. Neither is it made clear that the same energy exchange occurs between the second, metallic, selenium and the electrolytic version. That it should be the case seems to be an important part of his theory. He did, however, note the unstable nature of the second variety, using the following words.[44]

> 'Unfortunately, however, this second modification is not so stable as the first; when lowered in temperature parts of it change back into the first or metalloid modification by taking up specific heat, and in watching this effect a point is discovered at which the ratio of increase of conductivity with fall of temperature changes sign, or where the electrolyte substance begins to predominate over the metallic selenium. If cooled down to - 15$^{o}$C the whole of the metallic selenium is gradually being converted back into the first variety.'

A simple interpretation of the change in conductivity of selenium samples can be based on the relative abundance of electrolytic and metallic modifications. If, and this is an important preposition, the ratio of the two forms is affected by light then one has a ready explanation for the existence of photoconductivity. This Siemens assumed to be the case, but he had no direct evidence that the action of light could catalyse such a direct action in selenium other than the change in resistance. With a strange circularity Siemens supported his own thesis. This is the essence of Siemens first explanation of the effect of light on selenium, (quoted above p 36); it is by no means equivalent to his second mode of expression, (also quoted on p 41). Are we to see specific heat release as the cause of molecular change, the cause of conductivity change or merely a concomitant of an allotropic modification? Siemens is not clear. A causal link between specific heat and conductivity is suggested with a reference to Helmholtz' work.[45]

> 'The physical conditions here arrived at may be said to be an extension of Helmholtz' theory that the conductivity of metals varies inversely as the total heat contained in them.'

There is, therefore, a hint that the specific heat release may itself cause an alteration in conductivity but Siemens did not press this point; rather he preferred to see the release of specific heat as a cause of modification of molecular condition. He pointed out that the gradual reduction in sensitivity of selenium to light as the time of irradiation increased could be due to a 'readjustment of specific heat throughout the mass, notwithstanding a continuance of the disturbing cause.'[46]

His second statement can be rephrased thus.

Light impinging on the selenium surface causes a release of specific heat. Thence a modification of the surface material occurs giving rise to the metallic form. On removing the light the liberated heat is reabsorbed and the substance returns to its initial condition. One great difficulty was present in Siemens' initial proposal, and one that was to remain in all theories of this type. It was soon observed that the action of light was instantaneous in producing an increase in conductivity. Yet removal of the stimulus was not immediately followed by an increase in resistance. Furthermore different specimens, indeed cells made of the same material, reacted very differently in their recovery from illumination. Siemens' solution was to assume that the modification of the condition of the surface was immediately consequent on irradiation but that the reforming of the electrolytic modification took time. There was no justification for this or for the assumption that the release of specific heat was instantaneous and its reabsorbtion slow.

However it is easy to be overcritical. There were many problems associated with the study of selenium, and later other semiconductor materials; not all of which were a function of theorectical shortcomings. The manufacture of suitable devices relied very much on the skill of the experimenter; he who could construct reliable cells could produce reliable results. The performance of selenium is so dependent on various physical factors - its crystalline state, its impurity content, the efficiency of the contact made between the selenium and the connecting leads, the ambient temperature and so on - that these had to be recognised and 'sorted out' before any real understanding could be obtained.

## 5.0. The Researches of Adams and Day.

An early attempt to do this is represented in the work reported in a paper by Adams and Day published in Philosophical Transactions[47] of 1877, read in May the previous year.

These workers recognised that there was not one interesting electrical phenomenon to be studied but four, possibly competing, effects.

a) Photoconductivity.

b) Rectification.

c) Photovoltaic action.

d) The marked effect of temperature change on the resistance of selenium.

While not the first men to report the existence of these facts they appear to have been the first to recognise all of them in the same material.[48]

Adams and Day set out their aims very clearly, and ambitiously.[49] They intended:-

> '(1) to determine whether this change in the resistance of selenium is the direct result of radiations, and if so, whether the dark heat rays, the luminous rays, or the chemically active rays produce the greatest changes.
>
> (2) To compare the changes of resistance in the selenium due to exposure to light from different sources and also to light which has passed through various absorbing media.
>
> (3) To determine whether the action is instantaneous or gradual, and to measure as far as possible the intensity of the action.
>
> (4) To examine into the character of the electrical conductivity of selenium when kept in the dark.
>
> (5) To determine whether light could actually generate an electrical current in the selenium.

Had it been possible to complete this programme successfully then much would have been learned about the different phenomena; but the character of the material was against definite conclusions. The variability found is well illustrated in a table which appeared in an appendix to the published version of the talk.[50]

| Cell No. | Resistance May 76. | Resistance May 77. |
|---|---|---|
| 7 | 1525000 | 3950 |
| 8 | 612500 | 5000 |
| 10 | 7600000 | 745 |
| 11 | 14900 | 19000 |
| 14 | 460000 | 207000 |
| 21 | 120000 | 1123 |
| 22 | 570 | 272 |
| 24 | 55 | 60 |
| 25 | 68 | 28.5 |

The variability of the properties of selenium continued to dog the work. Adams and Day had no method whereby strictly similar specimens of selenium could be prepared; neither could they guarantee that the same specimen would yield similar results throughout its life. For example on resistance they stated that[51]

> 'The resistance of any particular bar of selenium is so constantly altering, owing to the action of any currents that may be sent through it, that measurements of the resistance of the same piece, at the same temperature and with the same battery-power, made on two consecutive days, will hardly ever be found to give exactly the same results.'

Beginning with a continuation of the work of Smith[52] and Sale[53] Adams and Day confirmed that light interacted directly with selenium to produce a lowering of resistance; that this effect was not due to the action of heat or actinic rays neither could an alteration of temperature have confused the results. (They were of the opinion that temperature rises would increase the resistance of selenium.) However the discovery of the property of rectification caused them to turn their attention to this phenomenon. There can be no doubt that they realised the significance of this effect, for they wrote[54]

> 'If the electrical conductivity of selenium followed the ordinary laws of metallic conduction, this difference would not exist; and as it seemed probable that a careful investigation of these phenomena might afford some clue to the causes of the peculiar behaviour of selenium under certain conditions, we have of late been devoting especial attention to this branch of inquiry.'

The discovery of the rectifying action of selenium was a matter of some importance for Adams and Day, for it gave them, and later workers, a possible means to explain the properties of selenium. They carried out a long series of investigations on the flow of current through various specimens of selenium kept in the dark and at constant temperature and concluded:-[55]

> '(1) That, on the whole, there is a general diminution of resistance as the battery-power is increased.
>
> (2) That the first current sent through the selenium causes a more or less permanent 'set' of the molecules, in consequence of which the

> passage of the current, during the remainder of the experiments is more resisted in that direction than it is in the opposite one.
>
> (3) That the passage of the current in any direction, at any period of the series of observations, produces a slight 'set' of the molecules, which tends to facilitate the subsequent passage of a current in the opposite, but obstructs one in the same direction.'

Without doubt Adams and Day laid bare some real effects, although their explanation was premature. The first conclusion can be explained in terms of the properties of an inefficient, rectifying contact; as a surface effect or as a result of high internal field strength.[56]

The discovery that the resistance of selenium depended on the initial direction of the current flow is the first example of 'forming' : a process that was to enter later into the commercial manufacture of selenium rectifiers. It was in use, certainly, as late as 1949; an account of the process being given in Henisch's Metal Rectifiers.[57] Their explanation in terms of a 'set' was, of course, premature, for rectifying action is a property of surfaces, or junctions, rather than volumes. Adams and Day seem to have been unaware of the work of Braun [58] who had demonstrated that the rectification at point contacts on metallic sulphides was a property of the contact rather than the body of the material. It is not at all clear what was meant by 'permanent "set" of the molecules,' the point was not taken up later in the paper; perhaps they were thinking of an analogy with magnetic or electric dipoles.

They were faced, therefore, with a rather puzzling asymmetric phenomenon and with little previous experience to go on turned to electrolytic effects for an explanation. It is interesting to compare this with the work of Braun who was convinced that electrolysis did not occur and pointed out some conjunction between the conduction of electricity at point contact junctions and in electric arcs. (See for example Thomson J.J. and Thomson G.P. Conduction of Electricity through Gases).[59]

Since under certain conditions the process of electrolysis can be considered to be an asymmetric one it was not unreasonable for Adams and Day to turn to this for an explanation. They wrote:-[60]

> 'The experiments. . . . seemed to indicate that the electrical conductivity of selenium is electrolytic. It was therefore important to discover whether, after the passage of an electrical current through a piece of selenium, any distinct characteristic of polarisation could be detected. The existence of polarisation may be considered to be established if, after the current from a voltaic battery has been passed for some time through the selenium, and then the electrodes have been disengaged from the battery and connected with a galvanometer, a current in the opposite direction to that of the battery is found to pass through the galvanometer.'

It is true, of course, that in many cases the action of electrolysis produces polarisation or a 'back e.m.f.' but it is not a necessary conclusion that if polarisation effects can be detected then electrolysis has occurred. As Lark-Horovitz points out[61] the best test of electrolytic conduction is the strict application of Faraday's laws of electrolysis. Nevertheless Adams and Day did not use this criterion, relying solely on the presence of polarisation. They were not out of step in this belief, for in 1885 Lodge in a report for the British Association entitled On Electrolysis[62] gave four defining properties of electrolytic action; visible decomposition; polarisation; non-agreement with Volta's series law; transparency.[63]

They succeeded in measuring some very small polarisation currents and demonstrating that these were not thermoelectric effects,[64] but as normal with selenium, their results were characterised by the usual lack of good repeatability. Adams and Day interpreted their results as polarisation due to electrolytic action;[65] however, this would seem to be a doubtful conclusion, for they did not detect any products of electrolysis; although in fairness it must be pointed out that these might have been too small in magnitude for their analytical techniques. More significantly the relatively high conductivity of selenium compared with that of known electrolytes would seem to preclude the possibility that a similar action was taking place here. For example Lark-Horovitz makes the following points:-[66]

> 'Since the conductivity of silver sulfide and cuprous sulfide is far larger that the maximum conductivity expected for any electrolyte (for instance the conductivity of molten silver chloride is only 5 mho/cm while that of molten copper sulfide at its melting point is 1.3 x $10^3$ mho/cm), it is unlikely that these high conductivity materials are electrolytes.'

Later in the same paragraph he opines that from the calculation of mobilities similar conclusions may be drawn and, following Lark-Horovitz's lead, the conductivity of Willoughby Smith's sample was 2.0 x $10^{-5}$ mho/cm to be compared with $10^{-7}$ mho/cm for silver chloride at a similar temperature.[67] There may have been a small amount of electrolytic conduction, but it was not likely to have been substantial.

Sensibly, Adams and Day had carried out these polarisation experiments while the selenium was kept in the dark. As light affected the resistance of selenium it was conceivable that illumination might affect their results; they therefore determined to try exposing their selenium specimens to light while a polarisation current was being measured. They stated that:-[68]

> '. . . there appeared to be a slight increase in the intensity of the polarisation current during exposure, and a decrease in the intensity on shutting off the light.'

This modification of the magnitude of the polarisation current was a property of all the specimens they examined and they were led to conclude:-[69]

> 'Here, then, seemed to be a case in which light actually produced an electromotive force within the selenium which was, in this case, opposed to and could overbalance the electromotive force due to polarisation.'

If, they wondered, light could affect the polarisation current could it also produce a current in the selenium acting on its own? In answering this question they found, for the first time, the direct production of electricity by the action of light.[70] They wrote:-[71]

> 'The question of course at once presented itself as to whether it would be possible to start a current in the selenium merely by the action of light.
>
> Accordingly, the next morning the same tube, No. 15, was placed on the commutator and its electrodes were connected through the galvanometer. While unexposed there was no action whatever. On exposing the selenium to the light of a candle at a distance of about an inch from it, there was at once a deflection of 150 scale-divisions. On screening off the light the deflection came back at once to zero. Hence it was clear that a current could be started in the selenium by the action of light alone.'

This quiet pronouncement was later (1885) seen by William Siemens as 'a completely new physical phenomenon of great scientific importance; the direct transformation of light energy into electrical energy.'[72]

All the specimens they examined in this manner, with all the selenium surface being exposed to the light, showed some sensitivity; in that their results were consistent. Once again, however, their unreliable specimens gave them, and can give us, no confidence in the quantitative results they obtained. Even if sensitive devices were made from the same bar of selenium this was no guarantee that the same values of current would be recorded under similar lighting conditions. A forming process seemed to be necessary for on illuminating three specimens prepared from the same piece of selenium through which no current had been passed, one gave no deflection at all when illuminated by a burning magnesium ribbon; one a slight deflection of 3 divisions; and one a deflection of 40 divisions. They suggested a reason for this difference:-[73]

> 'Hence it appears that three pieces of the same length, which were made from the same rod of selenium, and which were annealed together, may, owing to some slight difference in their molecular condition, be very different as to their relative sensitiveness to light.'

The meaning of 'slight difference in their molecular condition' is obscure; unfortunately they neither expanded nor explained this statement. Possibly as they were acquainted with the work of Siemens and his method of producing sensitive cells[74] they were referring to the existence of allotropes and postulating that minute differences in the quantity of the various forms of selenium would account for the observed variations in sensitivity to light, although they gave no mechanism whereby this difference would be manifested.

There remained one important investigation to do; to examine the many specimens for any variations in longitudinal sensitivity to light, and to distinguish effects due to radiation from possible thermoelectric currents. Accordingly they arranged their apparatus so that small areas of the selenium plates could be illuminated. They were interested both in the strength of any current and in its direction. The results they obtained were important to them, and are important historically for, as mentioned above, they represent the publication of the discovery of what is now called 'the photovoltaic effect', (called by Adams and Day 'photo-electric' currents),[75] and demonstrated to their satisfaction that thermoelectricity played no part in the production of electricity. On page 53 below, Adams' and Day's discursive account is reproduced in tabular form where the numbers refer to galvanometer deflections.[76 77]

These results together with observations taken while a current was passed through the specimens[78] were interpreted as evidence in favour of the direct production of electric currents by the action of light, the existence of thermoelectricity being discounted.

| Specimen | Marked End | Unmarked End | Centre |
|---|---|---|---|
| W.S.* | 40.<br>Pt.- Se | 0 | 0 |
| 11 | 6<br>Se - Pt | 15<br>Pt - Se | Variable |
| 7 | 7<br>Pt - Se | 4<br>Pt - Se | Not given |
| 25(1)** | 6<br>Se - Pt | 11<br>Se - Pt | Not given |
| 25(2)** | 25<br>Se - Pt | 30<br>Se - Pt | Not given |
| 23 | 9<br>Se - Pt | 16<br>Se - Pt | 22<br>UM - M |
| 24 | 12<br>Se - Pt | 42<br>Se - Pt | 6<br>UM - M |
| 21 | 75<br>Se - Pt | 21<br>Se - Pt | 0 |
| 14 | Record of the results obtained with this specimen are unclear, see ref.(75) | | |
| 15*** | 10<br>Se - Pt | | 50 |

* W.S. = Willoughby Smith's sample.

** Two sets of measurements under different lighting conditions.

*** The direction of the current obtained when the light illuminated the centre portion is not clearly stated; there was, however, quite a definite and distinct difference in the value of the photocurrent. This was a particularly sensitive specimen.

Evidently candle and gas flames would not be expected to produce much heating, but in a later experiment when focused sunlight was employed heating could have been a problem. As in most cases the photocurrent was in the direction Selenium to Platinum and Adams and Day assumed that platinum stood above selenium in the thermoelectric series, then any thermocurrent would be in the opposite direction. At the time of their original publication, (received May 18, 1876), they cited the work of Matthiessen who, in 1858, had published a paper dealing with the thermo-electric series.[79] Matthiessen's researches provided data for some three dozen materials compared with silver and copper, but were generally limited in temperature range, and in the case of selenium seem to have concerned one specimen only. In retrospect this might have been important, for, as we know the properties of selenium depend strongly on the microstructure of a particular sample, as well as on the purity of the material. However Adams and Day were aware that the manufacture of their cells involved modifying the structure of the material and hence, possibly, its thermoelectric behaviour; their own words indicate that they realised this possibility quite clearly.[80]

> 'It has been suggested that, considering the changes produced in selenium by the process of annealing, it would be well to try the thermo-

> electric properties of the several pieces used in the above experiments.'

Unfortunately they were not able to obtain consistent results and could not, therefore, claim to have dispensed with thermoelectricity as a source of the 'photocurrent'. The unreliability of the results and their lack of weight can be put down to two factors, one the variability of selenium itself, (mainly a result of the manufacturing process), and two the doubtful experimental procedure they appear to have employed. Using focused sunlight as a source they showed that the passage of a current was eased when the specimen was illuminated; this cannot be interpreted as the result of a photovoltage being developed. Without the passage of a current the expected photocurrent was obtained. For producing the thermal effects they employed the heat of the hand or of a minute air-blast obtaining, by this means, variable results. About one half of their specimens were above platinum, the remainder below platinum with no significant correlation between thermoelectric measurements and the earlier determinations of the photocurrent direction. All that can be derived from this section of their paper is that selenium lived up to its variability and that Adams and Day thought that the diverse results had something to do with the structure of the selenium forming their specimens.[81]

> 'It seems to be pretty well established by these experiments that the more complete the process of annealing, the higher selenium is raised in the thermoelectric scale;.........'

It is not possible, then, to agree that Adams and Day had established, without doubt, by these experiments that the photocurrent was due solely to the action of light; but an earlier inference is more convincing.[82]

> 'A thermoelectric current does not usually attain its maximum strength immediately, nor does it cease altogether immediately after the withdrawal of the source of heat.
> In these experiments we have invariably found that, on interposing a screen in the path of the beam of light, the current immediately ceased, and on withdrawing the screen, the current was at once renewed in its original strength. The phenomena noticed are exactly similar to those observed when a tangent galvanometer and a galvanic cell are joined up by a key in simple circuit. On closing the circuit, the needle swings at once up to, and then oscillates about its ultimate position of rest, and stays there while the current is passing. On breaking the circuit, the needle at once returns, oscillates on either side of, and then stops at zero.
> During these experiments we were frequently struck by the analogy of the two cases, and impressed with the idea that cutting off the light was, in point of fact, removing the electromotor of the current.'

This was a forceful phrase and a forceful conclusion. We have already remarked on Siemens' response to the discovery which added another link to the chain which, by then, had led to the formulation of the law of conservation of energy.

What is it about Adam's and Day's work that it warrants the detailed attention that it has been given? They proposed no major theoretical insights and their results, often variable, can be summarised briefly in the following terms.

1) Selenium has a large positive temperature coefficient of resistance.
2) That increasing the current through selenium decreased its resistance, possibly as a result of polarisation similar to electrolytic polarisation and the strength of the current depended on the direction of flow.
3) The action of light was to reduce the resistance of the selenium.
4) Change in electrical resistance was proportional to the square root of the illuminating power.
5) The strength of the polarisation current was increased by exposure to light.
6) A current was produced in annealed selenium by the action of light which generated an electromotive force among the molecules.
7) Different parts of the selenium produced different electric results.
8) That action of light alone resulted in a current termed, by them, the <u>photoelectric</u>* current.

An analysis of these results is rendered

---

* Not to be confused with the photoelectric effect found by Hertz.

difficult, for not only is a complete theory of the materials they used not fully developed,[83] but also precise information on their experiments and the purity of the selenium they used is lacking. Neither Adams and Day, nor for that matter, any later worker until recently,[84] considered it necessary to utilise extremely pure material in their researches. It would be sheer guesswork if an estimate of impurity levels were given, for no information has come to hand that is of any direct help. Only if their samples were of a purity orders of magnitude better that used by Bidwell, (see below), would they have avoided the masking of the real properties of pure selenium by the effects of impurities. Our modern theory informs us that to examine the properties of semiconductors, material of a purity greater than can be provided by chemical methods must be used; or at least the purity levels must be known to better than one part in a few million. We know from Bidwell's work, discussed later, that all his selenium contained amounts of silver and lead, for he cited these as necessary for the formation of selenides; and thus one must expect that Adams' Day's samples were similarly contaminated.

It would be pleasant if the analyses of their selenium were known, but that is not the case. We can suggest, however, that many of their results may be accounted for by the presence of impurities in their samples. Examining their results, one by one, we can put forward possible explanations for them.

The temperature coefficient of resistance of semiconductors, is, of course, negative for intrinsic material; although this can be complicated by the interaction of scattering phenomena with the thermal production of current carriers.[85] A simple explanation would be that their selenium was acting as an extrinsic semiconductor, which would display a positive temperature coefficient of resistance. We noted earlier that there were reported cases of the resistance of selenium decreasing with increased temperature, and will later take up this question when the work of Bidwell is considered.

The relationship between increasing current and decreasing resistance would be easy to explain if Adams and Day had noted a negative temperature coefficient of resistance; we could simply postulate the direct effect of Joule heating. Their explanation in terms of polarisation cannot be accepted for reasons suggested above (p 49 ) and also in light of the fact that polarisation might be expected to decrease the current, (i.e. increase the resistance); but if we take this observation together with their clear demonstration of rectifying action then we can suggest that they were, perhaps, observing the effect of sequential breakdown within the selenium. It is more likely that the phenomenon was purely a surface effect, a point made by Smith.[86] Nevertheless it is impossible to ignore their detection of, what for want of a better term, can be referred to as 'polarisation'. Their results seem to indicate, quite clearly, that after the passage of a current in one direction through their samples, they could afterwards obtain a current in the opposite direction, which while was small, substantial enough for measurement. We cannot reject polarisation effects out of hand but we can claim that if polarisation existed their demonstrations did not show, unequivocally, its presence.

The existence of photoconductivity is simply understandable in terms of the generation of current carriers within the selenium; that the change of resistance should be proportional to the square root of the intensity of illumination is more difficult to explain. All that can be said is that with low levels of illumination the resistance should change in proportion to the illumination, but as a simple analysis ignores the complex effects of recombination and traps and lifetimes on the generated carriers our explanation of this interesting result can only be incomplete.

The discovery that selenium illuminated by light could generate an electric current was the first reporting of the photovoltaic effect. This, now known to be due to the production of electrons and holes near the region of a junction, was another link in the chain of the conservation of energy, showing that the direct conversion of light to electricity was possible. Only Siemens[87] appears to have been struck by this; but the general acceptance of the law made such discoveries likely rather than surprising. Although there are hints in Adams' and Day's publication that the currents were, more often than not, produced in the region of the electrodes of their samples it cannot be claimed that they had demonstrated the importance of junctions. This reading of their discovery is slightly at variance with the manner in which this result is reported by Lark-Horovitz.[88]

> 'The first photoelement of this layer type was the selenium cell produced by Adams and Day in 1876. In this all electronic cell a photovoltaic e.m.f. was observed;......'

The difference, although one of emphasis, is important. Lark-Horovitz' choice of words imply a more or less determined attempt, on the part of Adams, to produce a barrier layer photovoltaic cell, whereas, in fact, their discovery was 'accidental'.

They expressed no awareness that the effect was developed in the barrier layer either between the electrodes and the selenium or at the surface of the material and only with hindsight can we accredit them with this discovery. For them the effect remained to be explained; they did not even put forward a tentative account in terms of the electrolytic mechanism they supposed was operating.

Nevertheless in spite of the irregular nature of their results, and the inherent weakness of their suggested explanation, their work is important. Its importance stems not only from early publication and the existence of a clear priority of discovery but also because the work they did was referred to by many of those who followed their lead. Their results were not substantially altered and the electrolytic hypothesis they hinted at formed the basis for some experimental and theoretical work for a number of years.

For example in an article published in Wireless World (1915) concerned with the properties of selenium the work of Adams and Day was referred to in the following words[89].

> 'The most generally accepted theory is that put forward by Profs. Adams and Day, in 1877, the results of their exhaustive investigations leading them to suppose that the "electrical conductivity of selenium is electrolytic."'

Yet the electrolytic idea was not the only one proposed by Adams and Day for in a slightly earlier, and much shorter publication they wrote.[90]

> 'Light, as we know, in the case of some bodies tends to promote crystallisation, and when it falls upon a stick of selenium tends to promote crystallisation in the exterior layer, and therefore to produce a flow of energy from within outwards, which under certain circumstances appears in the case of selenium to produce an

> electric current. The crystallisation produced in selenium by light may also account for the diminution in the resistance of the selenium when a current from a battery is passing through it, for in changing to the crystalline state, selenium becomes a better conductor.'

However the mechanism of current flow remained electrolytic.

Hence by 1877 two theories were available to account for the electrical properties of selenium, at least in part; the proposals of Siemens (above p 41) used the known existence of several allotropic forms and their (supposed) interconversion, while those of Adams and Day appealed to electrolysis. The work of Bidwell, to be described shortly, utilised the latter theory, while the discovery of the electron and its use to give a qualitative account of the conduction of electricity through solids was later to be employed via modifications of Siemens' ideas.

## 6. The Seat of Rectification in Selenium and the Reality of Photoconductivity.

A year after the publication of Adams' and Day's extensive researches (1877) Robert Sabine[91] produced a paper[92] detailing the results of experiments which 'were undertaken with the view of removing, if possible, some of the difficulties which I had found in the way of constructing constant resistances of crystalline selenium.'[93] Although he did not achieve his main aim, it being 'evident that selenium is, from its peculiar nature, a very unsuitable material'[94] he put forward the important conclusions that the rectifying action of selenium was an effect of the electrode - selenium junction and that the photoconductive property of selenium was a result of actual resistance changes rather than due to the production of an electromotive force. He agreed with Adams and Day that the properties of selenium could, in the main, be explained as surface effects,[95] but did not specifically conclude that the conductivity of selenium was electrolytic. His explanations of the light sensitive properties of selenium were, he admitted, tentative and were expressed in extremely vague terms.[96] He was content merely to hint at possible mechanisms, recognising, perhaps, that the state of theoretical and empirical knowledge was not sufficiently advanced for definite conclusions to be advanced. Nevertheless the methods he used to substantiate his two major conclusions are interesting enough to warrant a short examination.

He pointed out, quite rightly, that it was not known whether the resistance of a selenium cell resided in the junctions with the electrodes or in the mass of the material. He probably knew that for some substances, carbon for example,[97] the resistance to the flow of electrical currents was a function of the mechanical perfection of the contact between metal and carbon, and hence that some junction effect might operate in selenium resistances. Thus by employing a multi-element[98] connection he was able to measure the resistances of the junctions and of the body of the selenium. He showed that:-[99]

> '. . . . . a large portion of the observed resistance of a so-called selenium resistance may, and frequently does, reside in the junctions and not in the selenium.'

His results indicate that as much as a third of the resistance of a bar of selenium might be due to the junction regions.[100] His interest then shifted to determining the seat (his word) of the change of resistance when the direction of current flow was reversed. Adams and Day had first reported this phenomenon but did not investigate the relative contributions of junctions and mass of material. Sabine's method was to maintain a constant current through the selenium on reversal of direction hoping, thereby, to distinguish between resistance changes and polarisation effects. This was an important distinction to attempt. Unfortunately it failed for:-[101]

> '. . . . . the majority of specimens of crystalline selenium did not alter sufficiently to afford definite evidence; and those recently prepared specimens which showed a considerable change generally gave unsteady readings.'

He claimed more success in determining the seat of rectification, clearly being of the opinion that it occurred at the junction. His measurements were direct determinations of the resistances of the junctions and the selenium. Effectively he compared the resistance of his cells and junctions with two fixed values of the current flowing in each direction. His argument was that a difference between the values of the resistances measured under opposite conditions would identify the seat of the effect. The discrepancies he found[102], though not large, were sufficiently marked for him to claim for the junctions[103] 'that in them, and not in the selenium, lies the change in question', (that is the dependence of the resistance of a selenium cell on the direction of current flow.)

Sabine confirmed Adams' and Day's discovery[104] of the photo-voltaic effect and showed that the thermoelectric voltages were the same in type and direction as those produced by light;[105] in addition he devised an argument that differentiated between the two possibilities, as he saw it, that the lowering of resistance was either a direct effect or was due to the production of an electromotive force in the same direction as the battery current. His argument is sufficiently interesting to quote in full:-[106]

> 'Let the resistance between the wires of the selenium plate and of the galvanometer be r, the electromotive force of the measuring battery be E, and the observed current c. On admitting light the current increases to c', and one of two things must have happened. Either (1) the increment of current be due to a decrement (x) of resistance, in which case

$c = \frac{E}{r}$ has changed to $c' = \frac{E}{r - x}$

$$x = E\,\frac{c' - c}{cc'} \quad ,\ldots\ldots\ldots\ldots(I)$$

or (2) the increment of current is due to a photo-electromotive force (y) in the selenium, in which case

$c = \frac{E}{r}$ has changed to $c' = \frac{E + y}{r}$

$$y = E\,\frac{c' - c}{c} \quad ,\ldots\ldots\ldots\ldots(II)$$

With a single measurement it is, of course, impossible to discriminate between the two cases: but by a known augmentation of battery and of resistance, it is easy to find which supposition affords the better argument.

I increased E to 2E and inserted a known resistance ($r_1$) as nearly equal to r as I could make it. The resulting current, when the selenium was in the dark, was $c_1$; and it increased to $c_2$ when subjected to the same source of light as before. Then either

$c_1 = \frac{2E}{r + r_1}$ changes to $c_2 = \frac{2E}{r + r_1 - x}$

$$x = 2E\,\frac{c_2 - c_1}{c_2\,c_1}, \quad \ldots\ldots\ldots(III)$$

or

$c_1$ changes to $c_2 = \frac{2E + y}{r + r_1}$

$$y = 2E\,\frac{c_2 - c_1}{c_1}; \quad \ldots\ldots\ldots(IV)$$

It is plain that, if the values of (x) calculated by (I) and (III) agree better than those of y calculated by (II) and (IV), the change must be due to resistance.'

Sabine's experimental test of this theory[107] showed fairly conclusively that a real resistance change occurred[108] when selenium was exposed to the effects of light; thereby demonstrating that the photo-voltaic and photo-conductive effects were distinct. Sabine's hints that photo-voltaic effects and rectification were properties of the junction region reinforced the opinion already proposed by Braun[109] and noted by Schuster[110] but were not to be investigated with much thoroughness until the opening years of this century for two reasons. First the photoconductive process was more interesting for practical purposes, and secondly the main theory used to account for the properties of selenium, electrolysis, although concerned with the interactions between electrolytes and electrodes, was not exclusively limited to the junction regions.

## 7. The Researches of Shelford Bidwell.

The main researcher into the properties of selenium was Shelford Bidwell[111] who in a series of papers published between 1881 and 1895 examined most of the discoveries made by Adams and others. Bidwell was primarily interested in the light sensitive properties and paid little attention to the rectification that occurred in selenium. He became convinced early in his work that the conductivity was not merely analogous to the process of electrolysis but that this was, indeed the mechanism of charge flow.

He commenced his researches when the process of electrolysis was not at all well understood, but by the time of his final paper, to which reference will be made later, the work of Arrhenius added to that of earlier researches had fixed fairly conclusively the processes of electrolysis; from then the possibility of marked electrolysis occurring in solids became extremely remote. However for nearly fifteen years Bidwell pursued the idea with considerable single-mindedness, eventually, however, being faced with the conclusion that the effects he had found may have been due to the presence of moisture in his samples. Although he added little to the knowledge of the properties of selenium or other semiconductors, his experiments were ingeniously constructed, and were interpreted by him directly as tests of the existence of electrolysis. Indeed he produced some remarkable results which only became clear if the presence of moisture is assumed; for otherwise they suggest a considerable contribution by electrolysis to the electrical conductivity of selenium.

In the 'Whiggish' sense the work of Bidwell can be dismissed; for the theoretical constructs he produced were based on insecure foundations and they appear to have led nowhere. However the work demonstrates with great clarity, how the adoption of a particular picture of conduction preformed both the direction and the interpretation of research.

Within his work there was one long-lasting 'correct' result; his clarification of the temperature dependence of the resistance of selenium.

In an early publication[112] (1881) he had this to say on the resistance of selenium.[113]

> 'In this matter, too, there is a remarkable discrepancy between the authorities. Professor Adams[114] says that an increase of temperature increases the resistance of selenium. . . . . Dr. Guthrie, Messrs. Draper and Moss[115], and others make the directly opposite assertions that the resistance of selenium diminishes with heat.'

Bidwell disposed of this discrepancy fairly promptly although not without some, apparently random variations, for in the same publication he states:-[116]

> '....., it seemed as if the selenium was possessed by a demon which produced the variations in accordance with the caprices of its own unaccountable will. At length, when the confusion was at its height and the demon most bewildering, the true explanation was suddenly revealed, and so exceedingly simple is it that now the only marvel is that it should so long have eluded discovery. The secret of the matter is this: and it discloses one of the most remarkable properties of this most remarkable substance. There is a certain degree of temperature at which a piece of crystalline selenium has a maximum resistance. If a piece of selenium at this temperature is exposed to either heat or cold, . . . . . , its resistance will be at once diminished; and extremes of either produce a far greater variation than is ever effected by the action of light.'

Bidwell had demonstrated what is now a well known property of semiconductors that the temperature coefficient of resistance alters in sign from positive to negative as the temperature is raised. His first experiments were followed two years later by more careful determinations and in an 1883 paper[117] he determined the temperature at which the maximum resistance occurred; for eight cells this point lay between 13°C and 30°C. By 1895 he had found that the variation of resistance with temperature was sensitive to the method of attaching electrodes. He reported that:-[118]

> 'On further investigating the subject I have traced this curious fact to the action of the fused-in electrodes. So far as I know . . . a piece of crystalline Se into which wires have been fused <u>always</u> acquires a maximum resistance at a certain temperature. On the other hand, the resistance of a piece having external electrodes pressed into contact with it is <u>always</u> diminished by a rise of temperature.'

Bidwell concluded that the normal effect was the reduction of resistance with rising temperature; the initial rise being caused by the differential expansion between the metal electrodes and the selenium.

Bidwell's work on selenium was concerned with the production of repeatable results and with the light sensitive properties, particularly photoconductivity. In his search for consistency he investigated the effects of impurities and methods of manufacture. His study of the photoconductive phenomena, and other electrical properties, was governed by his early belief that the electrical properties of selenium could be accounted for by electrolysis. During his fifteen years of research his work followed a clearly discernible pattern. Beginning by repeating the work of Adams and Day he adopted the electrolytic hypothesis which he attempted to demonstrate by a series of experiments, that were not restricted to selenium but encompassed experiments on sulphur and carbon and various sulphides. Finally he showed that many of the results he had discovered could be the secondary effects of adsorbed moisture.[119]

Bidwell was impressed, as were many others, by selenium's reaction to illumination. He often referred to the 'remarkable property' or the 'curious property' of selenium to lower its resistance when irradiated by visible light. Bidwell was a cautious reader of the literature appertaining to his research and in the following paragraphs his published papers will be used not only to provide information of his own findings but to introduce some experimental results that were produced by other workers.

In an early publication[120](1885) he opened the discussion on the possible electrolytic character of current flow in selenium with a reference to Adams and Day[121] writing that 'As the results of numerous experiments, these gentlemen were led to form the opinion that "the electrical conductivity of selenium is electrolytic",[122] Bidwell pointed out, quite correctly, that Adams and Day had not considered that the actual behaviour of the selenium was due to electrolysis, but 'rather that the molecular structure or crystalline condition of the substance was altered or modified by the action of a current of electricity in such a manner as to produce effects analogous to those which would have occurred if the selenium were an electrolyte and actually decomposed by the current.'[123] Bidwell had in mind, of course, an electrolytic mechanism. His belief was supported, he thought, by a form of selenium cell described in 1883 by C.E. Fritts of New York.[124] [125] The essential features of Fritts' cell were that the sensitive substance occupied the centre of a sandwich whose extremities were formed of a transparent electrode, a thin film of gold leaf for example, and a thick base electrode with which the selenium would combine. Fritts' reasons for this method of construction were dictated by his interpretation of the experimental situation. He began one publication with the paragraph:-[126]

> 'In all previous cells, so far as I am aware, the two portions or parts of the selenium, at which the current enters and leaves it, have been in substantially the same electrical state or condition. Furthermore, the paths of the current and of the light have been transverse to each other, so that the two forces partially neutralise each other in their action upon the selenium. Lastly, the current flows through not only the surface layer which is acted upon by the light, but also through the

> portion which is underneath and not affected thereby, and which therefore detracts from the actual effect of the light upon the selenium at the surface.'

This concept of a 'conflict' between two opposite 'forces' is obscure in meaning and carries overtones of Naturphilosophie and was not further explained. Even if based on false reasoning, his method of production resulted in devices that were relatively reliable and certainly extremely sensitive to the action of light. With them he confirmed most of Adams' and Day's results and included two extra findings.[127] The cells he made were extremely sensitive; he reported resistance changes by factors of up to 337.5 between darkness and sunlight; and he noted rectification with forward/reverse resistance ratios up to 1/22; and the photo-voltages he detected were sufficient to affect a telephone directly.[128] Without doubt the superior properties of his cells were due to their method of construction.[129] Yet what impressed Bidwell was not this but the inferential support given to his concept of electrolysis. Fritts gave no description of the causes of the phenomena he investigated,[130] but Bidwell wrote:-[131]

> 'It is impossible to read Mr. Fritts' paper without being impressed by the resemblance of some of the phenomena which he describes to those of electrolysis. The mere arrangement of the apparatus - two metallic plates with a third substance between them - is in

> itself strongly suggestive; while the unequal resistance offered by the two surfaces, and the generation of an independent electromotive force, in conjunction with the polarisation-effects above referred to, make it hard to believe that the conduction of selenium (in the form used in experiments) is <u>not truly and literally electrolytic.</u>'*

Be that as it may there was one profound problem opposing this suggestion; 'the only considerable difficulty in the way of this hypothesis arises from the fact that selenium is not an electrolyte.'[132] Bidwell knew that selenium was considered to be an element and it seemed unlikely that this position would be changed; but he saw in Fritts' paper a way out of this impasse; for[133]

> 'He spreads the selenium upon a plate of metal <u>with which it will form a chemical combination.</u> Now selenium will, I believe, combine more or less easily with all metals, forming selenides; and in experiments upon the conductivity of selenium, it has been usual to submit the substance to prolonged heating in contact with metallic electrodes.'

Thus Bidwell's structural picture began to emerge, and on this he built up a theory of electrolytic action in selenium. The electrolysis was not to be found in the selenium itself, for it is an element, but in the impurities present, particularly selenides; the conductivity was not a function of the selenides alone but how they were incorporated in

---

*My emphasis

the selenium. He supposed that there was a formal analogy between the putative selenides in selenium and the actual behaviour of a mixture of carbon and sulphur. Sulphur itself was a non-conductor but a mixture of carbon and sulphur allowed a current of electricity to pass. Bidwell had carried out some investigations on this mixture [134] and quoted the results in favour of his picture of conduction in selenium. He pointed out that while a mixture of sulphur and carbon conducted electricity, a similar result did not occur if the sulphur was replaced by shellac. The difference was accounted for by a structural argument.[135]

> 'The explanation which I have given of these facts, and in support of which a number of experiments are quoted is as follows:-
> The first mixture does not consist of a uniform structureless mass of sulphur,. . . : it is in fact an aggregation of little crystals of sulphur with carbon packed between them like mortar between bricks. The conduction.. [occurs].. through the carbon particles, which .. [extend] . . . in a series of chains from end to end of the mass. In the case of the shellac mixture, . . . . ... the resistance is . . . . infinite, because the structureless shellac penetrates between and completely surrounds the carbon particles.'

Hence Bidwell could give a qualitative account of the conduction by crystalline selenium while the vitreous variety remained an insulator. In the former the structure of the material allowed the 'chains' of selenides to form, while in the latter it did not. That commercial selenium contained many metallic impurities was well known[136] and these could have formed conducting selenides.[137] Throughout all of Bidwell's work it remained an open question as to whether selenides were, in fact, formed; but he thought in 1885[138] that he had circumstantial evidence that the conductivity of selenium that had been in contact with copper possessed a much lower resistivity than 'pure' selenium; the two differing in resistivity by three orders of magnitude. He did not know whether perfectly pure selenium would possess an infinite resistivity, he only required that this should be very high compared with the values for impure specimens.

If it were granted, then, that the selenium in use contained selenides which were conductors, and that these compounds were embedded in a matrix of crystalline selenium then several empirical facts could be accounted for.[139]

1. The reduction of resistance by annealing; a chemical and a structural effect.
2. The resistance of the cells depending on the material of the electrodes; a matter of chemical affinity.
3. The dependence of resistance on battery power; the 'disruptive' nature of the current flow.[140]
4. The apparent 'set' of the molecules as described by Adams and Day; a deposition of selenium upon the anode.

5. Electrolysis; resulting in polarisation effects.

6. The variation of the resistance of selenium with temperature; the result of two competing processes. First the mechanical contact between the selenides would, due to differential expansion, become less sure as the temperature rose resulting in an increase of resistance; second the specific resistance of the selenides was supposed to possess a negative temperature coefficient of resistance; taking the two together would produce the observed variation of resistance with temperature.

7. The diminishing of the resistance of Adams' and Day's cells with time; attributed to the slow formation of selenide by combination with the free selenium assumed to have been produced by electrolysis.

It was later to emerge that he envisaged the effect of light on selenium as a photo-chemical action; the quantity of selenides in the selenium would be increased by light, thus allowing an increased electrolytic current to be maintained. But in 1885 he had no certain evidence that selenides existed in selenium; this was a question that was 'only to be settled by the aid of refined chemical operations which I am incompetent to undertake.'[141] However the ready account of the effects that could be given by his speculative picture was obviously appealing; it was based on accepted modes of current transport, and known chemical facts. We have already suggested (p 76 above) that the evidence he held was circumstantial and indirect but Bidwell added more observations, which by analogy, were to be read as confirmation of his theory.

The chemical and physical similarity between selenium and sulphur had led to attempts to produce a sulphur cell which would also be sensitive to light, although, as Bidwell reported,[142] such attempts had failed. Driven by his picture of the electrical conductivity of selenium he was led to suggest that 'if this property of selenium were really due to the accidental existence of metallic selenides, then the admixture with sulphur of metallic sulphides might be expected to lead to similar effects'.[143] This line of analogical reasoning makes considerable sense. For it is not at all unreasonable to compare the properties of similar elements and chemical compounds. It was not possible to prepare a sulphur cell in the manner of selenium cells[144] for sulphur did not perform identically with selenium 'but if it is true that the virtue of annealing[145] really lies in the fact that a chemical union of the two elements is promoted by the action of heat, it is clearly immaterial whether the substances are heated together before or after the formation of the cell.'[146] Thus if sulphur mixed with metallic sulphides was used in place of annealed selenium to fabricate a cell, he expected that this would prove to be sensitive to light, and in general to display properties similar to selenium cells. Satisfactorily 'this turned out to be actually the case.'[147]

Since the behaviour of his sulphur cell was interpreted by Bidwell as indirect evidence in favour of his theory of conduction in selenium - and hence his theory of the light sensitiveness - the whole of the description of the manufacture of his 'Cell No. 1' is quoted below.[148] The method he used was as for selenium cells, but a significant departure must be noted. He found it necessary, after the first formation, to add further silver, which was probably converted to sulphide, to reduce the resistance of the device to measurable values; but in doing so he destroyed the analogy he was attempting to demonstrate.[149]

> 'Five parts of sublimed sulphur and one part of precipitated silver were heated together in a porcelain crucible for about two hours. The mixture was from time to time stirred with a glass rod and was finally allowed to settle, so that the bulk of the sulphide and any free silver which might remain fell to the bottom of the crucible. When the temperature was slightly above the melting point the liquid sulphur, which was perfectly mobile, though black with minute suspended particles of sulphide was poured off for use. Two wires of fine silver were then coiled side by side around a strip of mica 50 mm long and 27 mm wide; the wires were about 1 mm apart, and

> care was taken that they did not touch each other at any point. Some of the melted sulphur was spread evenly over one surface of the mica, the two wires being thus connected with each other through half their entire length by a thin layer of the prepared sulphur. When cold, this cell was connected in circuit with a battery and a galvanometer. It was found to conduct electricity, but its resistance was very high, being probably between 20 and 30 megohms. With the object of partially bridging over the intervals between the wires, the sulphur was melted by laying the cell upon a hot plate, and a piece of very thin silver-foil, measuring 25 mm by 10 mm, was laid upon its surface: this was probably entirely converted into sulphide before the cell was again cold.'

It seems almost certain that Bidwell had prepared what was, essentially, a cell of silver sulphide, now a well known semi-conductor, and that the effects he discovered with this were no more than an exhibition of the properties of this type of material.[150] Had he worked with pure silver sulphide, rather than mixing it with sulphur, his theory on the structural importance of crystalline selenium in determining the performance of selenium cells would have been difficult to maintain. Preoccupied, as he seemed to be, with an electrolytic mechanism, he never seems to have wondered whether pure sulphides or pure selenides would have exhibited the same properties as selenium.

Summarising his theory we note that the essential parts were that a mixture of a relatively poor conductor (selenium or sulphur) and an assumed electrolytic conductor, (selenides or sulphides), could account for the observed facts; the mixture was essential to his description. Consider his explanation of the photoconductive effect in his silver-sulphur cell for example.

The conduction of electricity through such a cell was presumed to be electrolytic, hence in common with all electrolytic processes, a separation of material would occur; in this case silver being deposited on the cathode and sulphur on the anode. The deposition of silver on the cathode would not affect the resistance of the cells, but if the sulphur did not combine with the material of the anode the action of the cell would gradually stop. With a silver anode the current would continue due to the formation of more silver sulphide.[151] The current carrying capability rested, then, on the possibility of combination between sulphur and the material of the anode. Bidwell changed one electrode from silver to iron and showed that the resistance of the cell was now distinctly asymmetric;[152] the ratio of the 'forward to reverse' resistance being about 30.[153] This asymmetry led him to conclude that the effect was not due to bad contact between the iron and the sulphur, but 'rather it seems that the resistance of the two anodes afford data for measuring the relative facilities with which sulphur combines with iron and silver.'[154]

His explanation of the photoconductive process was completed when he demonstrated that the reaction between silver and sulphur was enhanced by the action of light; thereby easing the movement of electricity by electrolysis and reducing the resistance.[155] Hence he was able to account for the behaviour of a sulphur-silver sulphide cell by means of a theory, which he had suggested for the description of the properties of selenium cells. Thus he could conclude his article with the words:-[156]

> 'So far as regards the explanation of the effect of light upon the resistance of selenium, I am aware that this paper contains little more than speculative suggestions, which are at present almost entirely unsupported by experimental evidence. It is, however noteworthy that these speculations led to the construction of a cell which, without containing a particle of selenium, behaved almost exactly, as if it were composed of that substance. How far this may be considered to prove anything with regard to selenium I do not know; but in any case the discovery of another substance possessing the same remarkable property seems in itself to be a matter of some interest.'

Bidwell's theory was not without opposition; but when he was acquainted with this he was able to dispose of contrary opinions fairly easily.[157] The most common alternative picture was one that ascribed the phenomena to be found in selenium, and other substances producing similar effects, to the direct or indirect action of heat. The direct action was envisaged as some form of thermoelectric phenomenon and was to be used in the opening years of the 20th century to give an account of rectification. The indirect action was interpreted, at least for some of the properties of selenium cells, in terms of differential expansion between the various component parts of the cell. We have already noted (p 78 ) that Bidwell in 1895 had used this argument to account for the increase of resistance of selenium with temperature. In 1885, however, his thoughts were turned towards the action of light on chemical change, i.e. the formation of silver sulphide from silver and sulphur, rather than towards mechanical explanations.

In a paper read to the Royal Society in June 1881 Dr. James Moser[158] had attempted to account for the 'microphonic' property of selenium cells in terms of varying perfection of contact between selenium, its selenides, and the electrodes of his cells. As Bidwell was to use the concept of electrolysis to form his theories, so Moser wished to use a single idea as the basis of his explanation.[159] He, like others, had noted that the incidence of intermittent light on a few samples produced a singing tone; and by analogy with carbon microphones[160] suggested that the action was due to the closer or more distant contact between selenium and electrodes and that the action of light lay in this effect. Bidwell considered that all the effects he investigated could be subsumed under the same explanation and supposed that light produced a direct action on selenides and sulphides; indeed he satisfactorily explained photo-conductivity, rectification and polarisation in his account, and in the same year (1885) he detailed some experiments that would allow a description to be given of the photo-voltaic effect.[161]

Although Bidwell never expressed his work in terms of the correlation of light and electricity, Siemens appreciated this possibility (p 61 above) as did Moser for he began his paper with the sentence[162]:-

> 'When I began these researches on the Transformation of Light into that of Sound by the Photophone, I held the opinion which is still common, that there are two kinds of photophone and three forms of light rays.'[163]

In fact he began his work believing 'that the photophone could inform us as to the direct correlation between light and electricity.'[164] However he became convinced by his work that the experimental results could be explained by the well known and accepted correlations; i.e., between light and heat and between light and chemical action. He experienced considerable difficulty in producing selenium cells, particularly when copper was used as an electrode. He took great care to ensure a good copper-selenium contact but found 'it was not possible to fix the selenium on the copper plate,'[165] eventually being forced to conclude 'that between the copper and the selenium, or rather the cuprous selenide, there is only a slight and imperfect contact.'[166]

Armed with this experimental fact, the use of a mechanical picture to account for the observed behaviour of selenium cells becomes obvious: a result of the heating of the selenium by the action of light, allowing for a better electrical contact and hence a lowering of resistance.

Moser appealed to the allotropic forms of selenium to account for the 'photo-effect' of Adams and Day; he simply assumed that the effect of light was to initiate a transformation from one allotropic form to another with a consequent release or absorption of energy which, under suitable circumstances could generate an electric current. Moser wrote:-[167]

> 'When, now, we no longer consider the selenium cells especially, but selenium in general, we find that light can produce in it, if the selenium is an element and pure,[168] no other chemical changes than those which induce the transformation of one of the allotropic modifications into another one.[169] But such a transformation is connected with development of energy; . . . With a proper arrangement (that is in a closed circuit) we shall get, instead of the development of heat, an electric current - just as, for instance two solutions of the same salt, but of different concentration, on being mixed together, give a development of heat, but, when brought into a circuit in a proper manner, produce electricity equivalent to this heat.'

Finally Moser concluded that, [170]

> '. . . . . there are two different effects which light may have on selenium and on selenium cells. The one is more of a chemical, the other more of a physical character. The one is a changing of modification,* and is not essential to the efficiency of the selenium photophone. In this latter we have to deal essentially with a heating effect, changing volume and contact - in brief with a microphonic action. . . . . . ; and I no longer believe that there is any prospect of finding an unknown power or a new relation of forces in this substance.'

This work of Moser's, which predated the first extensive paper of Bidwell's[171] by some four years, reintroduced the thought that the 'peculiar' properties of selenium might be ascribed to the action of heat. Adams and Day[172] had considered this possibility but had been led to reject the idea. The possibility that thermal effects were responsible for rectification was the subject of some discussion into the 20th century. The work of Flowers (1909-14)[173] effectively refuted this idea. Bidwell[174] examined Moser's explanation of photoconductivity and showed that it foundered on two important points. Heating did not, in general lower the resistance of selenium, at least initially; and more importantly the effects of heat are never instantaneous, neither in growth nor decay. On the subject of polarisation Adams and Day had written:-[175]

> 'That this is not due to a current arising from thermoelectric action in consequence of the

---

* i.e. transformation from one allotrope to another

could be no doubt, as Adams and Day[182] and Sabine[183] had shown, that,[184]

> 'In its peculiar sensitiveness to the visible part of the spectrum selenium seems, so far as our present knowledge goes, to stand almost, if not quite, alone,'

Thus Bidwell was free to establish firmly the links in his argument that the properties of selenium could be understood on the basis of electrolysis. The paper in which his views were first formulated[185] was read to the Physical Society on May 23 and June 13, 1885 and was followed on June 27, 1885, by a second paper 'On the Generation of Electric Currents by Sulphur Cells' published in Philosophical Magazine.[186] The experiments discussed by him were detailed and led to the conclusion that under suitable circumstances an electric battery[187] could be constructed completely from solid material; Bidwell announced his discovery to a wider public in Nature, August, 1885.[188] He considered that the cell, having silver and copper electrodes and an 'electrolyte' consisting of a mixture of copper and copper sulphide in the ratio of 1 to 5, was 'exactly analogous in its action to a Daniell cell.'[189] Although the effect of illumination was, generally, to decrease the electromotive force of the cell, the evidence was, on the whole, a support for his theory of the electrolytic conduction in sulphur-sulphide cells and in selenium.[190]

Bidwell stands alone, in this period, in attempting to produce a coherent description of the behaviour of selenium; his was a very plausible explanation using, as it did a well established mode of electrical conduction as its base; and was very hard to refute without careful measurements of the assumed 'electrolytic' parameters of sulphides and selenides. Bidwell's final paper on 'The Electrical Properties of Selenium' appeared in Philosophical Magazine of September 1895[191] and was largely a reiteration and reinforcement of his earlier work. As he had promised in 1885[192] he reported some researches into two problem areas - the presumed electrolytic conductivity of selenides and the effect of light on the formation of metallic selenides. It was vital to his case that positive answers should be given to these questions.

Bidwell's belief in the electrolytic action in selenium rested on Adams' and Day's notice of the polarisation currents that could be detected in their cells.[193] It has already been pointed out (p 48 above) that polarisation is not, in itself, conclusive proof of the existence of electrolysis and, as Bidwell was able to demonstrate, the polarisation currents were almost certainly due to the presence of moisture. His report of the experiments were unequivocal.[194]

> 'The electrodes of a Se cell were connected first with the poles of a battery, and then . . . . with a galvanometer: . . . . indicating an e.m.f. of rather more than 1/100 volt. The cell was then placed in a glass receiver over

> strong sulphuric acid, . . . . (The experiments were repeated)* After 18 hours the deflexion was only 3 divisions. The air was then exhausted . . . . 24 hours later no polarisation current whatever could be detected, even after prolonged connexion with the battery.[195]
>
> The cell was afterwards suspended for an hour in a receiver over a basin of water and then tested for polarisation. The spot of light was immediately deflected far beyond the limits of the scale.
>
> Probably therefore the polarisation results merely from the electrolysis of water; in any case the presence of water seems to be requisite for its production.'

These results did not mean, of course, that electrolysis did not occur; the conductivity of selenides might yet have been due to this cause. Bidwell tried to determine the character of electrical conduction in selenides, but while he was able to produce some apparent effect with moist selenides he was totally unable to discover any electrolysis in the absence of water. He wrote:-[196]

> 'Many abortive attempts were made to ascertain whether cuprous selenide conducts electricity entirely like a metal, as is generally believed, or like an electrolyte,[197] as required by my hypothesis. The experiments.. . . show that if the conduction is not altogether electrolytic, it is under certain conditions, at least partly so . . . . the results . . . . cannot be regarded as conclusive.'

Thus the search for electrolytic action was rendered inconclusive;[198] similarly attempts to

---

* My parenthesis

demonstrate that the formation of metallic selenides was enhanced by illumination proved disappointing. Bidwell had to rest content with experiments giving inferences only, not direct evidence.[199]

One can only sympathise with Bidwell, for after fifteen years he still persisted with a description that rested on ghostly, or rather vaporous, foundations, - the electrolytic conductivity of metallic selenides and the increased production of these compounds under the influence of light. In 1895 he knew little more than Adams and Day in 1877; he had added some knowledge of the manufacture of relatively reliable devices and had shown the influence of moisture on the action of selenium cells; he had shown that the temperature dependence of resistance was not the single function that Adams and Day had thought, being complicated, for example by the material of the electrodes. Yet the summary of the results discussed in his 1895 paper[200] show that he still held to an electrolytic theory. He did not alter his earlier conclusions in the light of his discovery of the roles of moisture; using this only when describing effects previously unconsidered by him.[201]

Bidwell's results did not go completely unnoticed, but did not, in general attract much attention. The summary of his results indicate that if they were not exactly contradictory, they were, at least very inconclusive. Thus on the subject of the electrolytic conductivity of selenium he wrote:-[202]

> 'The conductivity of crystalline Se appears to depend principally upon the impurities which it contains in the form of metallic selenides. It is suggested that the selenides conduct electrolytically......'

But later we read.

> 'Crystalline selenium is porous and absorbs moisture from the air.
>
> The polarisation of Se after being traversed by a current is due to absorbed moisture.
>
> The photo-electric currents sometimes set up when light falls upon Se are dependent upon the presence of moisture.'

In spite, therefore, of providing fairly clear empirical evidence that the overt 'electrolytic' effects, polarisation for example, were dependent on the presence of moisture, Bidwell was not prepared to concede that his theoretical description of the light sensitiveness of selenium was inadequately based. It is an interesting anomaly that he allowed the possibility that the 'photo-electric' currents may be due to the presence of moisture. Yet his experiments leading to this conclusion were, perhaps, even less convincing than those which he thought supported his claim that selenides were electrolytic conductors and that a metal - selenium reaction was enhanced by the direct action of light. Our verdict on Bidwell's theory must be 'Not proven' and, of course, it never was; neither, in a sense, was it disproved, merely displaced by 'better' theories. Indeed, even when the theory of the solid state became established in device descriptions, older electrolytic ideas still retained some use. For example in Henisch's Rectifying Semi-Conductor Contacts (1957)[203] a short discussion of the role of electrolysis in rectifiers is given. Henisch wrote:-[204]

> '. . . . ionised centres within the barrier region are in a strong electric field which tends to move them towards the metal electrode. . . . . Electrolytic processes of this kind must be responsible - at any rate in large part - for the reversible changes which are associated with current creep phenomena and for the much less reversible processes which we call forming.'

And on the subject of polarisation effects in selenium rectifiers[205]

> 'The study of creep and forming processes has revealed new aspects of rectifier behaviour which, among all the phenomena discussed, are least satisfactorily understood. . . . . . .
>
> The results show some measure of agreement with the dry electrolytic model of the forming process . . .
>
> Any polarisation effect due to the movement of charged impurity centres would be expected to result in a back e.m.f. which should show itself immediately after removal of the external forming voltage . . . . this current cannot be distinguished from the thermo-electric current which is expected to arise from self-heating

> during forming. . .The polarisation effect . . . is believed to be associated with the formation of cadmium selenide* at the counter electrode interface.'

These remarks are not included to justify Bidwell's findings and theories for this they do not do. Rather they illustrate the fact that selenium is a complex material and the devices made from it were not at all easy to understand theoretically. Indeed, in retrospect, that Bidwell should have been able to achieve what he did, and that Fritts could produce a reasonably reliable rectifier is a matter for admiration. Finally to conclude this discussion of Bidwell's work we quote the words of J. Reyval who in 1896 wrote:-[206]

> 'La curieuse propriété que l'une des variétés du sélénium d'augmenter de résistance sous l'influence de la lumière a provoque de nombreuses recherchés sur les propriétés électriques de ce corps. Parmi ces recherchés, celles M. Shelford Bidwell, qui depuis 1881 étudie ce sujet, sont des plus importantes.'

We agree with this contemporary assessment of Bidwell's work; it is also possible to accept Reyval's judgement of the status and achievements of Bidwell's researches and conclusions.[207]

> 'On voit que les expériences de M. Bidwell, bien qu'elles ne démontrent pas complètement la justesse de l'explication proposée par l'auteur,** apportent un grand nombre de preuves en faveur de cette hypothèse. Elles marquent une étape dans l'histoire des nombreuses recherchés faites sur les propriétés électriques du sélénium et pour cette raison méritaient d'être exposées avec quelques détails.'

And for these reasons a detailed discussion of Bidwell's work has been included in this thesis.

*My emphasis. ** i.e. Bidwell.

## CHAPTER 3. Some Technological and Theoretical Considerations to the end of the 19th Century.

The discovery of the light sensitivity of selenium occurred when Smith was utilising the high electrical resistance of the material in a measuring system and from that date practical devices were suggested or constructed using the 'new' property laid bare by Smith. The bars of selenium used by him were not designed to demonstrate the results of illuminating selenium but the workers who became interested in that property attempted to produce reliable and sensitive devices that would suit their purposes; in the process they added knowledge to the technology of selenium. Some inventors, Alexander Graham Bell in particular, patented devices in which selenium photocells were important components. The property of rectification does not appear to have been incorporated, intentionally, in useful applications during this period. As the properties of selenium were found to be very dependent on methods of preparation of the selenium and of manufacture, a brief consideration of the technology of selenium cells is included in this chapter.

The theoretical accounts of electrical phenomena form a background to the experimental work on selenium. Yet, as we will see, the power of the existing theories was limited, with only Maxwell's electrodynamics being more or less fully formed. In other areas, electrolysis, contact forces, thermoelectricity and voltaic forces, agreement between various authorities was by no means present in the closing years of the 19th century. The major part of this chapter will be devoted to a study of the electrical theories current between c1875 and 1895; and an attempt will be made to assess the applicability of them to the phenomena found in semiconductors in general and, in particular to those in selenium.

## 1. Technology.

It was realised very early that selenium in its grey allotropic form was the conductor of electricity; but that the specific resistance of even this modification was, in general, very large.[1] When it was desired to construct light sensitive cells of high sensitivity, large area, thin devices were required. Thus methods of manufacture had to be adopted that would provide the cells with a lowish resistance in order that galvanometers could be affected; with good contact between electrodes and selenium - note that with this point Moser[2] had dissented; with large areas exposed to the effects of light and, finally, using selenium of the correct allotropic form.

Evidently, the requirements to obtain cells of low resistance yet thin and having a large surface area could be contradictory; and hence cell designs were dictated by these considerations. Producing the correct allotrope of selenium was merely a matter of determining the best annealing process to apply;

heating vitreous selenium at any temperature between about 100°C and the melting point of crystalline selenium, 217°C, followed by a slow cooling would permit the growth of the crystalline modification. It transpired, as was noted by Werner Siemens,[3] that both the resistivity and the light sensitivity of crystalline selenium were dependent on the temperature and duration of the annealing process. Werner Siemens' note in _Philosophical Magazine_ and the report of his findings to the Royal Institution by his brother William[4] indicate that he considered he had produced a third form of crystalline selenium by the methods he employed; it is unlikely that this was the case. Moss in _Photoconductivity in the Elements_[5] points out that, although there is a third crystalline form of selenium, its electrical properties are more akin to those of an insulator.[6]

The Siemens brothers did not, unfortunately, provide many details of their production procedures; the annealing was carried out at 210°C 'for several hours'[7] and then the selenium allowed to cool slowly. Adams and Day adopted similar temperatures, but did not see fit to include details of their methods. They describe their technique of annealing cells in the following terms:-[8]

> 'The pieces . . . . were either annealed in a sand bath or in a hot-air bath. The former has been found to give the best results . . . . A large

> iron ball is heated to a bright red-heat in the fire and then placed in a large iron bowl filled with sand, which is heaped up all over the ball, and then left for an hour. The ball is then taken out and the pieces of selenium, wrapped up in paper, are put into the hot sand, and left there for twenty-four hours. On removing the selenium from the sand, its appearance is a sure indication whether or not the annealing has been successful; for, in the former case, the bright and glossy appearance of the amorphous selenium will have changed to a dull slate-coloured one, and when this is the case the conductivity of the specimen will, in general, be found to be very good.'

This, evidently rather idiosyncratic process, begged several questions of quality control; temperature, purity and so on, and it is not therefore surprising that Adams and Day found it difficult to produce totally reliable results. Henisch made the point very clear, in 1957,[9] writing that 'in view of the complicated relation between rate of growth, nucleation rate, and temperature, the properties of micro-crystalline specimens depend sensitively on their thermal history.'

In the absence of accurate methods of temperature control visual judgement of the state of crystallisation was probably a not totally unreliable technique. Bidwell, while exercising greater care over the temperature and duration of annealing, continued to rely on the appearance of the selenium for the determination of the optimum effect. He used essentially the same method of production[10] throughout his period of experimentation; giving detailed instructions in his 1895 paper.[11] The substrate used by Bidwell in his work was invariably mica; the operation of producing sufficiently sensitive selenium being in two parts. At a temperature just above the melting point of selenium, 217°C according to him, the selenium could be easily applied to the mica;[12] the application was immediately followed by rapid cooling producing a layer of effectively infinite resistance and having a 'black and lustrous' appearance; patient and careful annealing then produced cells of the right characteristics. Bidwell's description of his method was perfectly clear.[13]

> 'The Bunsen flame having been turned down sufficiently to lower the temperature to about 120°, the cell is replaced upon the hot plate. In a few minutes parts of its bright surface become dimmed, and shortly afterwards the whole turns a dull grey colour. The temperature is then cautiously raised until signs of melting just begins to appear, generally near one of the edges. When this occurs the burner is instantly withdrawn and the flame slightly lowered. The darkened spot recrystallizes in the course of a few seconds, and the burner is then replaced and left for four or five hours, during which time the temperature of the Se should be only a few degrees below the melting point. Another hour is occupied in slowly cooling the cell, the flame being lowered and finally extinguished. This process of long heating and slow cooling is generally spoken of as "annealing".'

The material of the electrodes and their form varied from worker to worker as dictated by practical requirements. One common constraint was the desire to produce cells of low electrical resistance and large surface area; and in Bidwell's case to use electrode materials that would combine with selenium producing selenides. Most cells were variants of a basic form:- wire electrodes wound in flat double spirals or helices; Siemens made use of the former, Bidwell the latter, there being no particular advantage in either save that Bidwell's cells may have been easier to construct.[14] Siemens' cells had an effective electrode separation of 0.25 cms and a sensitive surface area of approximately 1.0 $cm^2$ with a thickness of selenium of perhaps .2 mm. The corresponding dimensions of Bidwell's cells were, 0.06 cm, .1 $cm^2$ and .2 mm. The methods of construction used by Bidwell, and Siemens allowed the resistance of selenium cells to be reduced from several megohms to few tens of thousands of ohms, making the measurement of resistance much more straightforward. It was essential to prepare specimens correctly in order to produce any results at all as evidenced by a letter to Nature by Draper (March, 6, 1873).[15] The careful empirical approach of men like Siemens and Bidwell played an important, although hardly dramatic, part in the growth of interest and understanding of selenium cells.

A striking contrast to the types of cell outlined above is afforded by those made by Fritts in

1883[16] to which we have already alluded. Unfortunately we can add very little to that which has already been written for Fritts gave very few details of the methods of construction and production. In contrast to the devices used by Siemens and Bidwell, Fritts' cells were very much more sensitive to the action of light; their performance being a result of their large surface area, (35 $cm^2$), and the very thin selenium layers employed, (.003 to .015 cm); where Bidwell and Siemens were finding resistance changes on illumination by sunlight of no more than fifteen[17] times, Fritts' cells decreased their resistance by between factors of 80 to 340.

It would be very agreeable to know the purity of the selenium used by the various workers, but, however, beyond making reference to the presence of metallic impurities in his samples Bidwell did not submit them to extensive chemical analysis, except in one case; but did remark that 'selenium as supplied commercially is never free from impurities, and indeed I have lately been informed by a distinguished chemist, who has given some attention to the subject, that perfectly pure selenium has not yet been obtained.'[18] Sadly he gave no values for the levels of impurity that might be expected, neither did he quote his source of information. Bidwell, of course, required that metallic impurities be present in his selenium in order that the conducting selenide be formed; and in support of his theory he did on one or two occasions add known amounts of selenide to his cells. This process which he entitled 'Sensitizing Insensitive Selenium' was reported in his 1895 paper.[19]

The Siemens brothers did not seem to be concerned with the purity of the selenium they used being content to accept the commercial material. Fritts, by contrast, attempted to purify the selenium he used discovering that the product would separate 'into a number of portions, having very perceptible differences of behaviour, both in melting and annealing.'[20] He pointed out that this behaviour was linked with material that was supposed to be the same chemical substance and absolutely pure. He concluded that 'commercial selenium is a mixture, consisting of several distinct portions, which must either be different allotropic forms of the element or new elements, similar in appearance, chemical reactions and physical properties, yet distinctly different in many respects.' Again, sadly, his work did not include an account of the chemical constituents of the selenium he used.

The possibility that the light sensitive properties of selenium could be utilised in practical engineering devices was too obvious to be missed and many suggestions were put forward. Thus on the occasion of the announcement of the photoconductivity of selenium (1873) Latimer Clark remarked that this property of selenium 'seemed to him to afford a most reliable means of measuring the intensity of light, and to constitute a perfect photometer'.[21] Werner Siemens in his communication to the Royal Society (1875) concluded that he hoped 'to be able to utilise them [the properties] for the construction of a reliable photometer'.[22] The very sensitive dependence of selenium's resistance on temperature allowed Adams and Day to suggest that 'a very delicate differential thermometer may be formed with two pieces of selenium balanced against one another' (1877).[23] Bidwell, in his lecture to the Royal Institution (1881)[24] gave details of a mechanism he had developed for the transmission of pictures by telephone or telegraph wires. His suggestion was to scan the picture to be transmitted by a small rotating aperture; allow the light to affect the resistance of a selenium cell which formed on half of a bridge circuit the other part of which consisted of a detector where silver iodide was electrolytically decomposed by the currents of varying strength. The picture would thus be reconstituted in continuously changing densities of silver. Bidwell's scanning principle was later introduced by Nipkow[25] in his early attempts at developing television.

Few, if any, of these early suggestions came to rapid fruition, the problems not being those of conception but of operation and production. Thus Adams' and Day's suggestion could not be realised when the thermal properties of selenium proved to be rather more complex than thought at first. Werner Siemens overcame, to a certain extent, the variable qualities of selenium photoconductive cells in the design of a photometer using comparison techniques; but the scheme he produced had no advantages over existing instruments.[26] Bidwell's 'picture transmitter', although perfectly feasible in principle and on a small scale, relied heavily on the possibility of maintaining mechanical sychronisation between sending and receiving stations; this problem was not solved by Bidwell who, nevertheless, maintained interest in the subject eventually suggesting the use of 90,000 selenium cells in a transmitting device.[27] Alexander Graham Bell's photophone, first suggested in England in 1878 at a meeting at the Royal Institution,[28] and the subject of patents in 1880,[29] was technologically feasible but, relying, as it did, on the passage of light through the atmosphere could not hope to rival the transmission of telephonic signals along wires. It is not my intention to discuss the details of Bell's invention for that would take us too far from the general course of this thesis; but the method he chose to announce his work and the reception this received is of some interest for priority claims were involved; a short discussion being engendered in the pages of Nature during 1880-81.

A note in Nature of April, 15, 1880, intimated that Bell produced a new invention 'worthy to stand beside the telephone or the phonograph in point of interest'.[30] This 'rumour' of which Nature had 'authoritative information' had behind it the fact that Bell had deposited a sealed package at the Smithsonian Institution containing a description of a 'new and very remarkable instrument first conceived by him during his sojourn in England in 1878.' A week later, April, 22, 1880, Ayrton and Perry, perhaps sensing a priority dispute and, possibly, patent rights had a letter published entitled 'Seeing by Electricity'.[31] They began their letter by pointing out that they were in complete ignorance of Bell's invention but that 'complete means for seeing by telegraphy have been known for some time by scientific men'. They gave short details of an extremely elaborate scheme that, by utilising the photoconductive property of selenium, could, in theory at least, allow pictures to be transmitted along wires. They admitted that the 'elaborate nature' of the scheme and its 'expensive character' did not allow its use in the form they suggested; 'but if the new American invention. . . . should turn out to be some plan of this kind, then this letter may do good in preventing monopoly in an invention which really is the joint property of Willoughby Smith, Sabine and other scientific men, rather than of a particular man who has had sufficient money and leisure to carry out the idea'. They had, in fact, guessed wrongly; Bell was interested in eliminating wires from his telephone system rather than using them to carry visual information. Further, his device did not rely exclusively on the use of light sensitive selenium cells.[32] However Ayrton and Perry considered that even if Bell's plan was much simpler than theirs, (and it was!), 'it is well to show that the discovery of the light effect on selenium carries with it the principle of a plan for seeing by electricity'. However, as Bell probably appreciated, the movement from principle to practice is hard and complex, involving rather more than mere knowledge; he was attempting to achieve something vastly more straightforward than 'seeing at a distance.'

A few months later, Nature, September 23, 1880, S.P. Thompson and Bell himself in the same issue gave more and detailed information on 'The Photophone'. Thompson repeated the content of the initial note and referring, possibly, to Ayrton and Perry remarked: 'In spite of those who ingenuously attempted at the time of our announcement to forestall Prof. Bell and to discredit the idea that he had done anything new, the discovery. . . . is a startling novelty'.[33] In Thompson's opinion the photophone bore 'the same relation to the telephone as the heliograph bears to the telegraph'.[34] Although the distances over which signals had been transmitted were rather short Thompson did not see that this would be a permanent disadvantage; signals could follow where a beam of light could go, and he expected that 'the slow spelling out of words in the flashing signals of the heliograph to be superseded by the more expeditious whispers of the Photophone.'[35] Bell was to be congratulated 'on this addition to his well-won laurels' and, maybe, his photophone would have 'a great, if not widely extended, future of usefulness.'[36]

Bell's report, initially delivered as a lecture to the American Association, outlined the history of selenium, and the developments that Bell and his assistant Tainter[37] pursued to produce the photophone as a practical proposition. His short paper only hints, of course, at the difficulties he must have met and overcome; but it leaves us in no doubt that he was the first to produce a practical device to eliminate wires from telephony. Whether or not his final comment was directed at Ayrton and Perry cannot be known; but talking of the telephone and its development as a practical proposition he concluded his lecture by saying:-[38]

> 'It is not only pleasant to remember these things, and to speak of them, but it is a duty to repeat them, as they give a practical refutation to the often repeated stories of the blindness of scientific men to unaccredited novelties, and of their jealousy of unknown inventors who dare to enter the charmed circle of science. I trust that the scientific favour which was so readily accorded to the telephone may be extended by you to this new claimant.'

Bell's photophone was given greater coverage in <u>Nature</u> of November 4, 1880 when a four page article was given to a description of the device.[39] It is evident from this description that Bell and Tainter had invested considerable labour in developing their machine, which owed less to any 'scientific' knowledge of the properties of selenium than to their own appreciation of the practical difficulties, and their desire to produce a working instrument.

Shelford Bidwell followed up the publication of Bell's work with a short article[40] illustrating the means whereby a photophone, of sorts, could be constructed by anyone with access to selenium and a few instruments. Needless to say Bidwell's photophone bore no comparison with Bell's for practicality.

A report of sufficient finality for this brief discussion appeared on March 3, 1881,[41] in which a short account of Perry and Ayrton's excursions into the production of a photophone. It is evident that they had not succeeded, as Bell had, in overcoming the formidable practical obstacles in the way of turning an idea into practice.

Even this short consideration of the technological factors involved in the investigations of the properties of selenium is sufficient to underline the importance of developing effective devices on which measurements could be made. The original 'bars' used by Smith were quickly superseded by the more carefully manufactured cells of Siemens, Adams and Day, Bidwell and others. The work involved in producing reliable devices indicated the need for understanding the properties of the material; and the factors influencing these properties, crystalline form, purity, electrode materials, and so on. In general, attempts to apply the properties of selenium in useful instruments were not successful, mainly for technical reasons; the only 'successful' innovation being the photophone of Bell, the main shortcomings of this device being the transmission of light through the atmosphere.

The action of rectification by selenium or other materials did not result in any technological output during the 19th century.* Rectifying 'devices' using solids did not appear until the early years of the 20th century for by then there was beginning to be a demand for the rectification of alternating current at a variety of frequencies and powers. Only Fritts produced selenium rectifiers of marked reverse/forward ratios; while Braun did not use manufactured 'devices', rather arrangements that reflected the different requirements of 'pure' research.

## 2. Theory.

There exists a large amount of primary source material that could allow a detailed history of the developments in the understanding of electricity and magnetism that took place in the last quarter of the 19th century to be written. Unfortunately there are no recent careful studies of this period that can serve as authoritative sources for this section. Hence the discussion which is given in the following pages has been based mainly on various secondary sources contemporary with the work that was being carried out on selenium and other materials of this sort.

---

* and there seems little reason to doubt that this was due to lack of demand.

These sources ranging from articles in journals such as Modern Views of Electricity[42] by O. Lodge, serialised by Nature in 1887-89, through various British Association Reports, Lodge's On Electrolysis[43] of 1885 for example, to textbooks. In the latter category J.J. Thomson's Recent Researches in Electricity and Magnetism[44] of 1893 and the first edition of E.T. Whittaker's History of the Theories of Aether and Electricity[45] have proved particularly informative. Indeed the former volume has been used to define the termination of the period in which theoretical considerations will be discussed. Studying such secondary sources as these allows us to give the answers to three questions that have bearing on the various interpretations given to the experimental findings discussed earlier in this Chapter. The precise role of Thomson's and Lodge's writings is not easy to define. Although, to a history of electricity per se they are secondary sources, in that their contents were edited and presented a selected view of the field, for the purposes of this chapter they fulfil the primary role of surveying the state of knowledge and the areas of controversy. In this they have proved invaluable. For this chapter is not concerned with the history of electricity but with assessing how the properties of selenium, and other non-metallic conductors, were received by scientists of note. Also with what confidence the existing theories could be applied to discoveries not immediately contained within existing areas of knowledge. The roles and values of Thomson's and Lodge's writings in the above sources is discussed more fully when they are considered in detail below.

It was not, until 1931 that a theoretical study of the conduction of electricity through semi-conducting materials shed light upon wider problems of the electrical properties of solids in general.[46] Until then researchers who devoted their energies to investigations of non-metallic solids were compelled to apply descriptive mechanisms that were developed from different bases and for other purposes. It is necessary, then, to attempt an answer to the question, 'What was the contemporary "received" theoretical opinion about the nature of electricity when the discoveries, discussed earlier, were made?' together with its subsidiary 'What, effect, if any, did the discoveries themselves have on current electrical theories?'

In spite of the great 'advances' in electrical knowledge achieved by the beginning of the 1870's it must not be assumed that the explanations of electrolysis, of the voltaic effect, or indeed of electromagnetism were totally satisfactory.[47] There remained, even as late as 1885, problems that were still the subject of, if not controversy, then certainly friendly dispute. We must therefore consider the query, 'What were the problem areas in the existing theories and, more importantly, those associated with descriptions used to account for the properties of selenium, metallic oxides and sulphides and so on?'

Although we cannot know, with any certainty, the depth of electrical knowledge possessed by the workers we have referred to earlier, in the case of one writer, at least, we can make a reasonable guess at his knowledge of up to date electrical researches. Here, in the example of Bidwell, we have in published work, a hint of his knowledge of electrolysis and we know from the work of others[48] that he was in a position to be acquainted with up to date researches. In a limited sense, then, we can assess the question, 'How good was the use made of existing theories and to what extent did the explanations given of photoconductivity, rectification, and so on, utilise very new ideas?'

## 3.0. Thomson's 'Recent Researches.'

The date of publication of Thomson's book, Recent Researches,* 1893, is a useful point beyond which we need not look for the theoretical background to the work on photoconductivity, photoelectricity and rectification considered so far. In this publication Thomson at that time Cavendish Professor of Physics at Cambridge, included a comprehensive selection of the facts of electricity and magnetism, and, wherever possible, wove them together with the aid of Maxwell's Electrodynamics. The general tenor of his writings is mathematical although 'a method of regarding the Electric Field, which is geometrical and physical rather than analytical'[49] was introduced.

---

*This shortened title will be used in future.

An interesting feature of this approach was that Thomson was able to discuss the effects and phenomena of electric currents without introducing the concept of moving charges; using Faraday tubes as explicative devices, and, of course Maxwell's equations as the mathematical tools. Over half the book is devoted to a more or less mathematical exposition of the phenomena of electricity - Chapters III to VI; a third is concerned with the passage of electricity through gases; while the remainder, mainly considering the physical description of tubes of force, deals with all other 'recent researches'. In this latter part three pages only are devoted to metallic and electrolytic conduction *per se*; it is this area which is of consequence in our study of the history of semiconductors. *Recent Researches* contained no mention of the various discoveries of Adams and Day, Bidwell and others; which suggests either that Thomson had no knowledge of the results, or he considered them not significant enough to include. The former suggestions seems unlikely for the discoveries had a wide currency when they were made;[50] it is more probable that Thomson considered that the then present theories would eventually prove sufficient for a complete explanation of metallic conduction.

For example in Chapter I of *Recent Researches*[51] he gave a description of the use of Faraday tubes in accounting for conduction of electricity through gases and electrolytes and for the action of a galvanic cell.

He shows how the contraction of Faraday tubes can be used to express the resistance of conductor, relating the average life of a tube in the conductor to the relaxation time of the medium as defined by Maxwell. There seems to be no doubt that at this stage and in this publication Faraday's tubes had a reality for Thomson and that electrification effects were secondary to the motion and presence of the tubes; for when talking about Faraday's conception of the tubes he wrote:-[52]

> 'Although the language which Faraday used about lines of force leaves the impression that he usually regarded them as chains of polarised particles in the dielectric, yet there seem to be indications that he occasionally regarded them from another aspect; i.e. as something having an existence apart from the molecules of the dielectric, though these were polarised by the tubes when they passed through the dielectric. Thus . . . . he seems to regard these tubes as stretching across a vacuum. It is this latter view of the tubes of electrostatic induction which we shall adopt, we shall regard them as having their seat in the ether, the polarisation of the particles which accompanies their passage through a dielectric being a secondary phenomenon.'

It is not my intention to analyse the foundation and evolution of Thomson's picture of electricity, this has been attempted by others,[53] but it seems that at this stage (1893) Thomson was identifying the ether and the processes within it as the 'cause' of electrical phenomena. Whether or not this opinion represents Thomson's inner thoughts on the nature of electricity must remain, for my thesis, a matter of conjecture. In any case what is of real importance are the thoughts that Thomson was transmitting in Recent Researches; for it is these that are likely to have affected workers researching into areas that were not linked directly with the fundamentals of electrical theory.[54] And from these we perceive the clear view that, essentially, metallic conduction was not unlike electrolytic; and that field theory, pictorially represented by Faraday tubes, could be expected to give an account of the conduction of electricity in metallic solids.

Thomson pointed out (p 51 of Recent Researches) that while there were obvious differences between electrolytic conduction (where the processes could be described by Faraday tubes with some clarity) and metallic conduction (where description was more difficult), the discrepancies were not sufficient 'to make it necessary to seek an entirely different explanation for metallic conduction.'[55]

Thomson cited three major differences between metals and electrolytes.

1. The conductivity of metals is very much greater than electrolytes.
2. The temperature coefficient of conductivity is of opposite sign; positive for electrolytes, negative for metals.

3. There is chemical decomposition in electrolytic conduction.

While not ignoring empirical evidence Thomson pointed out that possession of a particular set of properties did not necessarily place a material in one class or another; carbon, although not an electrolyte had a negative temperature coefficient of resistance for example, and there were similarities in the behaviour of metals and electrolytes to light. Thomson did not attempt any theory of the constitution of Faraday tubes, although 'the analogies which exist between their properties and those of tubes of vortex motion irresistibly suggest that we should look to a rotatory motion in the ether for their explanation'.[56] Although Thomson did not explicitly claim that the tubes were the 'reality' behind electrical effects, he ended his first chapter thus:-[57]

> 'Taking however these tubes for granted, they afford, I think, a convenient means of getting a vivid picture of the processes occurring in the electro-magnetic field, and are especially suitable for expressing the relations which exist between chemical change and electrical action.'

Thomson's book leaves the strong impression that the main immediate research programme into electrical matters should be the investigation of gases, and that much of the rest would be subsumed under Maxwell's electrodynamics. He made very little comment on the nature of electric currents, and said nothing about the possibility that electricity might be an 'atomic' phenomenon. The discoveries made into the conduction of electricity through solids and at the points of contact between solids found no place in Recent Researches.

Thomson's view of electrolysis was conventional. By which I mean, he took no account of Arrhenius's recently published[58] suggestion that dissociation of ions took place in electrolytes, and hence, that the electrical, and other, properties of ionic solutions could be explained by an actual motion of charged atoms, each carrying a distinct quantity of electricity. There was, of course, considerable controversy surrounding Arrhenius's ideas[59] controversy which continued for much of the remainder of the 19th century; and, by and large, Thomson's writings in Recent Researches avoided the discussion of disagreement. To obtain reliable results on electrolysis was difficult, complicated, as it was, by the inevitable chemical reactions that occurred when electrodes were inserted into reactive solutions. However the way around this difficulty had been found by Kohlrausch in 1879 utilising alternating currents in his work. It may have been that the 'ionic dissociation' principle suggested by Arrhenius was not acceptable to Thomson in 1893 for inclusion in a didactic work.[60] Whatever may have been Thomson's opinion of Arrhenius' theories in 1893 the published work we are discussing contains a view in which electrolytes are solutions of polarised molecules, dissociated, one by one, by the interactions of Faraday tubes; resulting, eventually, in electrolytic decomposition. Thomson's geometric description of electrolysis did not require separation of ions in solution; nor did it envisage ions moving freely in the electrolyte. Thus Thomson's picture of electrolysis was in terms of 'Grotthus' chains described by the interaction of Faraday tubes which could collapse or grow, thereby giving rise to the chemical action in electrolysis, or conversely, galvanic cells.[61] Evidently such a visualisation could, in principle be applied to solids, particularly compound solids; Bidwell was not, therefore, out of step with 'received' opinion.

Beyond suggesting that electric currents may be represented by rotations of Faraday tubes, that is as interactions between fields of force, Thomson did not further illuminate the question of the nature of electric current or charges.

## 4. The Hall Effect.

Yet a paper published by Hall in 1879[62] introduced a phenomenon that was claimed to be at variance with Maxwell's views and was later to be used, to great effect, in elucidating the facts concerning conduction in the solid state.

The 'Hall Effect' was simply that if a conductor through which a current was passing had a magnetic field applied to it at right angles to the direction of the current then an electromotive force was developed mutually at right angles to the directions of the current and the magnetic field. Hall's own account begins with the consideration of a problem, as he saw it, in Maxwell's interpretation of the effect that a magnetic field had on a conductor carrying a current. Hall quoted from Maxwell's Electricity and Magnetism.[63]

> 'It must be carefully remembered, that the mechanical force which urges a conductor carrying a current across the lines of magnetic force, acts, not on the electric current, but on the conductor which carries it. If the conductor be a rotating disc,.. it will move in obedience to this force; and this motion may or may not be accompanied with a change of position of the electric current which it carries. But if the current itself be free to choose any path through a fixed solid conductor. . . . , then, . . . . after certain transient phenonema, called induction-currents, have subsided, the distribution of the current will be found to be the same as if no magnetic force were in action. The only force which acts on electric currents is electromotive force, which must be distinguished from the mechanical force which is the subject of this chapter.'

Hall found this rather puzzling, for as he pointed out [64] the mechanical forces which were developed were totally independent of the material carrying the currents. He reasoned that if the force acted on the conductor then the substance of the conductor might be expected to affect the magnitude of the force; but this was not the case. Furthermore there were variances between authorities on this point. Suspecting that there was a force between the current and the magnetic field he first essayed to detect a resistance change when a magnetic field acted on a current carrying conductor.[65] He found no effect, the current was not, apparently, forced to one side of the conductor. He altered his approach and assumed that electricity was an incompressible fluid returning, thereby, to a much earlier concept. From this premise about the nature of electricity itself, he argued that while there may be no actual motion of the electrical fluid there may well be a tendency to motion, when there would 'exist a state of stress in the conductor, the electricity pressing, as it were, toward one side of the wire.' Acceptance of the basic assumption concerning the nature of electricity allowed Hall to calculate the velocity of the electric current in conductors and eventually, to determine its sign.[66] Hall did not commit himself on this, but pointed out[67] that if the force between two currents was as the force between two current carrying conductors then the current, in gold at least, moved from the negative to the positive pole in the gold, (i.e. the sign of the current carriers was negative.) Thomson's discussion of the Hall effect[68] is combined with a consideration of the rotation of the plane of polarised light when it is reflected from the face of a magnet, and beyond remarking that the two need not necessarily be connected, had very little to say. He certainly did not treat Hall's discovery as if it were due to the action of magnetic forces on the currents in the conductors; he did not refute the argument, he merely did not refer to it. Again we are left with the impression that, sooner or later, electrodynamics would prove fully effective in describing Hall's discovery. In fact, Hall's basic assumption that electricity was an incompressible fluid, was at variance with Thomson's picture that electric charges were the terminations of Faraday tubes.

It is not my purpose to follow the early history of the Hall effect; and were it not for the historical fact that the main character in the selenium story became interested in refuting Hall's explanation the discovery could be 'left in the air', as it were, until it became of instrumental use in defining the properties of solid conduction during the opening years of this century. In Bidwell's work on the Hall effect we see that he did know of some up to date researches and that he was unwilling to accept the theoretical consequences suggested by Hall. There were, of course, experimental inaccuracies in Hall's work, it would be surprising if in the first instance of any 'discovery', there were not; there were also alternative descriptions possible, and Bidwell's was particularly ingenious. Some of Hall's results appeared to be wrong or reversible but once the existence of the electron was accepted the Hall effect became a necessary consequence of the proposed mechanism of charge transport in all types of conductor; a minor example of the effect of a Kuhnian paradigm shift.

Bidwell showed, qualitatively only, that the Hall effect could be interpreted as thermoelectric e.m.f.'s developed between variously strained portions of the conductor; the strains produced by the magnetic force on the conductor, temperature difference by the current flow, and the transverse voltages by the differential heating of the strained material resulting in inhomogeneity of resistance.

Shortly after Hall's publication of his initial results Rowland produced a short note on the new effect.[69] He suggested that Hall's findings implied that the electro-magnetic equations then in use were 'only approximate, . . . applying only to some ideal substance which may or may not exist in nature, but which certainly does not include the ordinary metals.'[70] It also seemed to Rowland that the effect would 'constitute a very important proof of Maxwell's theory of light'.[71] Rowland hoped, as did others,[72] to demonstrate that the Hall effect was similar in character to the rotation of the plane of polarised light when the light interacted with a magnetic field; but we have already seen that Thomson, in Recent Researches, could not give, (in 1893), a satisfactory derivation of the Hall effect. Rowland produced an elaborate argument in a series of papers,[73] whereby assuming that magnetism was the result of the motion of an incompressible fluid, he was able to deduce the rotation of the plane of polarisation light. His result, according to Thomson,[74] was identical to that given by Maxwell, but was obtained by including the Hall effect as a new axiom into his theory.

## 5. Bidwell and the Hall Effect.

Bidwell produced three papers on the Hall effect. On February 14, 1884, a publication 'On an Explanation of Hall's Phenomenon' was communicated to the Royal Society and published in Proceedings of the Royal Society on February 24, 1884.[75] A more extensive paper 'On some Experiments illustrating an Explanation of Hall's Phenomenon' was read to the Physical Society on March 8, 1884; later published in their Proceedings[76] and noted in Nature.[77] A short note in Nature of March 27, 1884,[78] illustrated 'The Reversal of Hall's Phenomenon'. All these writings were aimed at the same point: namely to show that the Hall effect was a result of thermo-electric phenomena. In a sense Bidwell's opinions represented a challenge to the proposed method of interpretation in terms of Maxwell's theory. His was not a deep challenge, i.e. at the fundamental assumptions, but offered an alternative on equally acceptable basic grounds. The brief examination of his second paper[79] which follows is not intended to illuminate the history of the Hall effect but to throw some light on the questions posed at the beginning of this section.

1. The Hall effect as a 'problem area',[80] not

necessarily in its own right, which it was, but as one more puzzle in the conduction of electricity through solids.

2. Bidwell's knowledge of 'up-to-date' researches in electrical science.
3. Bidwell's approach to research.

Of Bidwell's papers only the second need concern us here; it was an enlargement of the first and not substantially different from it; while the note in Nature added a small piece of confirmatory evidence, at least according to Bidwell.

We have seen previously that in his work on selenium Bidwell was a careful and detailed observer; effects he discovered he attempted to confirm not simply by repetition, but by analogy and extension. (His work on establishing his belief in the electrolytic nature of conduction in selenium is the pre-eminent example in this respect.) He applied the same techniques to his support of his belief that the Hall effect was explicable in the terms outlined above.

Bidwell began his paper with a mixture of confidence and diffidence. He considered that the Hall effect 'might be completely explained by the operation of mechanical strain and certain Peltier effects'[81] and that to his mind 'saturated as it was with the matter, it appeared that such a statement afforded in itself overwhelming evidence in favour of the views which (he) had been led to adopt; and (he) believed that when once set forth, ........, they could not fail to meet with immediate acceptance'.[82] However Bidwell was reluctant to pursue the matter without due caution for the explanation of the phenomenon 'seemed to be in complete harmony with the views of Clerk Maxwell as to the existence of a rotatory coefficient of resistance'.[83] Furthermore 'it [the Hall effect] was believed to point to an intimate relation between electricity and light'.[84] (Whether this comment was intended to underline the Hall effect as confirming Maxwell's theory or to suggest another correlation between the forces of nature is not clear. Recalling the discussion of his work on selenium we will remember that he did not interpret his work on the light sensitivity as indicating a direct action between light and electricity, although others did.)

Bidwell gave details of his experimental arrangements and how he had overcome one or two instrumental difficulties in order to make his measurements. Having, apparently, reached the conclusion that Hall's explanation of this effect was not correct.[85] Bidwell turned to other alternatives. First there was the possibility that the effect of the magnetic field on the junctions between connecting wires and the thin specimens used was to modify the thermoelectric behaviour from whence a transverse voltage would be developed. This explanation proved ineffective. His thoughts then turned to the effect of a mechanical strain in the conductors; if a direct stress could produce e.m.f.'s in a thin metal sample then he had a possible explanation of the Hall effect. He was able to show the existence of the required electromotive force.[86] Bidwell was aware that thermo-couples could be fabricated between the same materials that had had different mechanical histories;[87] a thermoelectric voltage could be developed at the junction of an unstrained copper wire and a stretched copper wire, for example. He now proceeded to the account to which his experiments were proceeding.[88] He provided a descriptive picture only, unsupported with numerical calculations, but was able to indicate a correlation between the directions of the current between stretched and unstretched portions and the sign of the Hall effect.[89]

Although Bidwell's work on the Hall effect has been given a very short treatment only, the discussion, together with the extensive footnotes, serve to illustrate the care that he took. Indeed he was so convinced by his experimental argument that he concluded his paper with the words:-[90]

> 'Though it may not impossibly turn out, on further investigation, that the details of the action differ in some respects from those which I have suggested, I think no reasonable doubt can remain that Hall's phenomenon is simply a consequence of mechanical action combined with Peltier effects. . . . Having regard to the great importance of the subject, it seemed desirable that it should receive the most thorough and exhaustive treatment possible.'

This short consideration of Bidwell's paper serves to indicate that the Hall effect was a problem area, as Thomson was tacitly to acknowledge in Recent Researches and that although Bidwell describes, without magnitudes, how explanations might be given, his own conclusions were inadequate. He could have rejected them on the same grounds that he had rejected thermal effects in selenium, namely that no thermal effect was known to take place instantaneously, while the Hall effect made an immediate appearance once the currents were started. Again, although he took care to be qualitatively correct, he made no attempt to produce reliable quantitative results; for example the magnitude of stresses, the amount of heat generated at the junctions, the thermal e.m.f.'s and so on. However we must acknowledge that he appears to have been informed about very recent developments in electrical research and to be able to link these with earlier discoveries. This is certainly true of experimental work,[91] for he quoted his sources; but we cannot be so sure when theoretical matters are considered, for here, in contrast, he provided no indication of the basis of his knowledge and information.

In his work on the Hall effect, as for selenium, Bidwell tried to give support to theories that he formed fairly early in his work; and was constrained by his early opinions to interpret his findings rather rigidly. Although his work on the Hall effect was not nearly as extensive as that on selenium the same attention to detail can be seen but his dependence on descriptive theories, led him to qualitative rather than quantitative measurements, and to some rather complex mechanisms.[92]

## 6. Electrical Theory in the late Nineteenth Century.

Four aspects of electrical theory impinged on the research into the properties of selenium and of rectifying junctions, namely:-

1) Metallic conduction,
2) Electrolysis,
3) Junction phenomena,
4) Electro-magnetism,

of which four only the latter could be said to have reached a satisfactory state by 1893; and even that could not account for the Hall effect. In the other cases, although some empirical rules were well established and accepted, considerable controversy raged around the interpretation and understanding of the various phenomena, for a suitable model was lacking.

Thus for metals, beyond the knowledge that Ohm's law was obeyed to a high degree of accuracy over a wide range of current densities and that there was no sensible transport of matter there was no more that could be said. The electrical characteristics of different materials were a matter of measurement rather than calculation based on a common set of assumptions; even such a startling generalisation as the Wiedemann-Franz law could not be derived theoretically.

In the case of electrolysis Faraday's laws were well founded and confirmed but were not firmly based on generally agreed foundations. It was not until 1902 that Whetham could write about Arrhenius' dissociation theory of 1887[93]

> 'The theory of electrolysis described in this chapter has proved one of the most stimulating hypotheses in the recent history of physical science. At the outset it met with much opposition, chiefly from chemists who held that its fundamental demands were inconsistent with well-established chemical conclusions. . . . As experimental arrangements approximate to ideal conditions the correspondence between theory and observation increases. . . . Some form of dissociation theory seems to be clearly indicated by the electrical properties of solutions, and, as at present formulated will be a guide in further investigations. . . . The complete theory of electrolysis needs further experimental data upon which to build, but the fundamental conception of ionic dissociation seems to secure a foundation for further development.'

However when Bidwell produced his 1895 paper[94] he could opine that the action of light on selenium 'would occur not only at the anode, but throughout the body of the Se, the recombination of the separated molecules of Se and the metal (forming the "Grotthuss chain") being (similarly) assisted.'[95] At that time, although, as we shall see below, Lodge queried the possibility of electrolysis in solids, the mechanisms involved in the conduction of electricity in electrolytes were open to dispute. Ten years later mobile atoms in solid materials seemed extremely unlikely, at least at ordinary temperatures. In 1880, however, electrolytic action was a likely candidate to account for the properties of selenium, for the performance of selenium cells had much that was qualitatively in common with electrolytic cells.

Junction phenomena were also within the scope of electrolysis for directional characteristics and the generation of e.m.f.'s were well known properties of electrolytes; but thermoelectricity, (the Seebeck and Peltier effects) and contact electricity, (the well established result that the contact and later separation of different materials produced a, sometimes very large, potential difference) were possible competitors for electrochemical processes. Yet again although old and well known empirical knowledge existed there was neither a satisfactory theoretical description of the phenomena, nor a generally agreed mechanism relating to thermoelectricity, the contact forces and Volta forces.

Consideration of the various problems associated with electrolysis and junction phenomena aroused, on occasions, considerable heat and differences of opinion; giving the impression of a state of knowledge that was extremely fluid, a fertile ground for experiment and theory;and analogical arguments, such as Bidwell used, could not be struck out of court very readily. Like the Hall effect, the efforts devoted to the understanding of these aspects of electricity are, in themselves, worthy of an extended piece of historical research.

In this thesis I can only indicate the areas of controversy which will serve to show that the lack of a suitable model of current electricity and a concentration on fields of force were the constraints which limited theoretical understanding of those phenomena which would have aided research into the properties of solids and the junctions between solids.

Berkson in Fields of Force[96] and Nye in Molecular Reality[97] provide us with excellent analyses of two problem regions in the history of 19th century physics. Berkson argues that Maxwell beginning from Faraday's intuitive conceptions of the nature of electrical actions tended to interpret electricity as the result of modifications and interactions of fields of force in the 'ether'; charge itself being a secondary property. Berkson puts the situation rather neatly in the following words:-[98]

> 'Up to this point[99] Maxwell had not considered the connection between electromotive force and charge. This may seem strange, since it would be supposed that a theory of charge would be the starting point of any theory of electromagnetism. But Maxwell had avoided introducing charge into his model, and instead had made current and its relation to the magnetic field fundamental. Although this enabled him to develop a unified theory of magnetism and current, he was unable to make charge an integral part of his model. Charge is a cause of displacement of the electrical particle outside the mechanism itself. To find the connection between charge and electric force Maxwell had to use a roundabout deduction, involving

all of the previous assumptions about the model.'

In his book Berkson returns several times to the concept of charge in Maxwell's theory[100] underlining, thereby, the limitations of his theory in this respect. Maxwell's reduction of electricity to the interactions between fields of force and his view of electric charge as a 'secondary' phenomenon is, paradoxically, at once understandable and strange. Understandable in that charge implies atomicity while Maxwell followed Faraday who did not accept that for electricity: strange in that Maxwell's work on kinetic theory was based on an atomic conception. It may be that in the case of atomic electricity and atomic matter the fundamental problem was not whether either hypothesis could give an account of observed phenomena, but whether the theoretical expression indicated the actual reality within the basic assumptions. As Nye expresses it in the introduction to her book:-[101]

> 'In attempting to understand the chemistry and physics of the nineteenth and twentieth centuries, it is readily apparent that a watershed of fundamental significance marks the years leading into our present epoch.
>
> Yet something is missing in many (of these)* histories, or perhaps too much is assumed. (There is a)* tendency to assume what so many of the physical scientists of this pivotal period did not for one minute assume - the discontinuity of the matter which underlies visible reality . . . . . . . , one perhaps fails to realise that the focus was

*My parenthesis

> not simply upon the nature of the molecules, ions and atoms, but upon the very fact of their existence. The alternative to a wave conception of cathode rays, for example, could not be couched in simple 'either - or' terminology, for the 'or' was not recognised by a sizeable segment of the scientific group as even a possible alternative.'

If Nye is correct, and she makes out a very good case for this view in her book, then as the study of electricity and an understanding of the phenomena were deeply woven into the picture of the microscopic properties of matter it is not surprising that agreed knowledge about electrolysis and junction phenomena was confined to the experimental results. Conversely, if the molecular view of matter was firmly based by the late 1870's then Helmholtz's famous lecture of 1881 would have been superfluous.[102]

## 7. Lodge's Reviews and Views.

As was indicated above (p 111) contemporary review type[103] papers will be used to indicate the range of the problems for a detailed examination of the primary sources would take me too far from the main purposes of this thesis, i.e. the early history of semiconductors. It is fortunate that Oliver Lodge produced a series of publications which not only give us some indication of his interpretations of the various electrical theories between 1885 and 1900; but include his summaries of the controversies, developments and predictions existing within the subject. Of particular interest is his Modern Views of Electricity.[104]

for here he attempted a survey of the total field; venturing into areas of speculation which in other publications might have been avoided. His reports to the British Association on Electrolysis[105] and to the Institution of Electrical Engineers when he wrote On the Seat of the Electromotive Forces in a Voltaic Cell[106] were written in an almost polemical style that serves to accentuate the problem areas. The difficulties were discussed until the close of the nineteenth century, before the electron theory provided a common ground for all electrical phenomenon. Almost the final "shots" in the argument were presented in a series of papers by Lodge[107] (1900) and a work of Kelvin's (1898).[108] Both works discussed contact electrification and voltaic electromotive forces.

Lodge's overall description of electricity and the phenomenon associated with it is briefly given in Modern Views*; much of which gives substance to Duhem's oft quoted remark 'We thought we were entering the tranquil and neatly ordered abode of reason, but find ourselves in a factory.'[109] Mechanical models abound for the description of purely electrical phenomena; the mechanical representations being analogies for the Maxwellian theories that Lodge assumed accounted for electrical properties of materials. Lodge was careful to emphasise that the use of mechanical models must be tempered with caution for the real nature of electricity did not necessarily reflect the properties of the assumed model. For example when he introduced the idea that electricity

* This shortened title will be used in future.

could be treated as an incompressible fluid he wrote:-[110]

> '. . . . it is natural to express the phenomenon[111] by saying that the electricity behaves itself like a perfectly <u>incompressible</u> substance or fluid, of which all of space is completely full. That is to say it behaves like a perfect and all permeating <u>liquid</u>. Understand, I by no means assert that electricity <u>is</u> such a fluid or liquid; I only assert the undoubted fact that it behaves like one; i.e., it obeys the same laws.
>
> It may be advisable carefully to guard one's self against becoming too strongly imbued with the notion that because electricity obeys the laws of a liquid it therefore is one. One must always be keenly on the look-out for any discrepancy between the behaviour of the two things, and a single certain discrepancy will be sufficient to overthrow the fancy that they may really be identical.'

Lodge does not make it too clear what this liquid was intended to describe; in some cases he seems to be identifying it with the ether, while in other cases with electricity itself, which he seems to envisage as something embedded in the ether. The models he described were, as might be expected mechanical representations of Maxwell's imaginary wheels and vortices; but he was less than clear:-[112]

> 'We have nowhere asserted that electricity and the ether are identical. If they are, we are bound to admit that ether, although fluid in the sense of enabling masses to move freely through it, has a certain amount of rigidity......If they are not identical, we can more vaguely say that ether

> contains electricity as a jelly contains water, but that the rigidity concerned in the transverse vibrations belongs not to the water in the jelly but to the mode in which it is entangled in the water.[113] However all this is a great and difficult question into which we shall be able to enter with more satisfaction twenty years hence.'[114]

The somewhat indeterminate nature of Lodge's fluid analogy did not restrict his description of electrostatics; which he interpreted as strains in the all-pervading fluid or in the 'jelly' in which the fluid was embedded. However the particular model he chose did not affect the issue greatly, for as Berkson shows the phenomena of electrostatics are independent of the model chosen to represent electricity; indeed a model is hardly necessary at all.[115] Where interactions between static collections of electricity were being considered Lodge's model was neither more nor less satisfactory than other representations.

Throughout Modern Views Lodge was careful to stress that his pictorial representations were merely analogies and only served as aids to establish the mathematical relationships; nevertheless he was able to provide graphic, if somewhat cluttered and unlikely, mechanical models of the electromagnetic field and its manifestations. He was relatively successful here, of course, for there is a formal analogy between the field equations of Maxwell and the actual performance of the systems Lodge used as illustrations.[116] Where no formal analogy existed or where Maxwell's theory included no basic assumptions Lodge was totally unable to provide a plausible description; and this applies to those properties possessed by semiconductors, (photconductivity, rectification, development of photovoltaic electromotive forces and so on) to metallic conduction and, of course, to the Hall effect. He devoted very little attention to junction problems in the version of Modern Views published in Nature, although the later book edition included some additional material on that subject.[117] Only two columns of Nature were devoted to the subject of metallic conduction[118] after which Lodge was content to leave 'the obscure subject of conduction in metals'[119] and to pass 'to the consideration of the way in which electricity flows through liquids.'[120] In his treatment of electrolytic conduction Lodge dispensed with a mechanical model in his detailed consideration and closed his sections on liquid and gaseous conduction with the thought that electric current may very well be an actual flow of charged particles. For as he wrote 'a current, being merely electricity in motion, need consist of nothing but a charged body borne rapidly along.'[121] Such bodies could describe the responses of dielectric and electrolytes to electric forces but left the behaviour of metals and solids unexplained. For as Lodge wrote:-[122]

> 'Locomotive carriage is not to thought of in them; but, inasmuch as no new phenomenon appears in their case, it is natural to try and picture the process as one not wholly dissimilar; and this is what in

> one place we have tried to do; with, however, but poor success.'

In fact metallic conduction was a mystery, and was to remain without a satisfactory explanation for some years. Lodge's treatment of junction phenomena and electrolysis in Modern Views was scarcely more extensive, although they were considered at greater length in the book version. However the papers already mentioned[123] are of greater weight and consequence; and these have been used in preference to the interesting, but lighter approach in Modern Views.

The larger part of Modern Views considers the phenomena of electromagnetism;[124] but towards the end of the work[125] Lodge indicates the existence of some problems that, as yet, had no explanation. Among these were the Hall effect and the action of light on the conductivity of selenium. He, like Thomson in Recent Researches, accepted that the Hall effect was intimately connected with the Faraday rotation of light,[126] which it was not. He knew that there was no satisfactory Maxwellian explanation of the Hall effect and leaves us 'in the air' as far as his own interpretation is concerned. However he pointed out that the Hall effect was difficult to observe and as the interaction between magnetism and the resistance of materials was rather complex and straining materials could affect their thermoelectric properties the Hall effect might be a thermal effect. He wrote:[127]

> 'Now a metal conveying a current in a magnetic field is certainly more or less strained by mechanical forces, and hence heat will be developed unequally in different parts, by a sort of Peltier effect; and the result of this will be to modify the resistance in patches and so produce a disturbance of the flow which may easily result partly in a transverse e.m.f. This has been pointed out by Mr. Shelford Bidwell.'

The possibility that the Hall effect might be explained by a heating effect led Lodge to suggest that there might be 'real' and 'spurious' Hall effects; i.e. that there might occur an actual rotation of the lines of electric potential as a direct result of the action of magnetic fields on currents which is masked by resistance effects.[128] But as distinguishing between some effects as real and others as spurious is hardly allowable then it may be, argued Lodge, that all actions between light and electricity in materials might be the result of thermal effects. This would, at least, add new expressions to the idea of the conservation of energy and forces.[129] Left as a question in the conclusion of Modern Views was the photoconductivity of selenium. Lodge wondered whether it was a property of selenium alone or possessed by all matter to a greater or lesser extent. Lodge did not know, but he had slight evidence to suggest that glass conducted electricity better when illuminated by light.[130]

We may summarise Modern Views by commenting that as Thomson in Recent Researches shows how the mathematical theory of Maxwell could give an excellent account of magnetism and electrodynamics, but metallic conduction, the properties of electrolytes and junctions were little understood, so Lodge demonstrated, with his mechanical models, that pictorial representations of Maxwell's equations could be given but the mechanisms did not fit metallic conduction and junction properties with the same ease. We can only trust that Lodge's strictures on the use of his ideas were adhered to for if read uncritically his models could be too convincing.

Modern Views was intended as a 'popular' exposition, albeit for the 'higher class of students'.[131] Where existing problems were touched upon there lay behind them the belief that the explanations were to be sought in terms of the ethereal conception of electricity. For Lodge the ether was not a viewpoint but a 'conviction'.[132] and for him the real pressing question was, 'What is ether?'[133] However we have seen in Lodge's work and in Thomson's Recent Researches that in spite of their overtly different approaches neither provided a satisfactory account of the phenomena that appeared in the early experiments with semiconducting materials.

## 8. Problems with Electrolysis.

By far the most common and important description of the behaviour of semiconductors in general and selenium in particular was in terms of electrolysis, which, superficially, could provide a framework for photoconductivity, rectification and photoelectric effects. Occasionally thermoelectric properties were appealed to as well as various other contact forces.

In fact, scattered through the papers published during the 1870's and 1880's there existed fairly clear 'proofs' that these experimental facts could not give adequate and total accounts of the new properties. Thus while Bidwell[134] and Adams and Day[135] were demonstrating that thermal causes, were unlikely, Braun[136] showed, with some experimental skill, that rectification was not a result of electrolytic action. However it is a fact that the results obtained, often on a variety of materials, were not brought together; and only Bidwell had sufficient tenacity of purpose, for whatever reason, to hold to a particular theory and to work out, qualitatively at least, the consequences of his beliefs. In retrospect, electrolysis seems an unlikely candidate to explain the conductivity of solids, that is at the magnitude required, but even by 1890, although the facts of electrolysis were well known[137] the underlying mechanisms were the subject of, if not mystery, then certainly dispute. Since we know that Bidwell did not subscribe to Arrhenius' theory[138] the question is whether the existing theories of electrolysis allowed for the uses to which they were put by Bidwell. Although, as we shall see, the answer is that they probably did not, the state of agreement was such that a categoric denial of the validity of Bidwell's argument was not possible.

Not only was the nature of electricity a matter of some doubt but the nature of electrolysis was not clear. Although Helmholtz[139] had suggested that electricity was an atomic phenomenon the majority opinion was in favour of the ethereal view; and while some suggested that, in solution, electrolytes might be dissociated, the general tenor of opinion was not in favour of this interpretation. Lodge's 1885 report On Electrolysis[140] to the British Association makes the problems and difficulties of interpretation extremely clear, and serves as an excellent source for the 'state of the electrolysis art' in the 1880's.

Lodge did not like the subject of electrolysis, for although he saw it as immensely important he was 'to a great extent deterred by the immense area it covered, and by the somewhat repulsive character attaching to any borderland branch of science - in this case not wholly physics nor wholly chemistry - a repulsiveness perhaps only subjective, and probably to be attributed to a feeling of incapacity for grasping both aspects of the subject with equal completeness.'[141] In spite of his apparent reluctance to consider the subject Lodge produced a fifty page paper that highlighted the controversies within the subject of electrolysis and, occasionally, strayed into more general fields. It appeared to Lodge that much remained to be determined for, to him, the theoretical position was far from clear. He decided to 'direct attention to certain theoretical points which are undoubtedly of interest and importance, and to suggest the answers . . . . to debatable questions which bristle round even the most elementary facts; in the hope that, attention being thus directed to them, success in finally solving some of them may be attained by a more competent hand.'[142] It is interesting to read that even the definition of an electrolyte posed some difficulties and it was by no means certain that electrolytic action was not accompanied by metallic conduction.[143] Lodge's statement that 'an electrolyte is a substance which conducts electrolytically'[144] could encompass many substances, even solids, although Lodge was careful to write that:-[145]

> 'Electrolytes seem necessarily fluid, and it is difficult to imagine the locomotion of atoms which accompanies electrolysis to go on in a solid body.'

He was aware of Bidwell's claim that he had found solid electrolytes but exhorted his readers to be wary of accepting such an idea for 'extreme viscosity there may be, as in hot glass, but not the true rigidity of a solid, unless certain proof is forthcoming.'[146] Much of the report is concerned with the various theories of electrolysis and the empirical results supporting them; and in section V of the report Lodge summarises the various suggestions.[147] Three competing views were current, according to Lodge; the molecular chain of Grotthus, molecular dissociation ascribable to Clausius, and supported by Maxwell and finally the electrostatic theory of Helmholtz.[148] Lodge considered each of these theories in turn.

The chain theory of Grotthus he considered too familiar to require reiteration. He pointed out that some form of dissociation hypothesis was needed, for the chain theory necessitated a correspondence between the strength of chemical binding and the ease with which electrolysis occurred; but no such relationship could be found.[149] However complete and permanent dissociation of the atoms of the electrolyte was not necessary, 'a momentary dissociation would be sufficient, but no hypothesis which involves a tearing asunder of molecules in the interior of a homogeneous electrolyte can be permitted.'[150] Herein, said Lodge, lay the distinction between electrolytes and dielectrics.

The dissociation theories, surveyed by Lodge, did not require permanent separation either. It being only necessary to assume a short lived parting; the process being seen as a dynamic equilibrium, where the lifetime of separated atoms could be as short as one thousandth of a second.[151] Interpretations as to the action of electric fields on the dissociated ions differed. Some assumed that all the ions were subjected to attractive forces while others considered the action to take place in the neighbourhood of the electrodes.[152] Lodge discussed three variants of the dissociation hypothesis; those due to Quincke, Wiedemann and Kohlrausch. The first of these he treated with some disrespect. Quincke had assumed that the components of the electrolyte possessed charges of opposite sign and of unequal magnitude; this theory, although it could account for dissociation, migration of ions and electrical endomose,[153] was not one for which Lodge had much liking. His opinion was firm.[154]

> 'Evidently the hypothesis is very elastic, and, if granted, explains the facts; but I must confess to an invincible repugnance to the idea of numerically unequal charges existing in the dissociated atoms of a molecule, as well as to the corresponding idea of all the molecules of an electrolyte being similarly charged.'

Quincke's hypothesis was based solely on the requirement to account for the different rate of migration of the ions in solutions but 'the facts of migration [did] not necessitate such inequality'.[155]

Wiedemann's and Kohlrausch's description were very similar; both presumed that ions carried charges of equal magnitude and opposite signs; both considered the facts of electrolysis to be accounted for by dissociation, They differed when the source of the charge was introduced; for Wiedemann the charge was induced by contact between the atoms;[156] for Kohlrausch Lodge implied that molecules were composed of charged atoms which became dissociated into ions. The velocity of ions presented a problem which Wiedemann solved by suggesting that the rate of diffusion was a phenomena connected with the ions and the viscosity of the medium through which they moved;[157] Kohlrausch attached a specific velocity to an ion in a given fluid.[158] Although Lodge considered Kohlrausch's theory to be 'beautiful'[159] he was able to show, to his own satisfaction, that contrary to Kohlrausch's hopes the ionic velocities could not be calculated from the data already to hand.[160]

Finally Lodge examined Helmholtz's theory summarised by him in one paragraph.[161]

> 'The root idea of this theory is that each kind of matter has a specific attraction for electricity, some kinds for positive, other kinds for negative; that, accordingly, work must be done to separate an atom from its electrical charge, or to remove electricity from an atom of high specific attraction and give it to another lower in the scale. Further, that chemical affinity is mainly due to the electrical attraction of oppositely charged atoms, and that when such atoms combine into a compound molecule they do not discharge into each other but retain their charge.'

Lodge, borrowing heavily from Helmholtz's 1881 lecture,[162] shows how his ideas can be applied to many of the facts of electrochemistry; both in the production of electricity in cells and in electrolysis. He takes issue with Helmholtz's claim that contact electricity, thermal e.m.f.'s and frictional electricity could be accounted for by the same mechanisms[163] and he had the authority to express doubt.[164] He pointed out that Helmholtz's ideas might be fruitful in producing a theory of chemistry stating that they implied[165] 'a theory of chemistry; in the form of a sort of kinetic theory of gases with electrified atoms.' While Lodge was impressed by Helmholtz's views he could not accept the idea of atomic electricity however much the facts of electrolysis demanded it. Indeed he wrote that 'the notion is repugnant, but it just wants considering; though I should hardly have ventured to suggest it but for the support Helmholtz has given to the idea.' Here Lodge was being conservative; for Helmholtz's theory allied to dissociation is not far off the ideas that Arrhenius was working on in 1885; but we have already seen[166] that for Lodge the ether was the real substance of electricity.

This brief analysis of <u>On Electrolysis</u> would be sufficient to show that while there were many facts concerning electrolysis there was not one theory more acceptable than another; and this is confirmed by a series of questions and problems which Lodge appended to his report, some of them so apparently elementary that it is clear that much of the mechanism of electrolysis was open to doubt. The list that follows speaks for itself.[167]

'1. Is Ohm's law exactly true for electrolysis?
2. Is Ohm's law obeyed by very bad conductors?
3. Are electrolytic and metallic conduction thoroughly distinct, so that no substance has a trace of both conductivities at once? Can any metallic alloys

conduct electrolytically?

4. Is there any relation between optical opacity and electrolytic conductivity?
5. Under what circumstances is solid matter deposited in the path of a current?
6. Is it possible for opposite corresponding ions to travel at different rates?
7. On the apparent relative velocity of opposite ions.
8. How much of the current is conveyed by the water and how much by the dissolved salt in any given case?
9. Is any quasi-electrolysis possible across an air space?
10. Does the energy of secondary action contribute to e.m.f. in a cell just as much as the energy of primary action, or do secondary actions directly generate heat?'

Electrolysis, then, unlike electrodynamics, was not a 'well formed' science in 1885. Although there were constraints on its invocation, (to account for conduction of electricity by elements, for example), sufficient haziness and disagreement existed that allowed it to be used in situations that, today, seem unlikely. No one could be sure that solids did not conduct electrolytically; and until they were Bidwell, and others, could describe their results in electrochemical terms.

Because of a lack of a clear and accepted picture of electrolysis it could be employed in describing the action of selenium, which, as we have remarked on several occasions possessed all the properties that are now associated with semiconductors; and although there were other contenders that might have been employed only electrolytic explanations were used with any consistency, notably by Bidwell. Siemens had suggested chemical effects but no one had followed this up: Moser put forward a mechanical explanation but Bidwell had shown this to be untenable.

## 9. Junction Phenomena.

In spite of the clear indications that rectification, and the development of photovoltages were properties associated with the junctions between materials, no one appears to have attempted to reconcile these phenomena with known thermoelectric properties[168] or with the development of potential differences in voltaic piles or batteries. Of course the application of electrolytic descriptions implied the production of polarisation effects and the developments of voltages; but as is clear from Lodge's paper 'On the Seat of the Electromotive Forces in a Voltaic Cell'[169] and the subsequent discussion of that work the underlying cause of the action was the subject of much dispute. As the lack of use of a model that was to hand is as interesting as the employment of an alternative, this chapter will be closed with a brief discussion of Lodge's summary of the knowledge concerning junction phenomena, and an assessment of the role of the various theories in developing an understanding of semiconductors in general and selenium in particular.

From the beginning of the 19th century, when Volta had demonstrated the existence of electric potential differences between both wet and dry metals, a considerable amount of work had been undertaken in order that the discovery might be understood, and possibly reduced to the same basic explanation. Even by 1885 it was still not clear whether the action of a pair of dry metals was the same as that when the metals were separated by an electrolyte. In addition the thermoelectric properties of junctions - the Seebeck and Peltier effects - compounded the difficulties. There were, therefore three experimental discoveries to be considered.

1. The 'Contact' force between dry materials.
2. The 'Volta' force as developed between wetted metals.[170]
3. The 'Thermoelectric' effects - the Seebeck and Peltier effects being recognised as complementary.

There was really no disagreement but that the Volta force was the product of chemical action; neither was there any doubt that where a current was produced some other action had previously occurred.[171] All knew that an electromotive force could be produced where dissimilar materials were in contact; but, according to Lodge, there existed doubt about where in a circuit the major part of the e.m.f. resided.[172] For Lodge this was the only question: in a zinc - acid - copper - zinc circuit which junction contributed most to the e.m.f? Lodge contrary to 'most physicists (who would)* say . . . . that the major part of the e.m.f. of the cell resides at the zinc - copper junction,'[173] thought the zinc - acid junction the most suitable candidate for this honour. He pointed out that there existed some real experimental difficulties in the determination of the various components of the total e.m.f.,[174] and that some scientists had been guilty of gross errors of interpretation. He wrote this of the views of Pellat and Ayrton:-[175]

> 'Pellat, however considers the Peltier effect to be quite distinct from and have no relation to the true e.m.f. of contact. In explaining this he makes use of a piece of unpleasantly plausible reasoning, which I myself have heard Professor Ayrton use, and which, when unexpectedly suggested is so painfully benumbing that it is worth while to quote it and to indicate its weak point.'

Lodge proceeded to expound his version of Pellat's and Ayrton's opinions and to demolish them. Lodge concluded that 'the existence or non-existence of a Peltier effect has everything to do with the existence or non-existence of an e.m.f.'[176] His identification of thermal effects with true differences of potential at the junction between metals enabled him to point out that the contact forces between substances

---

*My parenthesis.

gave rise to much greater effects than those of thermo-electricity; the cause he ascribed to actual or potential chemical action. His account is reminiscent of Helmholtz' ideas of attraction between electrodes and the atoms of a dielectric. Hence the potential difference detectable between, say, copper and zinc was not a measure of an inherent difference between them, but represented the result of the different affinities they felt for oxygen. The weakness of Lodge's argument, which Perry gleefully exploited in the subsequent discussion, was the requirement that a third substance be present between the copper and the zinc if a large difference of potential was to be observed.[177] I do not intend to argue the merits of Lodge's case or of Perry's rebuttal of it for the discussion I give is simply to underline the fluid state of much electrical theory in the 1880's; but the extensive quotation of Perry's remarks that follows illustrates, clearly, the magnitude of the differences and the, somewhat, partial tone in which they were expressed.[178]

> 'Dr. Lodge's paper differs from those usually read at this Society in that it opens a debate; and my answer can hardly be regarded as merely a criticism of an ordinary scientific paper, but as opening the debate on the other side. Dr. Lodge (supports) Clerk Maxwell and other philosophers . . . I want to put before the Society . . . . what may be called the Thomson[179] side . . . . My strongest feeling just now is one of gratitude to Dr. Lodge;

he has treated us mercifully on the whole. When one mounts the steed of physico-chemical speculation as to what is going on in a voltaic circuit there is no reason for drawing rein at one place rather than another. Why should he stop anywhere in particular? It is only enjoyment to him this careering about in a new world where there is neither north nor south, where one plain fact is an enchanted giant error, that must be borne down by the spear of downright denial, and another plain fact is simply a plain fact with no enchantment about it. I say again that I feel grateful to Dr. Lodge, because there is no doubt that he has the power of speculating for years and years on a subject of such interest as this. He accepts the contact theory of voltaic action; he acknowledges that the electromotive force of a voltaic circuit is equal to the sum of the contact-forces, as measured electrostatically, of the various substances. These are the plain facts; now for the enchantment. He says it is absurd to imagine that there is a considerable difference of potential between two metals, say zinc and copper, in contact with one another. He says, "Yes; experimenters have certainly found an apparent difference of potential; they have measured apparent differences of potential in air, and they are due to air effect." Yet they have measured these differences of potential, when, instead of air being the dielectric, there has been no air, and there have been other gases quite different from air, but still he says their results are due to an air effect. They have even measured these differences of potential in fairly good vacua, but still Dr. Lodge says they are air effects. Not only does he say that this is the case, but that if you could experiment in as perfect a vacuum as has

> been obtained by Mr. Crookes and obtained the same result, as we might suppose you might, still he says it would be due to an air effect. Now, when Dr. Lodge makes a statement of that kind, it is quite obvious that there must be some very strong reason for his discarding evidence; . . . . and I assume that if we can show Dr. Lodge that this strong reason is baseless - has no existence - then he will probably be willing to leave again this region of speculation to the sole enjoyment of the leader from whom he already differs a little, Dr. Exner.'

Perry's criticism of Lodge's views continued in a like vein for some time; an approach excused in the opening remark by pointing out that Lodge was opening a debate; by his acceptance of the challenge and taking an opposing stance he acknowledged that a real debate existed. The main substance of Perry's criticism lay in a matter of definition; that is the distinction between e.m.f. and potential difference; and the existence of the latter, implied Perry, did not necessarily entail the production of the former. Thus it could be that contact forces, although producing large potential differences, did not contribute greatly to the production of the e.m.f. in a voltaic circuit. Hopkinson agreed that the 'question is one very largely of definition,'[180] although he preferred Lodge's manner of interpretation, and thought that, on the whole, the experimental data supported Lodge. Fleming suggested new experiments to test the importance of the medium in the phenomenon of contact electricity,[181] but

Forbes considered the question to hold no more interest than 'metaphysical speculations as "How many angels can stand on the point of a needle?" '.[182] Forbes regretted that Lodge had provided no new experiments, while rejecting the interpretations of the old ones, and suspected that Lodge would not accept the results of new experiments as conclusive. Others entered the arena. Ayrton, with some experiments, supported Perry, as might be expected[183] and Swinburne attacked some of Lodge's conclusions based on the heat of formation of metallic oxides,[184] and so the debate continued. S.P. Thompson supported Lodge, and was, in turn, criticised by Ayrton. Lodge, as in any good debate, was given the opportunity of summing up,[185] (there were a couple of written communications that were included in the published version). He attempted to demolish his opponents' arguments and concluded his discourse with a picture of the action in a voltaic circuit in terms of lines of electrostatic force. This perhaps is the key to Lodge's opinions. His interpretation of the contact force as being a chemical action was particularly suited to the introduction of these concepts and it may be that his opinions were more directed by his adherence to the ether and strains in that 'medium' than by a desire to be truly receptive to opposing opinion.[186]

However that is not the point I wish to investigate, however interesting it might be. I began this section on junction phenomena by suggesting that the known, and accepted, experimental results were not explained by a generally agreed model. This point has been made by the introduction and acceptance of a debate concerning the nature of all contact electricity.[187] The lengthy extract of Perry's words has served to illustrate not only that the differences of opinion were real, and possibly profound, but also that the discussion was conducted in a manner typical more of a debating chamber than a scientific dispute.

## 10. The Relation between Experimental Discoveries and Theories.

Most of the discoveries associated with semiconducting materials were made while Maxwell's theory of the electro-magnetic field was being established as the prime, and perhaps the only, theory of electricity. It cannot be doubted that the effect of this theory was notable as, one by one, rival constructs were abandoned as inadequate; in particular, as Berkson indicates,[188] Hertz's demonstration that electro-magnetic energy could be radiated in the form of transverse waves identifiable with light finally confirmed the strength of Maxwell's approach. Thus while J.J. Thompson in his report to the British Association on Electrical Theories,[189] presented in 1885, considered it necessary to compare Maxwell's field theory with alternative descriptions, by 1893 in

Recent Researches[190] he 'adopted exclusively Maxwell's theory' and did not attempt 'to discuss the consequences which would follow from any other view of electrical action.' Indeed this is understandable; for Maxwell's theory not only encompassed all the experimental observations of static magnetism and electricity but also made predictions, later confirmed, about radiation, absorption of light, reflection of light and so on. It was entirely natural to apply Maxwell's theory to all electrical phenomena, although some were ill suited to this purpose, and we find Thomson, Lodge and others[191] attempting to describe metallic conduction and electrolysis in field-theoretic terms. Yet, perhaps because the action of electricity in closed circuits and in chemical reactions was rather complex, Maxwell's theory was not applied successfully in these areas. More importantly the 'hidden' assumptions of Maxwell's theory[192] - absolute space, the ether, mechanical forms, charges the manifestation of ethereal strains - militated against a successful description of conduction processes themselves. For in field theory attention was focused on the processes in the field itself; yielding a paradigm that was not applicable to phenomena involving knowledge of the mechanisms of current flow. We have seen how the Hall effect was not amenable to treatment by Maxwell's theory, in spite of several attempts to achieve a successful solution;[193]

although, on the face of it, representing, as it did, an interaction between magnetism and electricity electromagnetic field theory should have yielded an answer. Rowland's inclusion of the Hall effect as an additional empirical 'axiom' in field theory was not accepted; for this step was not seen as necessary.[194]

Acceptance of the Maxwellian model and its corollary, rejection of the atomic nature of electricity, particularly by Lodge,[195] opened areas of debate, such as that on electrolysis and the sources of voltaic e.m.f's.[196] The discussion on these topics has illustrated that differences of opinion existed in these fields, not so much concerned with experimental data, but with the interpretation of this information.

It is thus easy to appreciate why the discoveries of Smith, Adams and Day, Siemens and others were something of a by-way in electrical researches in the 19th century and why Bidwell was able to maintain his electrolytic theory of the action of selenium. It remained a by-way for it included some complex interactions and, moreover, the effects were not totally unexpected; at least in the retrospect of the times. The major research effort was devoted to the study of conduction in gases, inherently much simpler, and to the extension of Maxwell's theory;[197] no major figure appears to have contributed anything to the study of semiconducting materials at this stage in their history[198] thus emphasising the 'fringe' nature of the research. Highlighting this point still further we find no mention of selenium and its properties in Recent Researches and there is only passing comment on the phenomena in Modern Views; and Whittaker in the first edition of A History of the Theories of Aether and Electricity ignored the field entirely.

Of those who investigated selenium, and other substances[199] only Shelford Bidwell maintained a consistent attitude and interest; as was detailed in Chapter 2. His attachment to electrolysis in selenium becomes cogent when the theoretical points discussed in this chapter are remembered. Qualitatively at least electrolytic action accounted for the properties of selenium; and Bidwell is to be congratulated, in retrospect, for his persistence with his ideas. For him they seemed to possess all the qualities of a definite research programme; leading him to investigate solid electrolytes, the rates of reaction under the influence of light; and in his writings his theories appear respectable and plausible. Without exception, however, they were not quantitative;[200] he did not attempt to check whether Faraday's laws of electrolysis were obeyed, neither did he try to determine the level of impurities, particularly the presence of selenides, in his samples. So enamoured was he of electrolysis that he maintained his stance even in his last paper on the subject where he showed the importance of water if the phenomena were to be obtained.[201] Why, we must ask, did he select electrolysis? There is, I think, a simple answer; no other theory was as satisfactory and Bidwell was unable or unwilling to invent a new theoretical construct. No blame or criticism can be attached to him for this for we have seen how existing theories of conduction were unable to account for even the simplest of experimental facts, Ohm's law. We have seen how the empirical statements relating to electrolysis and to the action of batteries and to thermal effects were hedged around by controversy; this situation was both satisfactory and unsatisfactory. Satisfactory in that without a clear picture of the mechanisms of electrolysis the ideas could be applied to selenium, whereas by 1900 the concept of mobile positive and negative ions in solids appeared to be unlikely. Unsatisfactory in that without a clear picture of electrolysis or junction phenomena the experimental phenomena discovered by Smith et al and Braun were not interpreted as problems outside the scope of accepted explanations; there were none. Bidwell, having rejected thermoelectricity, had to accept electrolysis unaware that Braun had shown, in a restricted case at least, that this was not good enough.

To the familiar 'breakdowns' of classical physics we can add those of rectification, photoconductivity, photovoltaic effects and the Hall effect; problems whose solutions were to lie in the already nascent electron theory and quantum theory. At the time these difficulties were expected to be resolvable within the existing framework, but no such explanation was ever given.

## CHAPTER 4. Experimental Work to 1920.

The first two decades of this century witnessed an increasing interest in the properties of solids. Although, as in the previous period, very few workers appear to have been sufficiently motivated to devote their main and continuing effort to the story in which I am interested. A majority of the work on semiconductors, building on the foundations laid in the nineteenth century, was directed at a deeper understanding of the properties of selenium. By the end of the 1900's a few German researchers were beginning to investigate the properties of a large number of non-metallic solids; to such effect that by the end of the next decade a new class of materials could be defined. The class we call 'semiconductors'.[1]

The volume of primary material from which a history of semiconductors could be written begins to assume vast proportions and as little of it has been examined historically the problems of selection, both of sources and subjects, becomes difficult. However, as the work on selenium was divorced from that on other materials, it has proved possible to disentangle the important parts of the story of selenium as it developed between 1900 and c1920; with only occasional references to other materials.

As in the previous period the history of selenium was examined through the work of a few men, so in this chapter the work of an American, Brown,[2] has served as the core around which the story has been written; for between 1905 and 1917 Brown authored, or co-authored, a score of papers concerned with the electrical and optical properties of selenium. The main content of the chapter will be a discussion of the experimental work carried out on selenium.

## 1. Selenium - An Overview.

It was suggested earlier that the approach to selenium possessed a Baconian character in the nineteenth century; everything that might have had an effect was tried. To some extent this was also true during the first twenty years of this century. It seems as if all physical causes were investigated for their effect on selenium; radium rays,[3] X-rays[4] and N-rays[5] were hurled at the element; its surface was abraded;[6] it was subjected to the influences of mercury vapour;[7] and the effect of high pressures was investigated.[8] Few workers indicated the ends to which this experimental activity was directed, although, as we shall see later, Brown[9] did at least make some attempt to codify his results. The Baconian character of some of the work is well illustrated by a series of papers produced by McDowell[10,11,12] in Physical Review (1909, 1910). By contrast two papers by Pfund in 1904[13] and 1909[14] indicate how effectively experimental work may be combined with theoretical considerations either for the purposes of confirmation or denial. Bidwell's electrolytic theory of the action of selenium[15] did not survive long into the 20th century. Although Martin in a review article in Wireless World of 1915[16] wrote that 'the most generally accepted theory is that put forward by Professors Adams and Day, in 1877, the results of their exhaustive investigations leading them to suppose that the "electrical conductivity of selenium is electrolytic" ',[17] he was not, in fact, reporting a correct state of affairs for by 1915 the most acceptable account was based on the electronic theories of Lorentz[18] and Thomson.[19] The concepts of the electron theory were not applied immediately to the problems of selenium, and for a time two competing theories existed side by side. Brown devoted considerable effort,[20] theoretical and practical, to a chemical interpretation. In a manner reminiscent of Siemens' suggestions[21] he pictured the properties of selenium as a result of the equilibrium between the various allotropic forms in which it could exist. As we shall see his experiments constrained him to reject his interpretation and adopt an electronic description which was more, although not completely, successful.[22] While Brown was developing his 'allotropic modification theory' others, Pfund for example,[23] were suggesting that electronic theories would serve and while the concept of the electronic theory of solid conduction began to produce a unification within the study of the electrical properties of solids, (a point of view which will be considered in Chapter 5), it is true to say that no attempt to work out fully the consequences vis a vis selenium was made.[24] (In fact partial success was only achieved when the early electron theories were applied to metals or to simpler materials than microcrystalline selenium).[25] The electronic and chemical theories were not mutually incompatible. For what was at issue was not whether the electrical properties of selenium were due to the presence of electrons but whether the action of light, for example, was manifested as a direct action on the electrons or whether the equilibrium between the various allotropic modifications was disturbed. Electronic theories could then, possibly, account for the electrical differences observed.

## 2. The Demise of Bidwell's Theory.

We have seen in an earlier chapter[26] how Bidwell enlarged the work of Adams and Day[27] and taking their suggestion that the electrical and electro-optical properties of selenium might be electrolytic phenomena produced a convincing qualitative theory. We showed that his theory depended on four assumptions; that selenides were always present in selenium; that the electrical properties of selenium cells were dependent on the properties of the selenides; that selenides were electrolytic in nature; and that the concentration of selenides in selenium cells could be altered by the action of light. It was argued that in spite of much effort Bidwell was unable to provide conclusive experimental evidence for his theory and further that his last paper (1895)[28] indicated that his evidence for electrolysis was based on the presence of moisture in his cells, although he did not fully take this point.

The repudiation of Bidwell's theory was not, of course, immediate, but, by 1911, Brown, when proposing his own theory of the action of light in selenium,[29] could write:-[30]

> 'That the effect of illumination on certain varieties of light-positive[31] selenium is to produce a genuine change in the selenium itself has not been questioned since Pfund[32] and Berndt[33] showed that selenium cells made by using selenium of the highest purity[34] and carbon electrodes were sensitive to light.'

This passage from Brown's writings indicates, correctly, that Pfund and Berndt attacked what was the weakest link in Bidwell's chain of argument: namely the essential presence of selenides in selenium cells. It is evident that if selenides were shown to be unimportant to the operation of a selenium cell then the chances of the action being electrolytic, or due to the formation of chemical compounds, would be minimal.

Pfund directed his researches to two questions, both contained in Bidwell's theory. First could the necessity for the presence of selenides be sustained and second was there any evidence for a chemical change or molecular rearrangement at or near the surface of the selenium?

Pfund pointed out that in the accepted theory 'the phenomenon is ascribed entirely to the selenide, it seemed worthy of interest to undertake experiments with cells containing different selenides'.[35] Noting that the maximum sensitivity of the cells fell in the visible portion of the spectrum Pfund decided to see whether 'the position of the maximum might be a function of the metal in the selenide'.[36] Pfund was careful to produce selenium that was as pure as possible and remarking that 'distillation does not effectively remove impurities'[37] selected a chemical technique which, he claimed, yielded a product 'sufficiently pure for atomic and molecular weight determinations.'[38] To minimise indeterminate contamination with selenides he, like Berndt,[39] used cells with carbon electrodes. Before adding the selenium to the electrodes a definite quantity of selenide[40] was added. Spectroscopic measurements were made with the aid of a normal spectroscope and great care was taken to standardise the amount of energy falling on the cell at different wavelengths.[41]

Pfund was also careful to underline the speed of response of various cells, being the first worker to emphasise this point; although others, Adams and Day for example,[42] had pointed out that while there was an immediate response to illumination, a steady resistance was reached only after a relatively long time had elapsed.[43] The performance of a particular cell determined the exact experimental procedure Pfund adopted.[44]

His early investigations into the wavelength sensitivity of selenium, had demonstrated the presence of a 'prominent maximum'[45] at .7 μ. Thinking that the position of the maximum might have been a function of the metal of the selenide he repeated his measurements with cells of different electrodes and containing known selenides. 'However the maximum of the curve was not shifted.'[46] In the conclusion to this set of experiments he wrote:-[47]

> 'In these experiments the only substance present in every case was selenium, and it appears to me that, after all, this is probably the determining factor rather than the selenide. In view of the fact that the amount of selenide added to the cell was approximately that necessary to produce highest sensibility,[48] the conditions favourable to a shift in the maximum could not have been better. The persistence of the maximum in the same position indicates that the nature of the metal in the selenide does not control the selective sensibility of the cell.'

Of course, Pfund had not demonstrated that the presence of selenides was unnecessary to the production of light sensitivity in selenium, as Brown was to claim,[49] but he was to suggest that the action of light was on the selenium rather than the selenides; a step away from Bidwell's interpretation. Attempts to link the electro-optical properties of selenium with optical absorption measurements proved unsuccessful; although Pfund had good reason to believe that such a relation should have existed.[50]

His experiments on the sensibility of selenium cells thus gave him reasons to believe that the function of the selenides was not primary to the action of a selenium cell; although their presence was assumed by him to be necessary.

Turning to Bidwell's theory as expressed in an 1885 paper[51] Pfund pointed out a weakness:-[52]

> 'In Bidwell's theory the phenomenon is explained by assuming that light facilitates the molecular rearrangement in the surface layer of a selenide "through which an electric current is passing."* The experiments just described show that apparently the changes in resistance occur independently of the flow of current.'

Pfund had made use of the fact that a selenium cell took some time to recover from illumination, and had shown that the behaviour of a cell after illumination was the same whether or not a current had passed through it. This was an important

---

*Pfund's emphasis and parenthesis.

conclusion; but more importantly Pfund raised a greater difficulty. For as he indicated, Bidwell's theory found it 'most difficult to account for the role played by the large excess of free selenium, whose presence is absolutely necessary to the development of sensibility in a cell.'[53] We have already discussed Bidwell's picture and have noted that selenium played a structural and a chemical role but Pfund was quite right, such a large excess was hardly necessary. Yet Bidwell had shown[54] and Pfund had confirmed[55] that maximum sensitivity was obtained with a selenide content of about 3%; Pfund therefore found it essential to rethink the theory of the action of light on selenium. (The role of selenides in producing high sensitivity was not discovered).

Pfund's development of his ideas gives us a glimpse of a 'halfway house' between Bidwell's electrolytic theory and Brown's extension of a description based on allotropes. Pfund assumed that electrolytic conduction in selenides provided the current path; ascribed a definite role to the selenium; accounted for the fact that the action of light produced a change in the cell whether or not a current was passing; and gave a possible explanation of the independence of the position of maximum sensibility with respect to the metal of the selenide. Pfund couched his explanation in the following terms:-[56]

> 'Granting that in a selenium cell most, if not all, of the conduction is electrolytic in character, due to the presence of a selenide, it follows that there is an actual motion of the components of the selenide towards the electrodes of the cell.
>
> Any cause which will increase the velocity of these components will decrease the resistance of the cell. Selenium is known to exist in at least four allotropic modifications,[57] the metallic or crystalline form being represented in the selenium cell. As . . . . light affects the character of certain crystalline compounds . . . . light, in falling upon selenium, might also change its crystalline character, and that this new modification might offer less resistance to the components of the selenide as they wander towards the electrodes, thereby producing indirectly an increase in their velocities, which is equivalent to a decrease in the resistance of the cell. This view gains in plausibility if, with Bidwell, we think of the particles of selenide being packed in between the particles of selenium. Assuming that this new modification of selenium is stable only in light, it would revert to its original condition when light is cut off, the change taking place more rapidly at first and more slowly afterwards (comparable perhaps to the molecular changes in soft iron when the magnetizing force has been withdrawn). This would decrease the velocity of the components of the selenide, which would mean eventually bringing the resistance of the cell back to its original value.'

Pfund's theory highlighted serious difficulties in Bidwell's, namely the importance of selenides and the role of selenium; but he still retained the fundamental assumption that electrolysis was the seat of the electrical properties of selenium. However his re-emphasis of the importance of the various allotropes[58] pointed the way to an alternative theory of the electrical and electro-optical properties of selenium. Although in 1909 Pfund was to write,[59] 'At the present time it is quite generally acknowledged that the conduction in selenium is electronic and not electrolytic in character,' in 1904 the electron theory of solids was not sufficiently developed, and perhaps not sufficiently well known for it to be applied, even tentatively, to the case of selenium.[60]

In the same year as Pfund's paper, (1904), Berndt also produced the results of his experiments on selenium cells;[61] and he rejected the explanation in terms of selenides and electrolysis.[62] Beginning with pure selenium[63] he showed that it still retained its sensitivity to light; thus bringing into stark relief the role of selenides. He, like Pfund, referred to Bidwell's theory, writing in his introduction:-[64]

> 'Seit den Untersuchungen von Bidwell[65] war man meist der Ansicht, dass die Widerstandsabnahme von Selenzellen bei Belichtung auf chemische Prozesse zurückzufuhren sei.'

Berndt pointed out that Bidwell's cells included materials that combined with selenium and that if a cell was made using components that did not react with selenium and if the selenium were as pure as possible, then one could determine whether or not selenides were vital to the action of cells.[66] Since he knew that carbon did not react with selenium[67] a selenium cell with carbon electrodes would test Bidwell's theory for 'der Theorie von Bidwell durften also Selenzellen auf Kohle keine Lichtempfindlichkeit zeigen'.[68] He employed cells with carbon as electrodes and glass substrates on which his pure selenium was deposited[69] and was able to demonstrate that these behaved in substantially the same manner as Bidwell's cells.[70] Ignoring for a moment the possibility of impurities already present in his selenium, it can be seen that he was driven to the conclusion that selenides were not necessary to the development of the light-sensitive property of selenium; although he did not rule out the possibility that oxidation processes might be enhanced by the action of light.[71] Nevertheless in his conclusion he claimed that the effect of light on the conductivity of selenium was not a chemical process and finished his paper with the words:-[72]

> 'Da die Abnahme des Widerstandes bei Belichtung durch chemische Vorgänze nicht zu erklären ist; habe ich die folgende Hypothese gebildet: Ich

> Vermute, dass krystallinische Selen in zwei Moifikationen existiert, welche in dynamischen Gleichgewicht miteinander stehen; durch Belichtung wird dieses allmählich verschoben, nach Aufhörer der Belichtung kehrt der uhrsprüngliche Zustand allgemeinen allmählich wieder züruck. Wird die Zelle, aber irgendwie strapaziert, so bildet sich von der einen Modifikation soviel, dass ein Teil derselben einen stabilen Gleichgewichts-zustand annimmt und an dem dynamischen Gleichgewicht nicht mehr teilnimmt, oder - wenn die Belichtung weniger stark war, dass das Gleichgewicht erst nach längerer Zeit wieder eintritt. - Eine Entscheidung über die Richtigkeit dieser Hypothese ist vielleicht durch Untersuchungen der Empfindlichkeit bei möglichst zu erwarten, die ich, sobald ich durch andere Arbeiten nicht mehr verhindert bin, in Angriff nehmen werde.'

Pfund's and Berndt's papers although not containing definite refutations of Bidwell's theory, for there were too many unknowns in their experimental equations, began to amass circumstantial evidence against it. Berndt was 'bolder' than Pfund. However both suggested further work: Pfund pointed to the need to examine the absorption spectrum of selenium to establish, if possible, a link with the sensibility curves; and Berndt put forward a more significant test - the measurement of the sensitivity of selenium over a wide temperature range. Evidently if considerable sensitivity remained at low temperatures then considerable doubt would be cast on a chemical hypothesis; for the rate of chemical reaction decreases rapidly with decreasing temperature.

Thus, in spite of Martin's comment,[73] it is evident that if Bidwell's theory was not entirely dead by 1904 it was, at least, breathing its last breath.

## 3. The Work of Brown - A Methodological View.

As has been mentioned above (p 164) Brown[74] sometimes alone and sometimes with a co-worker produced a series of papers concerned with the electrical properties of selenium. The majority of his works were brief, although occasionally a longer publication appeared in which the work of previous papers was summarised and collated. For example a paper of 1908[75] contained work of the previous three years and an extensive quasi-theoretical paper published in 1911[76] developed a picture he had outlined previously. This method of reporting gives his researches a certain coherence; but it is impossible to decide, however, whether the coherence derived from an inductivist approach or whether he subscribed to a theoretical framework which controlled the course of his experimental work. Without unpublished material, apparently non-existent, only a study of public sources can provide us with a picture of his methodology. From this it can be seen that Brown's approach changed sometime around

1914 - 1915 when he began to investigate the optical properties of single crystals of selenium. Upon finding that these behaved similarly to microcrystalline material he abandoned his first theory and substituted one based on the electron theory of conduction. The former theory seems on the face of it to be purely Baconian in origin in that he moved from observation to theoretical generalisation; while the latter experiments he did were directed at verifying a previously adopted theory. His later papers, therefore, present a different aspect to us, than do his earlier writings. It is possible, however, to offer an interpretation of Brown's methodology that puts all his work into similar structural form.

Brown's longer papers were faithful reflections of the matter in his shorter works - indeed the suspicions cannot be avoided that asserting priority of publication formed a large part of his chosen method of presentation[77] - and they are good sources for an examination of the development of his experimental and theoretical ideas and will, therefore, be used as such.

All of Brown's work on selenium to 1911 can be seen as being in support of the theory that he published in that year. It was well known that three or possibly four allotropes of selenium existed[78] and that under some circumstances they appeared capable of changing one to another; temperature certainly and pressure possibly could produce this effect. The resistance of the allotropes differed markedly; a fact that first Siemens[79] and then Berndt[80] and Marc[81] used in their accounts of photoconductivity.

If we assume Brown was acquainted with these ideas, then his researches take on an ordered aspect, leading smoothly to the establishment of his first theory. Although there is no direct evidence in support of this assumption we know from a comment in a 1905 paper[82] that he had made a search of the literature connected with selenium and must surely have read the allotropic theory. The attractiveness of this idea had been enhanced by the refutation of the electrolytic theory.

However there were severe problems to solve. There was little evidence that light could act directly on selenium to produce any changes, visible or otherwise, in its physical and chemical condition. Bidwell's attempts to detect such alterations had not been successful. Brown at no stage published any work connected with this problem but appears to have utilised a roundabout line of reasoning to support his own theory. We can express his presumed reasoning symbolically.

If $A \rightarrow B$ and $A \rightarrow C$ then (maybe) $A \rightarrow B \rightarrow C$ and
if $D \rightarrow C$ then (perhaps) $D \rightarrow B \rightarrow C$

If 'C' is identified with change of resistance; 'B' with modification of allotropic form; 'D' with illumination; and 'A' with any effect that changes the resistance of selenium: then if in 'A' we have any effects that can be shown to produce allotropic transformation then, maybe, we have circumstantial evidence in support of an allotropic theory.

Applying this type of reasoning to Brown's experimental papers allows us to present his work in more sympathetic light than merely dismissing them as 'Baconian'; although the published works themselves contain no overt statement of theoretical intent until 1911 and could be laid aside as 'Natural History'. Thus his 1908 paper contains a list of experimental situations which, in the light of the above argument, are arranged to provide the circumstantial supports for the allotropic theory. Brown there reported the results of applying six agencies to selenium cells:[83] pressure and light sensitivity as a function of pressure; temperature and light sensitivity as a function of temperature; hydrogen peroxide and radium rays.

Brown's expressed reasons for testing all these agencies and combinations of them do not support the assumptions we have made concerning his methodology; but if the only purpose of the experiments was 'to examine the effects of various agencies that change the resistance of the selenium cell and to correlate them in so far as possible'[84] why should he have limited himself to merely a few possibilities? We cannot but express reasonable doubt but that he was searching for, or thought he already had, a consistent, general explanation for the electrical and optical properties of selenium. For he wondered whether all the resistance changes noted were due to the same cause but cautioned 'we cannot completely correlate our results but we hope that in the near future an hypothesis may be set up which will satisfactorily and completely explain all the various selenium phenomena'.[85] That he was considering a general theory, perhaps based on allotropes, is suggested by the final sentence in his 1908 paper. That, in so far as electrical conductivity is concerned, 'all these conditions seem to take the selenium to a certain equilibrium state'.[86] It seems not unreasonable then that his work was controlled by an assumed theory, and that the methodology outlined is applicable to Brown's researches where he lacked direct evidence for his assumptions.

## 4. Brown's Allotropic Theory.

In the previous section we have seen that if we make an assumption about Brown's knowledge and his methodology then his experimental work to 1908 was concerned with providing, in an oblique fashion, the factual basis for an allotropic theory. The methodological assumptions were based on Brown's presumed knowledge of the literature and also on the doubt that the relationships examined were chosen without the benefit of some sort of theoretical framework.

While it is difficult to believe that a Baconian approach would allow the examination of just those properties necessary for the support of an allotropic theory of electrical conduction, Brown's own introduction to his extensive paper of 1911[87] indicates an inductive approach.

> 'In a paper by Brown and Stebbins[88] it was shown that the light sensitiveness of a certain selenium cell was a function of its resistance whether that resistance was conditioned by temperature, pressure, light or other agencies. This conclusion, together with the results of recent investigations, has led me to formulate an hypothesis for explaining the changes in the electrical conductivity occurring in light sensitive selenium.
>
> The hypothesis is that all light-positive and light negative varieties[89] consist of various mixtures of three kinds of selenium which we will call A, B and C, and that under the action of light A is changed into B and B is changed into C according to the reaction
>
> $$A \rightleftharpoons B \rightleftharpoons C$$
>
> and that the changes in both directions are proportional at all times to the amount of the changing material.'

The basic assumption that selenium contained three allotropes that were in mutual equilibrium was founded not on direct evidence[90] but by analogy with the properties of sulphur. Brown wrote that as there were three components in sulphur which were mutually in equilibrium under the effects of pressure and temperature, then 'it would not be surprising to find later that the three components of light sensitive selenium may be identified and studied as separate allotropic forms.'[91]

In addition to this fundamental assumption Brown introduced four more, for some of which there was scant justification. The assumptions were:-

1. That the sensitive layer of selenium was thin enough for there to be a uniform intensity of light throughout the layer.[92]
2. That the conductivity of A kind approached zero, that of B metals and that of C was very much less than that of B.[93]
3. That if $\alpha_1$ and $\beta_1$ are the rates of change of A into B and B into C and $\alpha_2$ and $\beta_2$ are the corresponding reverse changes of C into B and B into A then $\alpha_1/\alpha_2$ and $\beta_1/\beta_2$ should be expected always to be increased by the action of light.[94]
4. That the conductivity of the selenium depended on the amount of B only and that the homogeneity and uniformity of the mixture of the three kinds should not affect the conductivity which would be given by

$$\frac{1}{r} = K_1 B$$ [95]

From this relation and five further equations Brown could derive an expression for the quantity of B as a function of time, and hence that the current would be represented by

$$i = K_1 \Big[ L/N + c_1 . \exp(m_1 t) + c_2 . \exp(m_2 t) \Big]$$ [96]

While in principle the parameters in the equation were capable of independent measurement and hence the form of the current-time curves were derivable from a base not within the theory itself, in practice Brown was driven to choosing the values of the constants to give results that agreed with experimentally determined relationships.[97] He was, therefore, forced to adopt what was, in effect, an elaborate 'curve-fitting' exercise. As he wrote:-[98]

> 'By a method of approximations[99] and guesses I have found specimen arbitrary values for the rates of change, which when taken with appropriate values of the other constants will establish the characteristic ways in which the conductivity i, will vary with the time of exposure to light.'

Reproduced below is Brown's Fig. 1.[100] illustrating that several types of response could be represented by his formula. Case 2 he rejected on theoretical grounds[101] while the others were considered to represent actual possibilities.
The form of the curves cannot be compared in any simple fashion, for although they depended entirely on the values of the constants mentioned above, these were themselves functions of a number of variables and constants, 18 in all.[102]

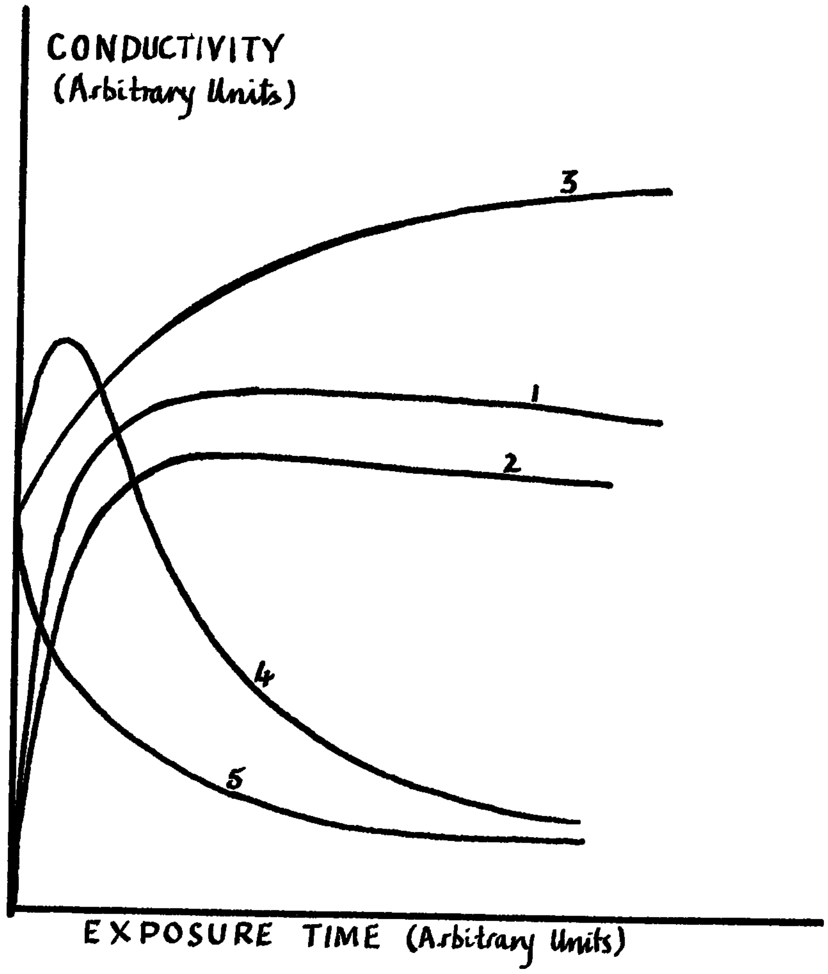


Fig. 3. Typical Responses of Selenium Cells: Brown's Theory.

Brown was later, (see section 5 below), to present empirical relationships between conductivity and time which by their correspondence with the theoretically derived curves were adduced as confirmatory evidence for his theory. He felt able to give a confident interpretation of his mathematics. However even if the fundamental assumption was correct, the additional assumptions he introduced rendered the final exercise '<u>ad hoc</u>'. For without the essential, independent verifications of the assumptions his theory became a conjunction of conditional statements; rendering his argument circular. The final 'truth' was interpreted as supporting the assumptions.

However notwithstanding the logical weaknesses of his argument Brown claimed that:-[103]

> 'The theory proposed is simple and attractive in so much as it rather implies that all the agencies that affect the conductivity of selenium produce the same kind of change in the selenium, namely a variation in the rates of interchange. Or stated in other words the selenium is in equilibrium under a variety of conditions. Each agency merely acts in a way to alter the equilibrium by changing the rates.'

Brown was, of course, overstating his case. Since his theory did not examine the underlying mechanisms of conduction in selenium generalisations to a variety of phenomena were out of order.

However this criticism is perhaps a little unkind. Brown did not claim to examine the electrical behaviour of selenium <u>per se</u>; he was, in effect using electrical measurements to investigate what he saw as the fundamental property of selenium; namely that the concentrations of its three allotropes were sensitive to the actions of various physical agents. He was simply searching for a 'mechanical interpretation of the theory'[104] and viewed the changing conditions of equilibrium as due to a 'distortion' of the selenium.[105] Hence the study of the change of conductivity could be regarded 'as merely a study of one of the processes taking place while the new equilibrium is being established.'[106] In spite of his detailed treatment and the confidence he expressed, he, in fact, added little to the understanding of the basic property of photoconductivity in selenium. His picture remained diffuse and ill-founded; a view illustrated perfectly by his verbal description of his theory. He wrote:-[107]

> 'Suppose a selenium cell in equilibrium in the dark in a condition which we will call $\phi$ . Next expose it to intense light and as a result of the existing distortion it changes <u>according to certain laws</u>* toward a new equilibrium condition which we may call $\theta$ . The changes can be shown by curves. Finally remove the selenium to the dark and again due to the distorted condition of the selenium it will return to its former dark condition $\phi$ . . . . The general movement of the change in the first case may be said to be in the positive direction and in the second case it may be said to be in the negative direction. The changes in the negative direction . . . . may be said to be the reciprocal of the changes in the positive direction and the time taken for the selenium to go from $\theta$ to $\phi$ should be of the same order of magnitude as the time required for the selenium to go from $\phi$ to $\theta$'.

---

* My emphasis

This account is, of course, an alternative statement of the mathematical formulation and conforms with it; for the words and the mathematics are complementary modes of expression. The description does not represent, in any real sense, an explanation of the light sensitive properties of selenium, indeed it is difficult to understand the rationale behind some of the phrases. Why should changes in the 'negative direction' proceed at the same rate as those in the 'positive direction'? There is no compelling reason for this assumption, only that he found it necessary in order that he could 'fit' his theoretical curves to the experimental examples.

Brown suggested experimental tests of his theory. If, for example, the light sensitive properties were as in Curve 4, above, then other agencies than light 'should in all probability show the same two changes'.[108] Indeed if the changes in conductivity were to be explained by the same mechanisms in all cases then this would seem to be a necessary conclusion; but Brown went on to write that 'this conclusion is clearly not required'.[109] Whether he was referring to an experimental or a theoretical situation he did not make clear, but the tone of his words indicate that he recognised the shortcomings of his theory. For he suggested that the changes produced by light could be reproduced mechanically 'if there were a sudden application of mechanical pressure of the right amount'[110] and that 'the same argument would apply to the agencies of temperature and differences of electric potential.'[111] Implying, thereby, a critical test of his theory; a test which when carried out cast doubt on his theory, (see below p 200 ).

## 5. Experimental Justifications for the Allotrope Theory.

From a purely mathematical approach Brown now turned to the experimental justification of his theory; or at least, that is how his paper was organised. He was strongly attracted to a property of selenium that was not within the confines of his theory; that is the marked dependence of sensitivity on resistance. He was impressed with the 'striking relation between the resistance of selenium and its sensibility to light'[112] and quoted a series of results[113] that indicated such a relationship quite clearly, even though that was not the intentional outcome of the measurements.[114] However, like previous workers, Brown was careful to point out that the properties of selenium were variable and recorded some empirical relations that had been found linking sensitivity with resistance as examples of 'diverse facts concerning selenium which do not seem to [lead] to any conclusion'.[115] The variability, he thought, could be due to many reasons; different types of selenium; non-comparable experimental conditions; construction of the cells and so on.[116] Also divergent properties could have been a result of impurities present in the selenium and, what was for him an important question, how deep was the penetration of selenium by light.[117] The last he was to answer eventually[118] at the same time casting doubt on his own theory. He considered that the variability in the conductivity/illumination relationships found by different workers[119] demonstrated the 'futility of [the] search for a simple universal law connecting the conductivity of a selenium and the intensity of illumination'[120] and thus it was 'necessary to look to other relationships . . . . to connect the facts by simple laws'.[121] In accordance with his theory these 'other relationships' were to be the time dependences of the sensitiveness of various cells and for the time being the 'striking relation' was ignored.

The experimental results occupied some dozen pages of the 1911 paper and were mainly concerned with establishing the form of the conductivity versus time curves for different levels of illumination and for various types of cell. Brown's concern was to demonstrate that his theoretical curves accurately reproduced the experimental ones and in this he was not unsuccessful. He discovered cells whose characteristics were mirrored by each of the curves given on p 184 above, and in his discussion wrote:-[122]

> 'I may state that I found data for curves of no other character to be obtained, either from the theory or from any variety of selenium that has come to my notice. I regard the striking similarity between these experimental and theoretical curves as important evidence in favour of the proposed theory. It seems a waste of time to try to fit the comparison curves more accurately until further information is obtained concerning the depth of penetration of selenium by light.'

Three points of importance are contained in this extract.

First in spite of his confident claim that the evidence was strongly in support of his theory it must be emphasised that his theoretical structure taught nothing new, and, in itself, suggested no experiments other than those needed to establish the assumptions. As the theory developed into a 'curve fitting' exercise it is evident that the choice of constants was made to <u>produce</u> curves that fitted the empirical findings. Brown was not unaware of the difficulties inherent in his theory but he tended to underplay the problems at this stage in his work.

That all causes produced similar effects implied a single explanation, but Brown noted that the effects of other agencies was not invariably akin to those of light. He wrote:-[123]

> 'There are some instances where no relation can be traced between theory and experiment. The ordinary effect of a rise of temperature is to produce a change in the conductivity in the same direction as that by light. But in the high sensibility cell the change by temperature is opposite to that of light. But since the temperature effect is in the same direction as in the pure metals and of about the same magnitude, we may say that the temperature effect is metallic in nature and refuse to explain it further.'

Well that was a novel way to overcome a fairly important detail! It is difficult to believe that he held the opinion that under these circumstances selenium had a metallic character for while the temperature coefficient of resistance may very well have been similar to those of metals the resistivity certainly was not. High sensibility cells were equated with high resistances and resistivities, many orders of magnitude greater than those of metals. However while this discrepancy was an isolated instance in the case of light-positive selenium,[124] it still represented a serious blow to his aim for a single general theory. Confirmation or refutation of his ideas was not forthcoming from observations on the effects of pressure for the results were too inconclusive to allow any comparison with theory.[125]

Brown conceded that even if the theory satisfactorily explained all the observed phenomena, which indeed it did not, it said nothing about why the rates of change of the different varieties were variable. While he suggested possible causes for the variations, evidence was lacking. In his own words:-[126]

> 'It will still remain to be explained why different varieties should have different rates of change. It may turn out that these different initial rates of change may arise from impurities which act as catalytic agents, or it may be if peculiar initial arrangements of the components are once established in the process of making, that there is an accompanying pressure or potential effect which maintains that peculiar arrangement.'

The second point of interest is the suggestion made for further measurement, on which we have already remarked.[127] That is that the effective depth of penetration of selenium by light should be determined. Brown gave as his reasons for this measurement that absorption of light by selenium would confound his theory,[128] although he gave no reasons for this. That this was the case underlines the fact that the mechanism of the interaction of light with selenium, that is in the allotropic theory the effect of light on the change rates, was a mystery. He evidently did not believe that light acted directly to produce its electrical effect but, as in Bidwell's electrolytic theory, modified the physical structure of the selenium. Brown's suspicion that the action of light was on the outermost layer of the selenium, as indicated by the mechanical structure of the cells, was later confirmed. The thought does not seem to have struck him that the absorption of light by selenium could produce a direct electrical effect and that this was a less oblique assumption than any he had made.

The third point of interest is not contained overtly in the passage quoted on p 190, but lies hidden in the phrase 'I regard the striking similarity . . . . in favour of the theory'. While curves 1, 2 and 3 presented no problems and 5 was not too serious to deal with, curve 4 could be given an interpretation that included polarisation effects. (Such interpretations had been suggested earlier.)[129] Brown was impressed with 'the remarkable decrease in the conductivity'[130] which was 'just as remarkable as is the enormous increase at first',[131] and suggested that this had an important bearing on his theory. In his opinion:-[132]

> ' . . . . it is quite necessary to know if this decrease in the conductivity represents a genuine change in the selenium or if it is a polarisation phenomenon. This question is a particularly legitimate one in view of the fact that many selenium cells show extreme polarisation under the action of light and the electric current.'

Brown's experiments settled this question conclusively for his cells for he demonstrated that the action of light or electricity did not result in any polarisation.[133] While this result did not, of itself, refute the electrolytic hypothesis, taken together with the previous work of Pfund and Berndt[134] the idea that such action could account for the behaviour of selenium became more and more untenable.

## 6. The Allotropic Theory - A Summary.

It has been argued that Brown's work displays a pattern of thought that goes counter to the apparently Baconian structure of his researches. The experiments he chose to do seem almost random unless we assume he was interested in establishing the allotropic theory of the light sensitivity of selenium on a firm foundation. We have demonstrated some reason to believe that he knew of the theory well before he produced his own version, probably before he began his own experiments. Being unable to find firm independent evidence for the assumptions he made he was forced to invoke a rather complex line of reasoning to 'prove' his theory; compelled, thereby, to rely on circular arguments and to carry out a curve fitting exercise rather than relying on calculations from first principles.

He relied on circumstantial evidence to establish the reliability of his assumptions and the accuracy of his theory; even the manner of testing used by Brown never removed the 'insubstantial' quality from the theory. While the basic tenets of his arguments rested on physical assumptions that were, in principle at least, measurable, no one carried out the obvious investigations; for example to determine independently the values of the rate constants, or the quantities of the various allotropes present in light-sensitive selenium. While he subscribed to the allotropic theory, Brown always relied on indirect verifications of his ideas, often with an inherent circularity.

For example, shortly after his major theoretical paper was published, he produced another work[135] in which he claimed: that only one allotrope conducted; that the change in conductivity was proportional to the amount of changing material; and that the action of heat was essentially the same as that of light but not identical to it.[136] But again, these conclusions were not based on direct measurements, but on the shape of recovery curves,[137] (i.e. the form of the conductivity/time graph after the removal of illumination). Even though this paper was close in time to the major theoretical work, it contained strong hints that the allotropic theory was unsatisfactory. The work on the recovery curves indicated that the rates of change in the positive direction only were affected by light,[138] a conclusion contrary to the assumptions he had originally made.[139] He found that the recovery curves were sensitive to the initial quantities of illumination, leading him to the suggestion that only a small proportion of the selenium was affected by light at low intensities and that, maybe, 'the amounts...[of the allotropes]...are partially fictitious'.[140]

To summarise Brown's allotropic theory we may remark that had it been based on clearly defined and measured parameters, it would, indeed have presented a plausible aspect. It went through a little development by others but did not survive long past 1913. Although carefully developed it was, in fact no more than an ad hoc theory, in contrast to Bidwell's electrolytic hypothesis which was, at least based on independent observations of the fundamental assumptions; Brown's theory never broke out of its own confines.

## 7. Movement from the Allotropic Theory.

Whatever may be the verdict on Brown's methodology, whether he was led to his ideas inductively as he suggested or whether he was guided by theoretical considerations, there can be no doubt that after 1911 his work led inexorably towards an electronic theory of photoconductivity. That is towards a description that involved a direct interaction between light and electrons rather than by changing the quantity of the conducting component of selenium.

The path Brown followed to an electron theory is clearly discernible. He began by measuring the depth of penetration of selenium by light;[141] a measurement that followed his discovery that the effects of light and heat on the resistance were slightly different.[142] He had maintained that the thickness of the sensitive layer would be important in his theory an idea he may have drawn from Pfund who in 1909 had remarked on the significance of absorption for a 'resonance' theory.[143] Pfund had pointed out that the depth of penetration may well be a function of the wavelength of light, and had made some tentative measurements of absorption, as we have already noted.[144] As Brown had ignored the possible complications of absorption in the selenium when he developed the allotropic theory, he and a colleague in 1913, commenced measurement on the dependence of the sensitivity of selenium on the wavelength of light,[145] intending to provide an explanation in Brown's terms. Finally his substitution of single crystals of selenium for the polycrystalline material commonly in use, and his demonstration that these behaved in identical fashion administered the <u>coup de grace</u> to the allotropic theory. His rejection of the allotropic theory was covert, it was completely ignored for example in a paper of 1915.[146] We cannot know why he delayed so long before introducing a direct interaction electron theory, for his association with Richardson[147] and Pfund[148] indicates that he was well acquainted with the Lorentz electron theory. However while the electrons were visualised as 'free' within a conductor it was difficult to account for many of the facts of conduction in selenium.[149] Meanwhile the allotropic theory served a purpose; perhaps as a model, perhaps as a learning device;[150] but with the discovery of the photoconductivity of single crystals and that the reduction of resistance was not restricted to the point at which light was incident, the idea of a shifting equilibrium between different allotropes became less acceptable. Historically, although work on single crystals clinched the matter, Brown began to shift from his earlier theory following his and Sieg's investigations of the wavelength sensitivity of selenium already referred to.[151]

His first lengthy paper (1913)[152] on this subject was controlled by his 1911 theory but in his second paper[153] he was evidently moving towards a fully fledged electron theory of the photoconductive effect. Brown and Sieg demonstrated that the sensitivity of selenium was a complicated function of wavelength and not comparable from cell to cell.[154] Their measurements and Brown's theoretical insights allowed them to separate out the effects of time lags in the responses and recoveries of selenium cells and thereby suggest a test for a theory of selenium action based on the electron theory of another researcher.[155]

The conclusions to the second paper (1914) represent a significant move towards an electron theory; from no mention of the mechanism of conduction in the 1911 paper to a possibility that maybe the change of conductivity under the action of light could be accompanied by electron release, (within the material that is). From his earlier theory Brown had concluded that there were two sorts of change, rapid and slow, and that the balance between them produced all the experimental curves.[156] More importantly he believed that both changes were due to the same cause, that is alteration of the change rates. Now he was not so sure. For while he believed that the slow changes in conductivity were due to shifts in crystal structure,[157] (i.e. A to B, C to B and vice versa) he was now prepared to entertain the idea that the rapid changes were the result of electron release during these structural alterations; a dual theory. The results of his measurements on the wavelength sensibility proved impossible to represent by a simple set of mathematical postulates. Moreover the structure and properties of selenium seemed more complex than before;[158] for his analysis now seemed to require 'at least two separate light actions in the selenium'.[159] While 'the slow changes accompanying the light-action were the result of crystal changes . . [there was] . . doubt concerning the rapid changes. [It was conceded] that perhaps light might expel electrons from the atoms in the transformation of one component to another.'[160] His belief that changes in crystal form were associated with conduction changes in selenium led him almost to an adumbration of the role of non-localised although bound electrons. For we find the following passage:-[161]

> 'But if there is one significant conclusion that can be accepted as a result of the variation of the sensibility curves, it is that light does not act on the atoms as units. Rather a larger unit, no doubt of the order of a crystal unit, is the seat of the disturbance by light action.'

And[162]

> 'We are compelled to recognise crystal boundaries when dealing with the flow of electrons in selenium, possibly also in other elements. Otherwise there is no apparent basis for the unification of our knowledge.'

Here for the first time we find clearly stated the importance of the boundaries between crystals; and, of course, with this recognition the possibility that experiments could be devised to distinguish between bulk and surface properties.[163] (A problem which was successfully tackled in the 1920's by Gudden and Pohl.[164]) Recognising that 'the phenomena of light action are almost unique' he pointed out in his conclusion that 'unification of knowledge' requires a non-generalised solution to the problems. Perhaps he realised that his approach and that of others to selenium and related materials was unsatisfactory and that a fresh examination of the theoretical base was needed.

## 8. Single Crystals.

In a series of papers published in 1914 and 1915 Brown completely undermined his original theory and replaced it with one based on the theory of electrons. Of his papers published in these years four are of importance: 'The Seat of Light Action in Certain Crystals of Metallic Selenium'[165] in Philosophical Magazine, (1914); 'The Electrical and Photo-electrical and the Electro-mechanical Properties of Certain Crystals of Metallic Selenium',[166] 'The Nature of Electrical Conduction in Selenium to Explain the Recovery Curves,'[167] and 'Some Experiments on the Nature of Transmitted Light Action in Crystals of Metallic Selenium',[168] in Physical Review, (1915). His use of single crystals enabled him to make something of a breakthrough in understanding the properties of selenium; for while he faced some hard technical problems, (growing crystals,[169] designing apparatus and so on), he was no longer tied to the use of very variable microcrystalline devices. As he put it in Philosophical Magazine:-[170]

> 'The advantages of a single crystal . . . . are perhaps obvious. The contact resistances are

> limited to the electrodes, and knowing this fact, the magnitude of such resistances can be determined. Also it makes it possible to locate the seat of light action as well as something concerning the nature of light action.'

In retrospect, of course, the advantages are indeed obvious, but Brown was the first to realise that this was the case. Other researchers were forced to 'make do' with naturally occurring materials or with devices constructed according to methods more reminiscent of the kitchen than the laboratory.

The sequential nature of Brown's approach to his subject allows us to give a chronological treatment of these papers. Investigating the relative significance of the electrodes and the bulk of the material Brown concluded 'that the light acts throughout the crystal, and that the conductivity is almost uniform throughout the crystal.'[171] As irradiating the specimen from the side on which the electrodes were situated or from the remote side made little difference to the conductivity change he was led to suggest 'either that the light penetrates the crystal without absorption, or that light on entering the crystal operates a mechanism which controls by secondary action the conductance of the entire crystal.'[172] However not only is it difficult to understand how light could act without being absorbed within the crystal it was also fairly obvious that the crystal was not transparent.[173] Hence the second conclusion should be the correct one.[174] Brown's use of the term 'secondary action' remains obscure for he did not explain the term satisfactorily. Taking the work to be discussed later and his earlier researches together it seems that primary action was the modification of the crystal structure of selenium while secondary action was the liberation of free electrons; but it is not possible to be sure. His own conclusion was:-[175]

> 'The fact that no light goes through the crystal compels us to believe that the crystal conductivity is controlled by sympathetic centres located throughout the crystal.'

In this work as in others, Brown discovered a new fact, one that he was to investigate further. He noted that the action of light in a crystal was transmitted to a distance. This 'amazing result'[176] was without any known explanation. Heat effects could not act quickly enough[177] and Brown thought that not only did single crystals display the same light sensitive properties as selenium cells but also they possessed 'a peculiar sympathetic structure limited apparently only by the crystal surfaces.'[178] He saw in the transmission of the light effect along a single crystal a 'new "Action at a distance" ' [179] as always he hinted at further experiments. Measurement of the rate of transmission of the effect should yield information concerning the mechanisms of transport: electronic transmission; elastic vibrations; or by 'the interaction of parts of the atoms moving with velocities approaching that of light.'[180] A crucial test would be, Brown thought, to determine whether the effect could be transmitted from one crystal to another.

Brown returned to the question in some later papers and was able to show that the light effect was transmitted across crystal boundaries, (provided, that is, that the crystals were grown in contact rather than put in contact.)[181] But however interesting this may have been what was important was his report that the effects of pressure and electric fields were not transmitted either along a single crystal or between crystals.[182] For him, and for me, this significant discovery refuted a claim of his earlier theory that all conductivity effects were, in principle at least, reducible to the same set of theoretical assumptions. His use of the known presence of allotropes in selenium was all-embracing; for it was possible to imagine that the actions of light, pressure, radioactivity and so on would all produce changes in the equilibria between the various components. Of course, when the light-effect was shown to be different in principle then this particular stretch of the imagination was unnecessary. Brown's reaction was admirable. He quietly revoked his own interpretations and turned to the electron theory of electricity for explanations. This theory and its relevance to the properties of selenium in particular and semiconductors in general at this time will be discussed in the following chapter.

I will close this discussion of the experimental work of Brown and his colleagues with a brief analysis of the fourth paper referred to above (p 201).[183] In this work Brown took up the question of the transmitted effects in single crystals of selenium and was able to state some startling, and advanced, conclusions. His determination of the velocity of the new effect at not less than 2cm/s was sufficient for him to conclude that it could not 'be transmission of a temperature change along the crystal'.[184] By the same token neither could it be ascribed to the 'equalization of electronic pressures throughout the crystal'.[185] If neither heat nor electrons were responsible for the transmitted effect Brown considered that only a 'mechanical' cause could be invoked.[186] (Here mechanical is to be interpreted as that which was not due to the action of heat or electrical forces.) He saw two alternatives. Either the light acts directly on the electrons tearing them free from the atomic structures thereby making them available for conduction or the light acts to create 'a certain instability throughout the crystal structure'.[187] In the first case either the electrons would disperse to all parts of the crystal or the increased concentration at the point of incidence would produce an effect analogous to that of increasing the quantity of gas at one part of a container.[188] In the second case the increased conductivity could result from 'an increased number of free electrons or a greater instability of the fixed electrons.'[189] Brown saw a distinct difference between the two possibilities. The first was largely independent of the crystal structure, while the second involved something akin to propagation through an elastic medium.[190] His experiments with light, mechanical pressure and electric fields led to conclusions which he regarded as notable. Indeed they were the only ones which he italicised. First:-[191]

> 'Thus we have the clear cut result that light action is transmitted along the crystal, but the pressure effects and the electrical potential effect, are not transmitted.'*

Second:-[192]

> 'The increase of pressure increases the light sensibility (i.e., the change of conductivity due to constant illumination) only when the pressure is applied to the part of the crystal where the conductivity is being measured.'*

Brown was impressed with these conclusions not for their own sake but for the deductions which he was able to draw from them. For him the fact that the effect of pressure was not transmitted implied

---

* Brown's emphasis.

that the enhanced conductivity that occurred at the point of application could not be due to free electrons. From this he was led to doubt that 'at atmospheric pressure' the conduction was due to free electrons.[193] Now while there was no real reason for this belief Brown was being driven by a reductionist argument leading him to the conclusion '<u>that electrical conduction in crystals of metallic selenium can not be due to the traditional free electron</u>'.* [194]

This surprising, and essentially correct, conclusion he saw as in no way opposed to the notion that in a metal the electrons were free as in 'the sense of the kinetic theory of gases,'[195] and he suggested that conduction in all non-metals was like that in selenium.[196] In this he was moving towards the same conclusion that was being reached in Germany, (see p 262).

Brown closed this paper with an outline theory of the conduction of electricity and the action of light on non-metallic crystals; basing his ideas on his experiences of selenium. He considered that, qualitatively at least, the picture he drew could account for the known facts, including the non-Ohmic behaviour of selenium. He wrote:-[197]

> 'The most satisfying unification of the experiments related that I have been able to conceive rests upon the hypothesis of conduction by electrons in semi-stable equilibrium. Scattered

---

* Brown's emphasis.

throughout the crystal structure are centers, . . . . in which are associated charges of electricity in almost unstable equilibrium. Electrons free to move about in the structure as gas molecules do not exist. True the electrons are fixed in number and position in the crystal structure, but the degree of their stability will vary with the agencies acting on the crystal. Electrical conduction consists essentially of a pulling out of these electrons from their moorings in the direction of the electrical stress. While out of position an electron might behave temporarily as a free electron in equilibrium with the heat and electrical forces about it . . . .

The fact that Ohm's law does not hold for these crystals or metallic selenium generally is against the free electron hypothesis. The conductivity increases very greatly as the electrical forces in the line of conduction increase, until a saturation value of the conductivity is reached.

On this view increased pressure or tension on the selenium reduces the electrons to an average lower degree of stability. Thus a given fall of potential across the crystal will be able to dislocate a larger number of electrons from their fixed positions, or will be able to use them on an average a longer time before they recombine.

Similarly, light by some mechanism yet undiscovered lowers the degree of stability of the electrons throughout the crystal or further the mechanism controlled by light frees the most unstable electrons throughout the selenium.'

Thus by dint of an effort that continued for a decade, together with a close knowledge of metallic conduction Brown gave a picture of the electrical properties of selenium that was remarkably close to a modern interpretation. He noted the fact that an application of Maxwell-Boltzmann statistics to the electrons in selenium led to contradictions;[198] and, if we replace 'lower the stability' by 'raise the energy' we can approximate the current view by Brown's words. Finally, unlike Bidwell, Brown changed his mind when experiments demanded it.

## 9. Brown's Use of Sources.

In the course of his publications on selenium Brown mentioned the work of some three dozen other researchers. From these he obtained a spectrum of ideas; from the starting point of theories to the processes required to construct reliable cells. Thus from Bidwell's work he learned how to construct good, sensitive cells;[199] from Marc's[200] and Kruyt's[201] publications he brought evidence for his allotropic theory; while from Richardson[202] and Nicholson[203] he derived an electron theory of the light-effect in selenium. There were, of course, many papers to which he made no reference either because they were unknown to him or because they gave him no new or useful information; in the absence of sources other than published work the question of his breadth of knowledge cannot be solved. While we can perhaps assume that he read much that was written on selenium he appears to have been ignorant of the work carried out by Koenigsberger[204] and Baedeker[205] on the conduction of electricity through solids. In a sense this is surprising, for Richardson, with whom Brown worked, thought the work of these men sufficiently important to give them some space in his book <u>The Electron Theory of Matter</u>, (1916).[206] However we have seen only in his later papers did he begin to realise that the mechanisms that he used to account for the electrical properties of selenium should also be applied in the case of other solid non-metals. Brown's concentration on the photo-conductive properties of selenium and his neglect of rectification and photo-voltaic effects delayed his realisation that the properties of non-metallic solids possessed common facets. Papers by Marc[207,208,209] and Saunders[210] gave Brown his justification for using allotropes of selenium and their relative importance in the light sensitivity. Strangely an extensive piece of work by Schrott,[211] (largely duplicating and extending the work of Marc and Saunders), was apparently unknown to Brown. The papers of these men, if put together, would constitute a sizeable publication, but for me, it is enough that they showed that an electrolytic theory was inadequate to account for all the effects of temperature and radiation on selenium. Schrott's interpretation did not agree with Brown's initial assumptions for he concluded that only the 'B' form acted as a conductor and was a light sensitive allotrope in its own right. He did not believe that any equilibrium, of the sort postulated by Brown, existed between the three allotropes but suggested that the light sensitivity of selenium was a purely electrical phenomenon.[212]

> 'Die Lichtwirkung dürfte in einer Ionisation des Selens B bestehen, welches bis zu einer Sättigung fortschreitet. Das Anwachsen des Widerstandes nach erfolgter Sättigung könnte vielleicht auf eine gleichzeitige Photopolymerisation zürückführen sein.'[213]

Schrott's suggestion of a saturation effect together with a reverse photopolymerisation has a flavour of electro-chemistry but was not worked out in detail. Marc's opinion, that the conductivity of selenium could be accounted for by two allotropes in equilibrium, was not sufficient for Brown; for he required two competing processes for his explanation. He appealed to analogy for more than two allotropes in equilibrium, comparing selenium with sulphur.

Brown's observations on the response of selenium cells to temperature, light and X-rays was confirmed by the work of McDowell,[214] Crum[215] and many others. Thus he could assert as experimental facts the various relationships expressing the variation of the resistance of selenium with temperature, light, time, radiation etc.; relationships which he was able to reproduce with his first theory.

His work with single crystals was spurred off by some experimental investigations by White.[216] White, working with blocks of selenium rather than thin cells, reached a conclusion that Brown found unacceptable, namely that 'the action of light on all selenium bridges* is to a large extent, but not wholly, to effect a change of resistance at the electrode contact.'[217] We recognise that, once again, the problem of bulk versus surface phenomena was raising its head, but while we recognise this now; Brown's theory depended on bulk properties. Thus to obviate contact problems, not only at electrodes but between microcrystals, Brown turned to single crystals and in so doing not only undermined his own theory but also pioneered the use of artificial single crystals of known composition and crystal structure.[218]

With the evidence of single crystals militating against an allotropic theory Brown was forced to consider an alternative. The electron 'resonance' theory, suggested by Pfund[219] and Ries,[220] although attractive had not been put into clear mathematical form; but in the year that Brown published his first work on the properties of single crystals Nicholson wrote a paper in which the theory was given a clear mathematical expression.[221] Brown acknowledged his debt to the work of Nicholson prior to introducing his own modification of the theory

---

* selenium bridges = selenium cells.

in 1915.[222] (It is interesting to note that the ideas of Nicholson were introduced to Brown by Pfund).[223] The relationships between Brown's and Nicholson's theories and with the electron theory of conduction in general will be discussed in the next chapter.

It is evident from the bibliography that a great deal of experimental work was carried out on selenium; the vast majority of it concerned with the optical properties of the material. Much of the work was known to Brown or repeated by him; his own really original contributions being the worked out allotrope theory and the use of single crystals.

While an examination of Brown's sources tells us clearly those which he knew; we cannot infer that the omission of a source implies ignorance of it. It is difficult to countenance the belief that a researcher, as indefatigable as Brown appears to have been, would have seen only those works that agreed with his own theory. Without more information than is contained in the published papers one cannot but suggest the, admittedly uncharitable, opinion that adverse theories were ignored by Brown; perhaps because he was so fond of his own. In one case at least he seems to have begun some work suggested by the researches of Pfund, without acknowledging the fact.[224]

Towards the middle of the second decade of the century Brown began to remark on the generality of his work. At about that time the rediscovery of earlier results on other photo-conductive materials and a reawakening of interest in rectification underlined the importance of Brown's thoughts, Some of this work will be discussed in the next section; meanwhile it can be noted that there are a great many questions posed but not answered in this thesis, for it may be that the answers to them represent substantial researches in their own right.

First the chemistry of selenium; how important and difficult was the purification of selenium for the researchers in the early 20th century? Brown remarked on questions of impurities in several of his papers but while referring to sources, gave little details of his own methods.[225] Was there ever any attempt to determine the reality of the equilibria between the three allotropes? That is did anyone ever attempt to determine the rate constants? Brown did not indicate any work in this area and did not carry out any himself. (I have not concentrated on Chemical or Physical Chemical sources in my research, in them may lie the answer).

In the physical area the most interesting question, and one that has been ignored in favour of a detailed study of Brown's work is the genesis and development of the 'electron resonance' theory. This will be discussed briefly in the next chapter but it is worth a long study. As noted above Brown eventually came round to this theory and, in the long run, the explanation of all the properties of conductors were seen to be reducible to the motion of electrons. This theory was rooted in the electron theory of metals and possibly in phenomena such as fluorescence[226] but a study of this theory, which is contained in many scattered papers, and sources is one for another worker in the history of semiconductors. It is probably on the 'direct trail' to band theory but Brown's work, which largely vanished, was always ingenious, occasionally original but, above all, represented continuous work over a long time scale and led him to the threshold of the modern view.

Selenium was not the only non-metallic conductor examined in this period. We find work being carried out on silicon,[227,228,229,230] galena,[231] bismuth and tellurium,[232] carbon,[233] copper iodide,[234] and a multitude of other solids. However little of this work was collated at the time and only towards the middle of the 1910's do we come across suggestions that all these substances had properties in common that could be explained by a single theory. Eventually it emerged that while metallic conduction could be accounted for more or less precisely by the Drude-Lorentz theory, albeit with some apparently minor shortcomings, the simple electron theory was a very inadequate tool to explain the properties of non-metallic, solid conductors.

In the following sections an outline is given of some of the work that was done on effects other than the photo-conductivity of selenium. The materials investigated were, generally, naturally occurring crystals that we now recognise as semiconductors, (galena, silver sulphide and so on); the properties studied were rectification, thermoelectric power and later photo-effects. A variety of measurement techniques were employed including the Hall effect.

## 10. Rectification.

The rectification properties of certain crystals continued to evoke interest throughout the period under discussion; with a considerable number of materials added to the list. The researches not only increased the known rectifiers but eliminated explanations other than purely electrical ones from the field. Although there was not a complete concensus, 19th century descriptions of rectification fell within three categories; viz: electrolysis, electric arc analogies and the effects of thermo-electricity.[235] While there were strong suggestions that rectification was a surface property complete agreement was not present. (I do not wish to imply that disagreements were voiced, for as was suggested in Chapter 2 the various researchers do not appear to have been familiar with each other's work). Lark-Horovitz claims that early investigations into the properties of 'many semiconductor - metal combinations . . . . as detectors. . . . [The] action of the detector was not completely understood and, with the mass production of radio tubes, interest in crystal detectors increased.'[236] However, be that as it may, an important step towards the reduction of the phenomena of semiconductors to a common theory was taken when it was demonstrated that rectification was a property of the materials and their contacts; and was, therefore, a property in its own right as was high thermo-electric power. Given that recognition, the observation could be made 'that high thermo-electric e.m.f., rectification, and photoconductivity are found together.' A link that Lark-Horovitz ascribes to Coblentz.[237]

The work of two men, prior to 1915, established many of the properties of crystal rectifiers; two men whose work was both typical of the investigations done and whose results were important in establishing the reality of a rectification effect distinct from thermoelectricity.

The work of Pierce is one of the few in the first decade of the 20th century singled out by Lark-Horovitz for a mention.[238] With a small number of other workers[239] operating independently of each other[240] the properties of crystal rectifiers were standardised. To a great extent each researcher seemed to be largely unaware of other work, although many mentioned the pioneering work of Braun.[241] If they understood his paper, and there is no reason to believe that they did not, then they would have known of his demonstration that rectification was not an electrolytic phenomena and also his less clear demonstration that thermal effects had no part to play. Nevertheless several pieces of research were concerned with refuting the thermoelectric theory as well as widening the list of known rectifiers and there was much, apparently unintentional, duplication of effort. The work of Pierce is typical of that which was done.

He produced three papers on the subject of rectification by crystals, all carrying the title 'Crystal Rectifiers for Electric Currents and

Electric Oscillations' and all published in Physical Review between 1907 and 1909.[242,243,244] Pierce was primarily concerned with the search for rectifiers rather than attempting to explain their action but in the course of his work he was able to refute the thermal theories of rectification. Thus in his first paper, concerned with the properties of carborundum, with the aid of some effective but unrefined experiments[245] he showed that thermoelectric effects were not the cause of rectification. In the same paper differences of resistance as a result of thermal gradients were shown to be insufficient to account for rectifying action.[246] Investigations on molybdenite, reported in his second paper, were even more conclusive for he found that rectification and thermoelectricity were in opposite senses and 'the opposition of the rectified current and the thermal current renders the thermoelectric explanation of the phenomenon of rectification highly improbable.'[247] Admittedly he was not too clear what he meant by 'opposition' of the two effects. His third paper concerned with iron pyrites assumed the refutation of thermal effects as the cause of rectification. Recognising that his own work and that of another researcher[248] showed that there was great similarity between different materials he concluded:-[249]

'We are apparently dealing with the same kind of

> phenomenon in the case of all the crystalline substances used as detectors for electric waves. The fact that all the crystal rectifiers have also large thermoelectromotive forces against the common metals may be due to the fact that rectification and thermoelectricity have a common basis . . . . if we suppose that the surface of separation of two conductors has such a character as to permit the passage of electrons more easily in one direction than in the opposite. . . . the boundary will act as a rectifier . . . .; it will also give rise to a thermoelectric force when heat is applied to the boundary, provided the velocity of the electrons is increased by an increase of temperature.'

Thus Pierce recognised the existence of a class of materials defined, in a manner like metallic conductors, by their electrical properties; but by properties which were rather more complex than simple resistance. The second part of the extract, while hardly a theory, was the closest he got to a theoretical description of rectifier action.

In 'Crystal and Solid Contact Rectifiers'(1909)[250] Flowers offers some intriguing results, more intriguing now than then.[251] With some neat experiments he showed that rectification was a surface action, either at the surface itself or in a film, and was independent of the material of the contact its shape or size. Rectification could be destroyed by high reverse voltages, (in his case high was about 15 volts) with apparent destruction of the film; and intriguingly 'The rectifying film can be produced artificially by electrochemical treatment with amorphous sulphur.'[252]

The last is a fascinating point. He had attempted to produce rectification in a non-rectifying galena crystal by various forms of chemical treatment. He reported that a copper point carrying amorphous sulphur[253] 'when set on a galena crystal that previously showed no rectifying properties would at first show little conductivity, but the passage of current first in one direction and then in the other produced in a few minutes a very fair degree of rectification <u>but in the opposite direction to that formed in native crystals</u>*'. Could he have been on the way to discovering the effect of variation from stoichoimetry on the electrical properties of semiconductors? Unfortunately[254] he was more interested in the applications of crystal rectifiers to practical problems than in investigating the physics of the devices as his 1914 paper indicated.[255]

Thus the controlling features of rectification were established by workers such as Pierce and Flowers. Rectification was a marked property of certain crystalline substances, generally compounds, although silicon had been shown to be a rectifier.[256] Rectification was shown to be a surface property and while dependent on the state of the surface was generally independent of the contacts used. From the

---

* Flowers' emphasis.

similarity of results from many different materials Pierce had suggested that the same mechanisms operated in all cases; and further that rectifying action was a result of barriers at the surface, a suggestion supported by Flowers. Finally while thermoelectricity was shown not to be the cause of rectification both phenomena should be explicable by the electron theory, for with good rectification went large thermoelectric electromotive forces, an inescapable link.

## 11. Photoconductivity in Materials other than Selenium.

There was in this area a considerable effort made. Lark-Horovitz refers to the work of half a dozen researchers,[257] who contributed a little knowledge, but no one man concentrated his efforts in this direction. Some of the early work by Joffe and Röntgen was, according to Lark-Horovitz,[258] of great significance to the later work of Gudden and Pohl, a claim that was confirmed by Pohl.[259] The metal halogens were particularly important to Gudden and Pohl who were systemisers as well as first class researchers [260] but during the period to 1920 Case and Coblentz began to search for photoconductivity. They began their work in the second decade of this century and continued past the end of the period to which this thesis is devoted. They both went some way to recognising the common quality of the property of photoconductivity in materials definable as semiconductors, but were more interested in the identification of photoconductive materials; they added nothing at this time to theory. (Case's paper of 1917 is a good illustration of his interests.)[261] The full value of their work does not become evident until the 1920's, when the optical properties of solids were used to great effect by Gudden and Pohl.

## 12. The Hall Effect.

As has been discussed[262] the Hall effect was not immediately explicable in the 19th century. However the introduction and ready acceptance of the electron theory provided a simple explanation. While the account was, in principle straightforward, the properties of semiconductors were not so easily understood. A few workers[263,264,265] used the Hall effect as an analytical tool in studies of the electrical properties of solids; but reported considerable variations in their results. Baedeker suggested that impurities and crystalline imperfections were responsible and Lark-Horovitz[266] considers that for this reason relatively little use was made of the Hall effect. In a sense Lark-Horovitz is at once right and wrong. If he is restricting his statement on the Hall effect to measurements that contributed to an understanding of electrical phenomena in semiconductors then he is right. If, however, all the work on the Hall effect, regardless of its theoretical import or not is considered then he is wrong. For a great number of papers were published concerning researches in which the Hall effect was employed;

but by far the larger proportion of them being of no significance to a modern scientist. Lark-Horovitz, as might be expected in a 1954 review paper, displays a Whiggish tendency.

It was made immediately evident that some substances, those we call semiconductors, gave rise to anomalous effects. Sometimes opposite to metallic conduction, sometimes the same; and some materials could be made, at will to produce either sign of the Hall effect. Baedeker, in particular,[267] used the Hall effect to show that, in contrast to metals, the number of electrons, (or rather current carriers) varied rapidly with temperature change; an important result for semiconductors and the electron theory. The existence of a Hall effect opposite to that in metals made it difficult to avoid the implication that, in some circumstances, free positive carriers were present.

## SUMMARY.

Brown's work has been singled out for a detailed study not because he was the first to discover and report new phenomena nor because his theories were totally original. But while others were content to produce one or two papers, Brown devoted considerable time and effort to his attempt to understand selenium. In the course of his work he achieved considerable insight into its behaviour; pioneered the use of single crystals and pointed clearly to the shortcomings of the simple electron theory as applied to selenium.

For most of the decade during which he researched into the properties of selenium he treated selenium as a unique substance; indeed it was one of a very small class of materials that possessed the property of photoconductivity.[268] Yet photoconductivity is but one of the electrical properties that characterise a semiconductor; rectification, positive temperature coefficient of conductivity, photovoltaic properties being the others. Brown's failure, and that of other workers, to investigate rectification in selenium contributed to the delay in placing it in a class with other non-metallic solid conductors that were being investigated.

We may therefore explain the historical fact that Brown's work vanished into the unremembered past. The route to modern knowledge of semiconductors was to lead through the use of pure single crystal materials, particularly the alkali halogens, enabling an important separation to be made between those properties of semiconductors that were associated with the bulk of the material and those which were dependent on surface and junction conditions. Such investigations were taken up by Pohl and Gudden in Göttingen during the twenties, and they appear to have been ignorant of Brown's work;[269] so although Brown introduced the use of single crystals to eliminate surface and junction effects, with the cessation of his work on selenium in 1917, Brown's influence in the field disappeared.

As Brown was led to an electron theory of selenium which pointed to the inadequacies of the simple theory, so, particularly in Germany, the same view had been reached[270] from studies of the electrical behaviour of various compound conductors. By the end of the second decade of this century a new class of materials could be defined; one whose properties were, essentially, determined by those referred to above. This classification, which we discuss briefly in the next chapter, was to include selenium, and presented Pohl and Gudden with a clearly defined area to examine.

There existed in the German sources alone all the necessary information to define the class of semiconductors.[271] Questions of purity had been considered[272] and techniques of measurement rather more reliable than Brown's, and of more generality, had been developed.[273] The materials, investigated by the German workers, although, in the main compounds, were, in fact, physically simpler than the polycrystalline forms of selenium; and their properties were more constant than the extreme variability that all too often was displayed by selenium cells. It seems plausible, therefore, to conclude that once a new class of materials had been defined, then experimental work would be devoted to members of the class that had the simplest structures and the most reliable properties: and that selenium was not such a material.

Thus Brown's work vanished because he investigated too few properties of the wrong material, and because he was, apparently, unacquainted with German researches.

The fame of a scientist seems to depend on very shaky foundations.

This chapter has examined but a very small part of the semiconductor story; the history of semiconductors is as yet a largely unexplored area. We have here outlined one thread in the history, a thread which, at the moment, seems to have been separate from the main flow of development; but which, nevertheless, is part of the whole picture.

## CHAPTER 5. The Theory of Electrons and Semiconductors.

In his paper[1] on the origins of Lorentz's theory of electrons Hirosige identifies four aspects in which the theory of electrons was historically significant. From the Zeeman effect it allowed development of a firm foundation for atomic physics; the discussion of the electromagnetic properties of fundamental particles, for example the electromagnetic mass of the electron, generated the theory of elementary particles; its completion of the pre-relativistic theory of the electromagnetic field prepared the ground for the theory of relativity; lastly, and most importantly from my point of view, some of the origins of solid-state physics can be found in Lorentz's theory of the conduction of electricity through metals by electrons. It is well known that the electron theory was able to give a convincing account of electrical conduction through metals, but agreement between theory and experiment was, at best, only a good approximation. In the case of semiconducting materials the 'free gas' electron theory was insufficiently precise for a good 'fit' between theory and experiment. It was evident to Pfund[2] and later to Brown[3] that, in selenium at least, the electrons could not be considered as completely free; while some were, the number being reflected in the conductivity of a particular sample, others were 'bound' to atoms to be freed by the action of light or by heat or by radium rays. In principle this account possessed elements of 'truth', but foundered on the experimental fact that, in semiconductors, the current carriers could be of either sign. The empirical validity of this knowledge was provided by the Hall effect measurements. Modification of the 'electron gas' theory by Sommerfeld[4] and others in the 20's allowed an accurate description of metallic conduction, but the unification of all types of solid state conduction was not possible until the band theory of semiconductors was proposed by Wilson in 1931.[5,6]

In retrospect it is easy to understand that quantum mechanics had to be invented and developed before the properties of semiconductors could be described, even in principle; but those who were interested in these materials made valiant attempts to provide theoretical accounts of their properties.

This chapter, then, will consider, in outline, the development of the electron theory of conduction and its relationship with the few attempts to provide a mathematical background to the experimental results obtained with selenium and other semiconductors.

## 1. Electron Theory - Sources.

The problem remarked upon in Chapter 3, that there was no detailed, extensive history of electrical theories in the 19th century which could have provided an authoritative analysis within which the descriptions of photoconductivity, rectification, etc., could have been included, reappears; for the conduction of electricity through solids has been ignored by recent historians. While modern publications concerned with semiconductors and other solids include historical material, this is arranged and selected for didactic purposes and has been of little use here. As for the 19th century, the problem has not been to find sources but to select those that would allow the background to the theories to be explored and would illuminate the controversies that existed. Location of sources presented no difficulties whatsoever, for even a cursory search demonstrated that the theory of electrons aroused immense interest. A large number of workers wrote a large number of papers on the subject and many books appeared in which the ideas were expounded. Indeed there is enough material available to provide not one but several researchers with theses. The problem was mitigated if not solved, by using Richardson's The Electron Theory of Matter*[7] and Thomson's The Corpuscular Theory of Matter**[8] as authoritative secondary sources[9] contemporary with the work on semiconductors that has been discussed. The fact that Brown, the main character of the last chapter, referred several times to Thomson's work and collaborated with Richardson renders the choice of sources sensible, rather than exhaustive. Recent historians of electricity, for example Whittaker,[10]

---

* In future will be referred to as The Electron Theory.

** In future will be referred to as The Corpuscular Theory.

have made little or no mention of the solid state and their writings are of no use for an overview of the development of the electron theory. Fortunately, Hume-Rothery's The Metallic State,[11] (1931), included a review of the competing forms of the electron theory which, while limited in scope, proved a useful introduction to an understanding of the pre-quantum mechanical electron theories. Additionally the theoretical difficulties have been examined through a restricted number of primary sources, produced mainly during the second decade of this century. Typical of these are papers by Lindemann,[12] Thomson,[13] and Livens.[14,15,16] The contents of these sources reflect contemporary concerns with the general tenets of the electron theory and with its application to special areas, for example thermoelectricity and superconductivity.

## 2. The Electron Theory.

Regardless of the accuracy of the descriptions or predictions afforded by the electron theory, as a heuristic device it focused attention on the common root of all electrical phenomena. With the electron at the seat of electricity apparently diverse phenomena, such as those discussed in Chapter 3, were conjoined and controversies that had produced considerable heat during the last quarter of the 19th century ceased to have any real meaning. Almost the 'last shots' in the arguments were fired by Lodge in 1900,[17] from then on theories, apart from electro-magnetism, ceased to display a phenomenological character becoming unified by the electron theory. This 'reductionism' is for me, the most important influence of the electron theory. No longer were there separate theories of electrolysis, contact electricity, voltaic forces and so on; the electron was the basis of all these facts. It now became a matter of how, in particular circumstances, electrons would behave to different disturbing influences.

As Hirosige informs us[18] Lorentz's original effort was to derive Maxwell's equations from the concept of an 'atomic' charge. Maxwell's own theory was noticeably silent on the nature of electricity[19] suggesting the pre-eminent significance of the ether. Lorentz's indication, that Maxwell's equations were recoverable from an alternative base, at least raised the possibility of electrical particles.[20] Thomson's demonstration of the atomic nature of electricity added powerful empirical evidence to Lorentz's theory, which until then was merely another viewpoint. With the electron established as a constituent of matter it was possible, in principle at least, to search for an explanation of two highly significant 'laws' of electrical conduction in solids; Ohm's law and the Wiedemann-Franz law. The validity of Ohm's law was not seriously questioned for metallic conductors after the careful and very accurate experimental work carried in the Cavendish laboratory in the late 19th century but the Wiedemann-Franz law was never more than approximately true.[21]

A 'simple' theory assuming only a 'free electron gas' obeying the laws of Maxwell - Boltzmann statistics, while capable of giving a fairly good account of Ohm's and Wiedemann-Franz's laws, could not be readily applied to more complex electrical phenomena; thermoelectricity or superconductivity for example. In the former case the methods of kinetic theory yielded several similar forms of equations, differing only in multiplying constants[22] and according to M'Whan:-[23]

> 'The formulae so derived are not open to test as against experimental results, containing as they do the ratio of the electronic densities in the two metals forming the couple: they have been shown, in addition, to be inconsistent with some of the known facts.'

M'Whan, following Baedeker[24] and others,[25] applied thermodynamical arguments to thermoelectric processes and demonstrated that the theory was 'essentially reconcilable with the standard Kelvin equations'[26] but pointed out that his treatment would not necessarily produce more information about the physical processes involved in thermoelectricity.[27] Leaving aside the question whether thermodynamics can, in fact, give any information about processes rather than systems, the conduction of electricity was, like other properties of solids, an insoluble problem for classical physics; a point elegantly made by Jammer in The Conceptual Development of Quantum Mechanics.[28] The roots of the difficulties were, of course, in the set of assumptions applied to the electrons in solids, and the relationship between the energy of the electrons and the atomic centres. Jammer[29] has traced the development of quantisation of electron energies and the theoretical structures in his book, and has shown that, as far as specific heat was concerned, the quantum theory was being applied to solids from about 1907; but this did not impinge on studies of electrical conduction, directly, until 1928.[30] The basic tenets were only rarely attacked, most workers being satisfied with modifications, often very elaborate, of the assumptions and mathematical formulations of the Lorentz theory.

At about the same time as Brown was concluding that the electrons in selenium did not obey Maxwell - Boltzmann statistics,[31] Lindemann published a short paper[32] on the electron theory of metals in which the shortcomings of the existing structure were pointed out, fairly forcibly. He agreed that the 'free electron' hypothesis could 'be made to explain most electrical phenomena in metals with fair accuracy.'[33] He outlined the description of electrical and thermal conduction in metals according to the theory but deemed it unnecessary to repeat the accounts of thermoelectricity, the Hall effect and so on. Each required secondary hypotheses none of which he found convincing; indeed he considered that the main points derived from the theory were 'in absolute contradiction with one another or with the facts.'[34] In Lindemann's opinion the expression 'free electron' 'suggesting, and intending to suggest, an electron normally not under the action of any force, like an atom in a monatomic gas, might almost be termed a contradiction in terms'.[35] He rejected the concept of an electron gas and suggested that 'the free electrons form a space lattice, which corresponds to a crystal at a very low temperature'.[36] That Lindemann should seek to refute the basic assumptions of the electronic theory of metallic conduction is evidence for the unsatisfactory state of the theory; but that he should replace it with a suggestion drawing an analogy between the electrons and a crystal at low temperature is extremely interesting. For by 1915 the low temperature characteristics of crystals were known not to be represented adequately by 19th century kinetic theory.[37]

The conflict between explanations of different electrical phenomena was considered by Hall in 1914.[38] In a paper presented to the American Association for the Advancement of Science he pointed out that while metallic conduction, particularly at low temperatures, necessitated the conduction of electricity by electrons not subject to the gas laws, thermoelectricity appeared 'to require the presence of free electrons within metals'.[39] Hall's solution was to elaborate the contribution to the process of two forms of metallic conduction; one borrowed from Thomson envisaging conduction by the direct transfer of an electron between neighbouring atoms;[40] the other the result of the motion of electrons in thermal equilibrium with their surroundings.[41] Hall concluded that there was some, although not total, agreement between his form of the electron theory and experimental results.[42]

Thomson, to whom the 'doublet' theory of electrical conduction was due, examined the problem of superconductivity in 1915. These phenomena which were 'of vital importance in the theory of metallic conduction'[43] constituted 'another, and fatal, objection to the theory that metallic conduction is due to the presence in the metal of free electrons which drift under the electrical force, for no permissible increase in the number of free electrons or in the mean free path would explain the difference between the ordinary and superconducting state.'[44] Thomson sought his explanation in classical terms, indeed he wrote:-[45]

> 'It is the object of this paper to show that the effects discovered by Kammerlingh Onnes are in accordance with the theory of Metallic Conduction which I gave in The Corpuscular Theory of Matter and which, with the substitution of an electron for a charged atom, is substantially the same as that given in my Applications of Dynamics to Physics and Chemistry, 1888.'

While some were investigating the electrical properties of metals others attempted to examine the interaction between light and electrons, Koenigsberger and Kilching[46] and Houston[47] for example. Although they were to suggest that some form of 'resonance' occurred, a point taken up by Pfund,[48] no effective description was to emerge.

This brief, and necessarily, inadequate, account of the electron theory is sufficient to make two points. First that the form of the theory available in the first twenty years of this century while able to give more or less satisfactory descriptions of thermo-electricity and the Wiedemann-Franz law, was quite incapable of subsuming the phenomenon of superconductivity within its structure. There were many attempts to produce conformity between theory and practice but they all foundered in one way or another. In consequence variations of the theory were produced, by Thomson, Hall, Lindemann and others, which it was hoped, would be more general in application. A history of the electron theory will, of course, examine the detailed relationships between the many modifications that arose; meanwhile it is sufficient to note that the 'simple', 'free electron', form of the theory was but one approach that was applied to electrical conduction in solids. It was not possible to be completely sanguine about any one formulation for while Livens opened one paper with the words:-[49]

> 'One of the greatest successes achieved by the so-called theory of electrons has been in its applications to the explanation of the details of the conduction of electricity in metals.'

And continued:-[50]

> 'Many of the more fundamental results in the theory have . . . . received verification and justification from several independent investigations,'

he was forced to qualify the successes:-[51]

> '. . . . it must be admitted that some of the results of these investigations have not always been so happily coincident as one might desire.'

Livens was concerned with numerical differences between formulae and seemed less interested in the basic assumptions; and his approach demonstrates the final intricacy of the theory while ignoring its fundamental weaknesses.

Second, and perhaps most importantly, the existence of the electron theory allowed a generalised approach to understanding conduction phenomena in solids. This point was made earlier, but it is vital to stress that the adoption of a widely applicable hypothesis unified electrical researches and generalised possibilities. Unique, ad hoc, theories were no longer necessary if an electron hypothesis could serve; and materials would no longer be unique if their properties could be described by an electron theory. Thus if the photoconductivity of selenium could be interpreted by means of the theory, then photoconductivity itself could be seen as a necessary consequence not of selenium, but of the electrons in selenium; and that was a significant change of viewpoint.

## 3. Pfund's Electronic Theory of Photoconductivity.

Pfund accepted[52] that conduction in selenium was electronic and not electrolytic in character. It was noted in the preceding chapter that he had, as early as 1904,[53] cast considerable doubt on Bidwell's theory and by 1909 he possessed further contrary evidence. Experiments with pure selenium, deposited on glass under vacuum, made it likely that photoconductivity was 'due to the selenium itself and not to the selenides, which are present as impurities'.[54] The increased number of electrons contributing to reduced resistance were supplied by the selenium itself.[55] Pfund considered that the emission was the result of a resonance set up in the atoms of selenium by the action of light; an 'internal' photoeffect.[56] His thinking was in 'classical' terms for when discussing the effective depth of penetration of selenium by light he wrote:-[57]

> 'In using the term "depth of penetration" it is tacitly assumed that the light is effective in producing changes in resistance only until the amplitude has died down to a certain minimum value, below which its effectiveness is lost. This fits in with the resonance theory, for the increased amplitude due to resonance must exceed a definite minimum value before electrons are expelled from the atom.'

Pfund had shown in his 1904 paper, and had confirmed his observations in 1909, that the sensitivity of selenium demonstrated a pronounced maximum at about 7000 Å; and that the absorption fell from a large value at 5000 Å to a much smaller one at 9000 Å, with a particularly rapid change between 6000 Å and 7000 Å. Modern theory suggests that there should indeed be a strong association between an absorption edge and sensitivity but to Pfund the experimental results were at odds with theoretical deductions. Quite rightly Pfund pointed out that absorption and resonance go together, but a continuous increase in sensitivity from red to blue was not observed.[58] To obtain, at least a qualitative, correspondence between his ideas and the results of his observations he cited the apparent 'critical' thickness of conducting metallic films. Citing the results of Longden, Vincent and Patterson and the theoretical work of Thomson,[59] Pfund showed that if the conductivity of selenium was restricted to a thin layer at the surface and if infra-red penetrated selenium more readily than blue light, which it did, then since the thickness of the selenium in his cells was much greater than the 'critical' thickness, the experimental results could be 'fitted' by the theory. In his words:-[60]

> 'Now then, beginning in the infra-red, where the depth of penetration of radiation is greater than the "critical" thickness, it is observed that the conductivity increases rapidly with increased absorption. However, in passing through the region of $\lambda = 7000$ Å where the absorption increases very rapidly, the depth of penetration and hence, the thickness of current carrying layer becomes equal to, and then less, than the critical

> thickness. It is in this region that the enormous decrease in conductivity with thickness makes itself felt and not only neutralises the effects due to absorption, but actually causes a sharp drop in conductivity.'

Pfund thus accounted for the form of the absorption and sensitivity curves, and further confirmed his prediction that increase in intensity of illumination would produce a shift in the sensitivity maximum to shorter wavelengths.

## 4. First Steps to an Electron Theory.

The first movement towards a mathematical theory of photoconductivity was taken not where the majority of the experimental work was done but in Australia. It was claimed by Barnard in 1931[61] that in 1910 a paper by Vonwiller[62] published in the Royal Society of New South Wales Journal and Proceedings contained the 'first definite mathematical expression of the electron theory . . of photoconductivity. .',[63] and there seems to be no reason to refute his contention. Vonwiller's work escaped the attention of the researchers in America and England, at least they made no mention of him, but since his theory was seen by Barnard as an adumbration of the 'modern theory'[64] (1931), and because it has the merit of simplicity, unlike some that followed, we will give it some attention.

The primary aim of Vonwiller's work was to explain the discrepancy between maximum sensitivity and maximum absorption. He like Pfund appealed to the effect of light penetration. Unlike Pfund, however, Vonwiller attempted to measure the depth of penetration of selenium; anticipating Brown[65] and using an experimental technique rather more elegant in design.[66] Vonwiller and Brown showed that light penetrated to a depth of the order of a few hundredths of a millimetre; rather greater than the depth required by Pfund, rendering his detailed suggestions doubtful. Vonwiller showed that the electron theory could be employed to provide a description of the variation of sensitivity with wavelength.

Vonwiller assumed that some selenium atoms had lost an electron, the loss being temporary and there being no more electrons than these. Recombination occurred continually and electrons were produced by the action of heat or light or any other agency that could supply energy to the selenium atoms. Assuming that the rate of recombination was proportional to $n^2$, where n was the number of electrons, then if b is the rate of production he could write,[67]

$$\frac{dn}{dt} = b - an^2 \; . \; . \; . \; . \; . \; . \; . \; (1)$$

In a steady state, $\frac{dn}{dt} = 0$, and $b = an^2$ . .(2)

In the dark, b was given the value

$$b_o = a_1 n_o^2 \; . \; . \; (3)$$

Vonwiller had shown, experimentally, that the rates of change of conductivity during irradiation were a function of the intensity of the incident light,[68] again anticipating Brown by two years.[69] Theoretically the empirical fact was expressed by allowing 'b' to be a variable constant. The dependence of the rate of recombination on '$n^2$' was decided by analogy with the situation in ionised gases, where it had been shown that the rate of recombination was proportional to the numbers of positive and negative ions. The differential equation expressed the empirical fact symbolically.

He tackled the problem that Pfund had discussed, namely that the peak of sensitivity did not coincide with the maximum absorption, which might have been expected. His mathematical approach was not dissimilar to Pfund's descriptive one, in that both depended on the variation of absorption with wavelength of incident light. However, whereas Pfund introduced the idea of a 'critical' thickness, of the order of $10^{-6}$ cm, Vonwiller demonstrated, in conformity with his experimental results, that this assumption was not required.

If $I_0$ is the incident intensity, and $a$ the coefficient of absorption then the energy absorbed at a depth x in the selenium is given by $aI_0e^{-ax}dx$. The exact form of the relationship between absorbed energy and electrical effect was unknown, despite thirty years' experimental work and much theoretical effort.[70] Vonwiller was compelled, therefore, to write the effect as an unknown function of the absorbed energy; giving at a depth 'x'

$$e_x = f\,(aI_0e^{-ax}) \quad . \; . \; . \; . \; (4)$$

Hence the total effect in a layer of thickness X would be,

$$E = f\ (aI_oe^{-ax})\ dx\ .\ .\ .\ .\ (5)$$

In general, as he knew,[71] the effect of light was not proportional to the energy absorbed, for the conductivity changes were less rapid than changes in intensity. An nth power law could be assumed for the function in (4) and (5) with $n < 1$ allowing (5) to be rewritten as,

$$E = a^nI_o^n\ \bullet\ e^{-anx}dx\ .\ .\ .\ (6)\ \text{(p a constant)}$$

which on integration yields

$$E = pa^{n-1}I_o^n\ (1 - e^{-anx})\ .\ .\ .\ (7)$$

Two extreme cases, X very small or X very large resulted in

$$E = pa^nI_o^n\ X\ .\ .\ .\ .\ (8)$$

and

$$E = \frac{pa^{n-1}I_o^n}{n}\ .\ .\ .\ .\ (9)$$

From equation (8) it could be inferred that as the absorption coefficient 'a' increases then the electrical effect becomes more marked, whereas the reverse is illustrated in equation (9). Thus for practically realisable thicknesses and variation in 'a' with wavelength it could be understood how the sensitivity maximum did not coincide with maximum absorption.

The importance of Vonwiller's theory lies not in the influence it had on later workers, for it appeared to have none; nor on its inherent 'truth'; for although it contained an explanation of one empirical fact, Vonwiller pointed out that its correctness could not be assumed.[72] Historically it is significant only as the first attempt to produce a mathematical theory of photoconductivity, that did not depend on the particular, and possibly unique, physical properties of selenium. The assumptions adopted by Vonwiller were well attested by independent observations, the existence of electrons was not doubted in 1910, and the law of absorption of light was well established. Vonwiller's pioneering effort, pre-dating others by some years, thus represents a move towards generality based on an electron theory which was to contribute to the recognition of a new class of materials, all the members of which possessed similar physical properties.

Vonwiller's approach possessed two main weaknesses. First he did not take into account any quantum effects and second his assumption of the dependence of the total effect on the intensity of light was by no means well established. The first omission is perfectly understandable. It was not generally agreed in 1910 that energy exchanges between light and electrons required a quantum-theoretical approach for a complete description. Einstein's work on the photo-electric effect while published in 1905[73] was still being treated with suspicion in 1913,[74] and it is fair to say that the liberation of electrons by light was, in the main, treated by the electromagnetic theory in its later modifications. The marriage between the quantum theory of light and photoconductivity was effected by the work of Gudden and Pohl in the 1920's.[75] The second point of criticism is also bound up with the first. In Chapter 2 reference was made to recent work on selenium[76] where it was pointed out that the behaviour of selenium was not completely understood in the 1950's; selenium, even though an element possesses some rather complex optical and electrical properties that were beyond the theory and the experiments of the first two decades of this century.

## 5. Nicholson's Theory.

Nicholson's elaboration of the electronic theory of the photoconductivity of selenium was unfairly treated in Barnard's The Selenium Cell of 1931. His short dismissal of Nicholson's ideas,[77] while understandable in a work that was not intended to be historical, underrated the laudable impulse to understand the varied properties of selenium that were known. (Barnard was writing, of course, as if the researchers of the 1910's were conscious of what would be known in the late 1920's).

Many effects that were later shown to be due to contact pressures, absorbed moisture, and so on, were, in 1914, considered to be real properties of selenium. Furthermore as many of the factors that affected the conductivity of selenium did so in analogous ways single explanations were sought. (Brown's attempt to satisfy this desire with his allotropic theory had already been discussed in some detail in Chapter 4.) Hence while Barnard could view Vonwiller's theory as very similar to that of 1927 and could pass by Nicholson's as including 'a somewhat involved internal photoelectric hypothesis'[78] Nicholson was trying to account for more empirically defined phenomena than could be encompassed by Vonwiller's theory. However it must not be thought that Nicholson's approach derived from that of Vonwiller's; he made no reference to the earlier work, and tried to reach a much more fundamental level of understanding in his own descriptions.

Nicholson recognised that the interaction between light and selenium was enormously complex and fully accepted that only approximate answers would be given.[79] Indeed he considered it necessary to omit many mechanisms that conceivably operated in selenium. His omissions were seven in all.[80]

1. Variation in the coefficient of recombination with strength of illumination; a point tacitly made by Vonwiller.
2. Diffusion of electrons from their point of production. Nicholson, citing the results of Pfund and Brown[81] pointed out that the effective depth of penetration was $\approx 10^{-3}$cms while the intensity of light would have fallen to one-thousandth of its incident value in a depth of about $10^{-4}$cms. Diffusion was, therefore, possibly 'a large factor'.[82]

3. If light acted very close to the surface of the selenium then a 'skin effect'[83] might exist. Nicholson considered that if such an effect existed then it would merely enter a constant multiplying factor into the expression for the number of electrons present and the magnitude of the current flowing.

4. Variation of the absorption coefficient with conductivity. The electron theory suggested that such an effect might exist and it had long been known that good conductors, metals for example, were opaque to light, while bad conductors often were transparent to much of the electromagnetic spectrum. However experiments had shown that such an effect was possibly very small.[84]

5. Non-uniform distribution of the electrons, most likely near the electrodes, but an effect which, thought Nicholson, would not be important.

6. Loss of electrons by the external photo-electric effect, which was probably unimportant at visible wavelengths.[85]

7. Secondary ionisation. Nicholson did not make this point clear, but presumably was referring to ionisation by collision, a phenomenon familiar in gases and one that Brown used to account for non-Ohmic behaviour.[86]

He pointed out that his theory might not be fundamentally different 'from that which assumes chemical effects as the cause of transformations; for such transformations, which in so far as they cause an increase of conductivity, mean simply a liberation of electrons'.[87]

Nicholson may have been preparing to meet criticism, perhaps from Brown, but, on the contrary Brown was to accept an electronic theory of photoconductivity. (The chemical allotropic theory was still sufficiently known in 1931 for Barnard to include a short discussion of it in his book.[88] However the fact that considerable light sensitivity was exhibited by selenium at the temperature of liquid air[89] was a powerful refutation of a chemical hypothesis).

Beginning with assumption very similar to Vonwiller's except that the effects of light and other agencies were separated, Nicholson wrote a differential equation.[90]

$$\frac{d}{dt}(nA\,dx) = AM^2\,dx + \mu AI\,.\,e^{-kx}dx \quad -\alpha^2 n^2 A\,dx. \quad .(1)$$

Where $n$ = density of electrons in active layer.

$A$ = area of selenium
$I$ = incident intensity/unit area
$M^2$ = number of electrons produced/sec in unit volume
$\alpha^2$ = recombination coefficient
$k$ = absorption coefficient
$x$ = distance from top
$\mu$ = a proportionality constant expressing the number of electrons expelled by resonance due to the absorption of light.

Nicholson solved this equation for n, at a depth x, and introducing the total number of electrons present, m, he performed the integration,[91]

$$m = \int_0^s An\,dx;\text{where } s = \text{thickness of selenium.} \quad .(2).$$

Unfortunately n was a rather complex function of a new variable, q, given by $q^2 = M^2 + c^2e^{-kx}$ in which c was a constant equal to $(\mu kI)^2$.[92]

After what was no doubt considerable algebraic manipulation he produced an expression that included the effect of illumination imposed on the dark conductivity. His total expression was the sum of three parts such that:-

Total number of electrons = number in dark + number due to illumination when conditions are steady - transient terms.[93] Making suitable assumptions and realistic approximations[94] he demonstrated that the increase in the number of electrons, and hence the conductivity under an illumination I was given by,

$$m - m_o = \frac{2A}{\alpha} \sqrt{\frac{\mu I}{k}} \quad . \; . \; . \; . \; (3)$$

i.e. that the change in conductivity was proportional to the square root of the illumination. Now there was some dispute as to the correctness of this 'law'. Some workers, Nicholson cited Rosse, Pfund, Adams and Berndt, had claimed such a relationship; others disputed its accuracy.[95] Nicholson suggested that any discrepancies could be readily accounted for; the absorption coefficient and the recombination coefficient were both functions of the wavelength and hence[96]

> 'In order to obtain a complete expression connecting change of conductivity, intensity of illumination and wavelength, it is necessary only to express $\mu$ and k as functions of the wavelength, correct I for loss of reflection, and insert its value in the equation. This problem does not at all seem hopeless.'

The last sentence expressed an optimism that had to await many years for its justification; and the route taken, as will be briefly discussed in the epilogue, was not to be via selenium.

Nicholson turned his attention to several facets of the properties of selenium; the dependence of sensibility on dark conductivity;[97] light negative selenium;[98] the 'inertia'[99] of selenium cells;[100] the effect of steady monochromatic radiation on sensibility; [101] the initial rate of change of conductivity;[102] the recovery from illumination and the time taken to reach a steady state.[103] In the main his theory was successful, in that it could give plausible accounts of the observed effects; it however failed completely to explain the long time required for selenium to reach a steady state. His inclusion of diffusion of electrons in his theory did not lead to a good solution.

While, in a sense, his theory was like Brown's in that he was forced to choose ad hoc values of the parameters he used, he had much more independent evidence for the fundamental assumptions he made. And in principle all the variables and constants he used could be subjected to independent measurements.[104] As we have remarked Brown's theory included assumptions that had doubtful validity, such as the existence of three allotropes whose rate of exchange could be affected directly by light, maybe Brown felt unhappy about this, particularly after his work on single crystals, for he was swift to adopt the electron theory of photoconductivity after becoming acquainted with Nicholson's approach. Nicholson summed up his own work in these words.[105]

> 'The facts accounted for are as follows:
>
> (a) Variation of change in conductivity with square root of intensity for long exposures.

(b) Variation of change in conductivity directly with the intensity when the time of illumination is short compared with that required to reach a steady state.

(c) High sensibility of cells of high resistance.

(d) Decrease of inertia with increasing intensity of illumination, absorption coefficient, and "dark conductivity". This also explains variation of sensibility with temperature and other disturbing factors.

(e) Dependence of rate of recovery upon the same causes.

(f) Change in sensibility when cell is illuminated continuously with a beam of light for whose constituents k is nearly constant.

(g) Decrease in inertia when this beam is red, or infra-red.

(h) Possible explanation of "light-negative" selenium and anomolous effects.

Finally Nicholson closed his wide ranging paper with an acknowledgment to Pfund,'who suggested the work and spared no pains in aiding me in every possible way.'[106]

## 6. Brown's Electronic Theory of Photoconductivity.

Brown introduced his own version of the electronic theory of photoconductivity in 1915,[107] following 'the line of attack made by J.W. Nicholson.'[108] While Nicholson was interested in describing the performance of selenium under the action of light, and developed an algebraically complex theory, Brown saw his own more straightforward account as serving a more general purpose. That selenium was one of a separate class of materials was not recognised by Brown; for him the allotropes of selenium could be classified as metallic or non-metallic - i.e. as conductors or non-conductors. He noted that there were several theories, all modifications of a basic electron—theory, that were competitors in the explanation of the electrical properties of solids. Metals, however, had not proved particularly fruitful in resolving the problems. For while 'the illuminating experiments of Richardson and his students and also the consistent agreement of theory and experiment involving the ratio of the electrical to the thermal conductivity of metals [had] made various modifications of the dynamical theory very popular'[109] the low value of the specific heat of all metals was a strong argument against the concept of electrons in thermal equlibrium with the molecules of the metal.[110] His writings clearly indicate that[111] he contemplated the possibility of deciding between two forms of electron theory: the 'electron-gas' concept and the 'doublet' theory of Thomson.[112] Given that the conductivity of selenium could be 'varied by so many physical conditions'[113] Brown thought that it would be possible to make a 'very definite choice'[114] as to which theory best applied. His results were, he considered, support for a theory of the 'doublet' type.

This theory is little known today, although according to Hume-Rothery, writing in 1931,[115] it 'aroused great attention in its time'.[116] In The Metallic State[117] (1931) Hume-Rothery pointed out that there were difficulties inherent in the 'electron-gas' theory; two being relatively important. Superconductivity being one area which was inexplicable and, as mentioned above, the problem of the specific heats of metals. Conductivity measurements suggested that in a typical metal the number of free electrons was at least as great as the number of atoms, and sometimes twice as great; yet if the electrons were to be in thermal equilibrium with the surrounding atoms then the specific heat of metals should have been much greater than it was. We have seen earlier that Lindemann's 'cold' electron space lattice concept gave a qualitative account of this discrepancy and Thomson's doublet theory represented another approach to the same problem.

Selenium's 'metallic' modification was responsible for photoconductivity and while, as in Brown's allotropic theory, this modification was considered to be one of three, two of which were non-conductors, then an 'electron gas' theory could be accepted, in a descriptive sense, as satisfactory. For the interaction of light with selenium produced no extra electrons directly, but acted to alter the equilibrium of the allotropes in the direction of the 'metallic' modification resulting in a greatly enhanced conductivity. Once it had been demonstrated that single crystals of 'metallic' selenium possessed conductivity then neither the shifting equilibrium of allotropes could be invoked nor was an electron theory any longer tenable. For in the first case only one modification was present, and in the second the additional electrons made available by the action of light must have been provided by an ionisation process; and the production of electrons would compete with recombination.

While the free electron theory did not, in itself, contain any denial of the possibility of the production of extra electrons by the action of light, the doublet theory of Thomson contained an ionisation process as a fundamental assumption. In Thomson's theory, outlined in Corpuscular Theory,[118] conduction electrons were continually being produced by dissociation of an electron and an associated positive centre, the two together constituting a dipole. While there were no 'free' electrons in the sense of an 'electron-gas' the conduction electrons were in thermal equilibrium with the atomic dipoles, whose energy distribution conformed to Maxwell-Boltzmann statistics. In essence the doublet theory was similar to electrolysis with only the negative charges mobile; in fact, as Thomson remarked, the reaction of the doublets to the action of an electric field took place 'much in the same way as the Grotthus chains in the old theory of electrolysis'.[119] (Hall was to extend this theory and combine it with the 'electron-gas' concept, giving a definite role to the positive electricity in solids.)[120] Evidently Thomson's suggestion that the process of electrical conduction in solids had a correspondence with the earlier dynamical equilibrium theory of Brown's; that is, it possessed time dependent qualities, and could be moulded readily into a pattern that would give a qualitative account of the photoconductive properties of selenium. Thus the dark conductivity would depend on the number of electrons available for conduction at a particular temperature; allowing light, or temperature increase, or X-rays and so on, to enhance the rate of production of electrons. The recovery process, well recorded for selenium cells, would then represent the time taken for the electrons to recombine with the doublets, or ionised atomic centres.

Brown decided to attack what was, apparently, an easy problem; namely the rate of recombination of electrons after the removal of the means of their excitation. He hoped that measurements of the recombination rate would 'enable . . [a] . . decision to be made with a minimum number of assumptions.'[121] Perhaps claiming a degree of priority he wrote:-[122]

> 'The author is not aware of any direct or indirect measurements having been made which consider any particular value for the rate of recombination of electrons with their positive residues, except in the conduction of electricity through a gas under the influence of an ionizing agent.'

Brown's choice of recombination for experimental purposes was a wise one. For not only did he possess a considerable quantity of data on the subject, but since only two processes were operating, (i.e. dark production of electrons and the recombination of the excess with the positive residues), the theory was, in principle, much simpler than Nicholson's. Again Brown's approach was of the 'curve fitting variety' but this time with the additional and important aims, to determine some fundamental properties of electrons in solids.

Brown agreed that the electrons in selenium were not free, as in a gas, but were liberated by the action of light; to recombine fairly rapidly with the atomic structure on removal of the illumination.[123] Assuming that the rate of recombination of electrons was given by a law similar to that pertaining in gases, and that the conductivity of selenium was proportional to the number of free electrons he wrote the following equations.[124]

$$\frac{dN}{dt} = -\alpha N^2 \quad . . . . (1)$$

$$i = k_1 N \quad . . . . (2)$$

$$\frac{di}{dt} = -\frac{\alpha i^2}{k_1} = - {}' i^2 \quad . . . . (3)$$

For equilibrium under illumination, if M is the rate of production of electrons by light and q the production rate under dark conditions, then,

$$\frac{dN}{dt} = M + q \quad . . . . (4)$$

and $\frac{di}{dt} = k_1 (M + q)$ . . . . (5)

Hence

$$i = k_1 \sqrt{\frac{M + q}{\alpha}} \quad . . . . (6)$$

Brown pointed out that equation (6) was eminently suitable for experimental verification but decided to defer that test until he had more data concerning the rate of production of electrons by light.[125] For the moment he was content to check the accuracy of equation (3), in its approximate form

$$\frac{\Delta i}{\Delta t} = -\alpha' i^2 \quad . . . . (7)$$

Of course, a more usual course would have been to integrate equation (3) and verify the equation,

$$\frac{1}{i} - \frac{1}{i_0} = \alpha t \quad . . . . (8)$$

as Brown fully realised;[126] but his theory was only truly applicable when the distribution of electrons was fairly uniform, and this would not necessarily be the case after a considerable time had elapsed.[127] Using data from an earlier paper and applying this to equation (7) he produced the earliest measurements of the recombination coefficients for electrons in selenium.[128]

Although he had by no means verified his particular form of the electron theory, he demonstrated that the properties of electrons in solids and the interaction between them and the positive atomic residues were susceptible to measurement. His expression of the recovery of selenium from illumination in terms of a modified electron theory, possessed a plausibility that his earlier attempt lacked. The allotrope theory, while capable of yielding expressions which could be made to agree with experimental data, was based on assumptions that boasted only mild support; and was a complex theory developed in terms of parameters whose direct measurement was either impossible or very difficult. As was discussed in the previous chapter the presence of three forms of selenium was indispensable, yet the evidence for three distinct forms of selenium inter-convertible by the action of light was not strong.[129] Brown appears to have postulated the existence of three modifications by analogy with sulphur,[130] and assumed mutual inter-convertibility under the action of light from the observations of Bidwell.[131] Certainly he never attempted to determine the relative quantities of the three types, or the rates of conversion, other than by his 'curve fitting exercise', nor did he suggest independent methods of verification. His tests of the allotropic theory were circular in character. By contrast a theory based on electrons, not only assumed the presence of a well established entity and a generally agreed outline of conduction processes, but also, by its nature, was capable of independent verification. (The recombination rates of electrons were eventually to yield to theoretical analysis, and to be measured by a variety of techniques). Furthermore, while the exact form of the electron theory remained a mystery Brown's work on selenium indicated quite strongly, that in that material at least, the assumptions of the 'simple' theory were inadequate to describe the properties of the element.

Brown was not content to rest with an outline explanation of the photoconductivity of selenium, he extended his description to its non-Ohmic behaviour.[132] Adams and Day had shown that Ohm's law was not obeyed in selenium, the current rising more rapidly than the voltage. While they had no explanation for their observation, Brown, by splitting the current into two parts, suggested a possible mechanism. Supposing that the increase of current to satisfy the law arose 'from increased velocity of drift of the electrons'[133] and that the excess current was due to 'additional electrons in the conducting state,'[134] he pointed out that there were two possible causes of the excess. 'Either a magnified rate of production or . . . . a diminished rate of recombination'[135] would yield the necessary increase in the number of electrons available for conduction. His explanation of the two possibilities was not unreasonable:-[136]

> 'The increased rate of production might be expected because of bombardment of semi-fixed electrons by the faster moving ones or the greater electric intensity might be considered as lowering the degree of stability of all the electrons of a certain class in the atomic structure. Consistent with either of these views, it would be reasonable to expect a diminished rate of recombination as the voltage is increased. An increased velocity of drift would lessen somewhat the chance of an atom to capture an electron and also a lower stability of the atom would indicate a smaller attractive force for the electron.'

While Brown's account is not completely out of place, for modern theory has room for a similar picture,[137] the departure from Ohm's law is rather more complex than he could imagine.[138] Indeed at the levels of field strength at which he was working, the departure from Ohm's law was more likely to have been a surface phenomenon than an intrinsic property of selenium;[139] but, nevertheless, the explicative power of the electron theory is underlined by Brown's writings. His acceptance of the electron theory and his application of it to selenium showed how a basically uncomplicated structure could provide a very understandable picture of some of its electrical properties; and illustrated that experiments on selenium had an importance that was far more general than simply understanding the properties of one element.

## 7. The Class of Semiconductors.

While metals presented a few problems for the early theory of conduction the major difficulties were offered by those materials which we now classify as semiconductors. We have investigated in detail how the properties of one material were examined; and, in particular, how the phenomenon of photoconductivity did not admit of a ready explanation. We have remarked that while this property exercised the thoughts of several workers other equally remarkable properties were ignored.[140] The typical characteristics of semiconductors had been noted in selenium cells as early as 1880;[141] that is, photoconductivity, rectification, photo-voltaic effects, negative temperature coefficient of resistance, and high thermo-electric power. Brown's work and theories had been directed towards internal phenomena of selenium, while rectification and photo-voltaic effects were properties of surfaces and junctions. Even though Brown had recognised some similarities between the electrical properties of selenium and those of crystal contacts as early as 1913, he did not extend his own work to cover this area and in his later work[142] went to considerable trouble to avoid the interference of junction phenomena with his observations on photoconductivity. Coblentz's recognition that the above properties were found together in certain materials, a point he made in 1916, may have paved the way for a conjunction of ideas, that seemed to have occurred in work of Gudden and Pohl, (a point we will return to in the Epilogue); but during the larger part of the first two decades of this century those who investigated the electrical properties of non-metallic solids did not seem fully cognisant of the work being carried out on the optical properties of selenium, and vice-versa. A notable exception can be found in Das elektrische Verhalten der variablen Leiter und der Beziehungen zur Elektronentheorie a paper written in 1914,[143] in which Koenigsberger reviewed the state of knowledge concerning the electrical properties of non-metallic solid conductors. Koenigsberger was himself responsible for many researches into the properties of substances of this sort, and his results, together with those of Baedeker, figured in the initial efforts of Gudden and Pohl.[144] While he referred to the photoconductive properties of selenium,[145] his treatment of the effect was very short and his citations limited.[146] His own writings, and those to which he referred, (mainly of German origin), illustrated the effective use to which the Hall effect was being put to identify the significant properties of semiconductors.

Koenigsberger suggested a three-fold classification of electronic solid conductors; metallic, alloy, and variable conductors.[147] Referring to Baedeker's pioneering work in 1907,[148] he suggested that,[149]

> 'Seitdem haben die Ergebnisse vieler Beobachtungen deutlich auf Notwendigkeit hingewiesen, eine Klasse metallischer Leiter, die variablen Leiter, von den eigentlichen Metallen und von den festen Elektrolyten zu trennen.'

In Koenigsberger's opinion the arrangement of 'metallic-like' conductors into alloys, true metals and variable conductors, was made possible by the electron theory.[150] As Brown had used his own work on selenium to examine the validity of the simple electron theory of metals, so Koenigsberger wrote that the existence of 'eine besondere Klasse von Leitern, die für die Elektronentheorie der Metalle von Bedeutung ist;'.[151] For, as he remarked, the properties of these conductors could be tested against the electron-theoretical predictions.[152] The studies of Brown and others on selenium[153] had indicated, quite clearly, that the electron theory, while relatively successful for metals, was insufficiently detailed for direct application to the phenomenon of photoconductivity. Similarly, according to Koenigsberger, the empirical work on 'variablen Leiter' demonstrated similar shortcomings in the electron theory. For:-[154]

> 'Die Experimente zeigen . . . . , dass die einfache kinetische Theorie zwar kein getreues Abbild der Nature, doch eine vorläufig brauchbare Skizze ist.'

For Koenigsberger the Hall effect, resistance and thermoelectric power were particularly significant features for study. These offered clearly defined problems to the electron theory for they were described simply in physical terms and their mathematical expression was precise.[155]

The Hall effect, thermoelectric properties and the variation of resistance with temperature formed the major part of Koenigsberger's review.[156] The Hall effect and thermoelectricity together yielded information on the number of current carriers available for conduction[157] while the resistance variations provided some knowledge of the strength of the binding between electrons and residual atoms, or, in other words, the activation energy of the electrons.

In this 1914 paper Koenigsberger made occasional use of the term 'halbleiter',[158] which today is translated as 'semiconductor' with all its attendant operational meanings.[159] Smith in his book <u>Semiconductors</u> claimed that Koenigsberger fully appreciated the distinction between metals and semiconductors.[160] Certainly he appreciated the distinction between metals and 'variablen Leiter', but considerably more historical research into the work of Koenigsberger and his German contemporaries, is required before a confident assessment of their understanding can be given. It is the case that the materials discussed by him fall into our class of 'semiconductors'; but Koenigsberger's 'halbleiter' formed a sub-class of his 'variablen Leiter'. This is quite clear in his paper[161] and was confirmed by Gudden in 1931.[162] Gudden stated Koenigsberger's definition of 'halbleiter' as:-[163]

> 'Elemente, die bei gewöhnlicher Temperatur nicht stark elektropositiv und daher elektroylisch abscheidbar sind, ferner die Verbindungen, von denen ein Bestandteil elektronegativ oder doch weniger elektropositiv ist.'

Thus copper oxide was in Koenigsberger's 'halbleiter' class, while silicon was not. Koenigsberger's 'variablen Leiter' classification was useful although not all that accurate for although by 1920 he had widened the list to include several elements and their oxides and sulphides only selenium, silicon, and tellurium are now accepted as elemental semiconductors.[164]

Without the detailed research and analysis which Koenigsberger's work demands, but which is, unfortunately, too extensive to be included in this thesis, to pronounce on his definitions and understanding is perhaps somewhat premature. Nevertheless it is a little strong to suggest that Koenigsberger 'fully appreciated' the distinction between metals and semiconductors. His application of the term was a restricted one, when compared to the modern sense: and his methods of classification led to the inclusion of materials in the class of 'variablen Leitern' which are not semiconductors. While he recognised that the materials he considered had properties sufficiently distinct to render them a separate class from the true (eigentlichen) metals, their electrical properties, were, for him, to be explained in terms of an electron theory.

Hence while the modern class of semiconductors was not recognised by Koenigsberger in 1914, or in 1920 for that matter, he, like Brown, fully appreciated that there were some substances whose properties were sufficiently distinct from those of other solid conductors to conclude that existing theories of metallic conduction were inadequate descriptive tools. With the recognition that photoconductivity was not a property unique to selenium[165] and with the inclusion of rectification the identification marks of semiconductors were widened.[166] However even with an extended range of tests unequivocal definition of semiconductors was not possible until 1931. For Wilson's band theory[167] of conduction was an essential ingredient of such a definition.[168]

## 8. Effect of Work on Semiconductors on the Electron Theory.

The basic tenet of the electron theory, that conduction in non-electrolytic solids was a result of the motion of electrons and only electrons, was not seriously doubted after Drude's extension of the original idea of Lorentz.[169] We have seen that while there were intractable problems posed for the theory, superconductivity and the specific heat of metals, on the whole the electron theory was reasonably successful when applied to conduction in metals; for semiconductors its shortcomings were obvious.

Those who devoted their attention to the properties of non-metallic solid conductors accepted the electron theory while recognising its limitations; and suggested various modifications to produce a more equable agreement between theory and practice. The electron theory had an undoubted influence on the descriptions of photoconductivity, for example, but one might well ask 'What effect did the work on semiconductors have on the refinements of the electron theory per se?'

Without doubt this question will prove of some significance in the as-yet-unwritten history of the electron theory of conduction, but within this thesis only a tentative, partial answer can be given. Even a superficial search of the sources yields a vast quantity of work devoted to the electron theory of metallic conduction, most of which has never formed the subject of an historical study; and suggests that there were two main streams of activity. The first, comprising mainly American and English sources, moved along the route of increasing mathematical complexity, with the arguments concerned with the magnitude of multiplying constants. The second, mainly German, while less detailed mathematically, was, unlike the former, apparently cognisant of the facts that Baedeker and others had laid bare. But, by and large, the movement of ideas and knowledge was in one direction: from the electron theory to the properties of semiconductors.

Thus in The Corpuscular Theory[170] (1907) Thomson made nothing whatsoever of rectification or photoconductivity. He was, however, forced to face the unpleasant facts of the Hall effect. If the conduction in non-electrolytic solids were due to electron flow then the Hall effect should always have the same direction. But it was well known that in some materials the sign of the Hall effect was opposite to that in metals.[171] An obvious explanation would be that the current was carried by positive and negative particles and the sign of the Hall effect would be related to that of the predominant carriers, but this Thomson was not prepared to accept. The most serious objection to this hypothesis, as Thomson pointed out, was that there was 'no evidence of the existence of positively charged carriers able to thread their way with facility through metals.'[172] Thomson, provided a qualitative description of the Hall effect that was more complicated, though more soundly based on experimental evidence, than the alternative of positive carriers. He pointed out that the simple theory of the Hall effect ignored the effect that the external magnetic field might have on the collisions between the electrons and the molecules of the metal. He argued that it was easy to see how[173]

> 'a magnetic field might make suitable molecules arrange themselves so that they produce a rotatory

> effect on the motion of a corpuscle when the corpuscle came into collision with the molecule, and that the sign of this effect might in some cases be the same as, in others opposite to, the rotation produced by the magnetic field when the corpuscle was travelling over its free path.'

Arguing that the molecules might be considered as magnetic dipoles, he showed how, in principle, the sign of the Hall effect might be recovered.[174] The Hall effect was described by two components 'one arising from the free path, the other from the collisions, and these terms would be of opposite signs.'[175] Thomson demonstrated that his doublet theory could, in principle, account for the direction of the Hall effect, but he appears not to have pursued this theory to any extent.[176] Thomson's suggestion that the Hall effect was a result of the combination of a direct action of an external magnetic field on the electrons and an indirect action via the interaction between the external field and internal fields was taken up some years later by a number of workers; of whom Livens, was typical.[177] Livens (1915) developed Thomson's ideas mathematically, at some length, and was at pains to show that the Hall effect and various linked phenomena were amenable to theoretical interpretation in terms of a modified 'free-electron' hypothesis. Livens' findings were quickly shown to be untenable in the light of all the experimental facts; and there the matter rested.

While rectification was largely ignored by theorists in this period, the other junction phenomenon, thermoelectricity, was the source of inspiration for a large number of papers. Far fewer difficulties were present in this field; and a two-pronged attack promised considerable success. The Maxwell-Boltzmann based electron gas theory, and the thermodynamics of Baedeker[178] were applicable to metals; and thermodynamics found some degree of success when applied to 'variablen Leiter'. However it seems to have been the case that in English sources, and Richardson's The Electron Theory supports this claim,[179] the properties of semiconductors were of little significance at that time in the development of the electron theory.

Why Thomson and Richardson should have ignored the truly remarkable properties of semiconductors remains a subject for speculation. Although it is possible to understand their reluctance to include positive carriers in their theories and to search, instead, for an explanation in terms of electrons, it is much more difficult to comprehend their reasons for ignoring such collocation of properties as the magnitude of the Hall coefficient and thermoelectric power. From as early as 1896[180] experimental work had clearly demonstrated that with a large Hall effect went a correspondingly great value of the thermoelectric power.[181] Of these the size of the Hall coefficient was the more significant; for it implied that the number of electrons available for conduction was many orders of magnitude smaller than was the case in metals; a radically different situation. Furthermore, as Richardson acknowledged, it was possible to vary the number of current carriers at will in certain materials[182] a state of affairs at odds with the properties of metallic conductors. There were, however, too many questions in the theory of electrons for the phenomena of semiconductors to be particularly important; they were, after all, a small and not very well defined class at the time. As Richardson wrote, rather than introduce additional assumptions into the electron theory it was more likely that the effects were 'all due to negative electrons, but that the theory only takes account of part of the phenomena'.[183]

Thus we can close this chapter with one definite although somewhat negative conclusion; and can include a tentative statement concerning the relationship between the state of knowledge of semiconductors and the development of the electron theory up to about 1919.

For those properties that were investigated, with the exception of the Hall effect, the electron theory permitted a sensible, though mainly qualitative explanation. Further as in the nineteenth century the existing theories of electricity were inadequate for a total description, the electron theory was presented with more serious problems by semiconductors than by metals. Such is the definite conclusion.

Tentatively we may say that, in general, the 'peculiar' properties of semiconductors did not produce a reaction on the development of the electron theory during the first twenty years of this century. The facts were too variable and too little known for them to impinge seriously on the fundamental assumptions of the electron theory.

# CHAPTER 6. Recapitulations, Conclusions, Epilogue.

## 1. Recapitulations and Conclusions.

This thesis has been mainly occupied with the story of selenium from 1873 to about 1919 and, although concerned with but a minute part of the history of semiconductors, represents an attempt to add some substance to the outline account of the history as is commonly known and normally presented.[1] Selenium, while not the most important material of its class today, was the first semiconductor whose properties excited the attention of many research workers. For most of these men and women by far the most intriguing property was the ability of selenium to respond to irradiation by light with a remarkable reduction in its electrical resistance. Besides this its other, equally remarkable, properties receded into the background. Thus while photoconductivity appeared as the subject in many experimental and a few theoretical papers, rectification and photovoltaic effects were largely ignored after the early work in the 1870's and 1880's.[2]

Throughout the period we have studied empirical discoveries were fitted into theoretical frameworks based on accepted pictures; but in general the theories were found wanting. The electrolytic theory, originating in the work of Adams and Day[3] was developed by Bidwell over a period of fifteen years[4] and had the obvious attraction that the gross properties of selenium could be described in terms of electrolysis. Bidwell found it necessary to assume the presence of selenides, presumed electrolytic, in selenium, although he later found[5] that most of the phenomena he ascribed to selenides could be accounted for by the presence of moisture. Electrolytic theories could, in principle, encompass sensitivity to light, for chemical reactions were known to be enhanced by illumination;[6] could account for polarisation and rectification for some electrolytic processes were known to be asymmetric in their reaction to the passage of an electric current;[7] and reacted to temperature changes in a manner similar to that found in most selenium cells.[8] The existence of allotropic forms of selenium suggested to Siemens[9] that transitions from one allotrope to another, catalysed by the action of light, could provide a description of photoconductivity. Demonstrations that electrolysis was unlikely to occur in selenium or to satisfy the experimental findings[10] were followed by the development of the allotropic theory, particularly by Brown.[11] In his hands it attained the form of a mathematical theory, but was swiftly replaced by an electron theory when work at low temperatures and on single crystals[12] showed that chemical theories or transformation theories were unlikely to be correct.

While the early work on selenium was rendered unreliable by the problems of forming selenium cells[13] the later investigations were not troubled in this way; for while Barnard may have been right to claim that 'much of the time spent in the study of selenium cells was devoted to the devising of instruments which finally proved inefficient'[14] this activity did, at least, lead to satisfactory and repeatable methods of producing selenium cells. Thus while we considered the technology of selenium in the nineteenth century the subject forms a different type of study in this; one devoted to technology per se rather than to the 'internal'[15] history of selenium.

The electrical properties of other non-metallic conductors were also investigated from an early date,[16] but, with the exception of Bidwell's attempt to verify his selenium - selenide electrolytic theory by analogy with sulphur - silver sulphide cells,[17] the work on selenium carried on largely separated from that on other substances. Consequently the suggestions advanced to account for rectification in iron sulphide, by Braun for example,[18] went unheeded by the investigators of selenium. His clear demonstration that electrolytic action did not accompany rectification by crystals had no effect on the electrolytic interpretations offered for selenium's properties.

The separation between selenium and comparable materials continued into the opening years of this century but it seems that convergent paths were being followed, to meet eventually in the writings of Koenigsberger.[19] The confluence of the lines of research occurred when electronic theories of conduction were applied to selenium and non-metallic compounds. For the qualitative, if not quantitative, power of the electron theory was enough to suggest that the phenomena of electrical conduction in different types of solids could be conjoined and generalised. From the conjunction of research and theory there arose a new classification of solid conductors. Within the broad group of solid conductors Koenigsberger recognised two main sub-groups:

electrolytic solids and metallic conductors, the decision resting on whether or not the conduction was wholly electronic.[20] His own work, and his knowledge of that of others, allowed him to separate metallic conductors into three distinct sub-sets: true metals, alloys and variable conductors;[21] the latter is now our modern class of semiconductors. Koenigsberger's classification rested not on theoretical distinctions but on the comparison and codification of observed properties: high thermoelectric power, positive temperature coefficient of conduction, large Hall coefficients and, to a lesser extent, photoconductivity.[22]

This history has been written around the work of five men who made special contributions to the study of selenium; Adams, Day, Bidwell, Pfund and Brown. None are remembered today but in their own time achieved a little fame[23] and all are referenced in the standard works of scientific biography.[24] Adams and Day were the first to subject selenium to a detailed study and to the already established property of photoconductivity they added rectification and photovoltaic effects. Their suggestion that electrolytic action was at the root of selenium's behaviour was taken up by Bidwell who, in the course of fifteen year's work, attempted to develop a coherent theory based on that idea.[25] Bidwell's development of manufacturing techniques largely removed problems associated with technology and allowed research to continue more or less unhindered by technical considerations.[26] From 1900 this history has been centred on the work of Pfund and Brown with the latter being particularly significant. Although Pfund generated many ideas,[27] often to be extended by others, Brown displayed a continuity of purpose allied to a flexibility of mind that led him to the threshold of realising that the special properties of selenium were representative of a wide class of substances; a point to be fully taken by Koenigsberger.

To the conclusions that have been drawn from time to time throughout this thesis the most important can be added: that much more historical research is required before the history of semiconductors between 1833 and 1919 will be fully known and understood.

The present study has demonstrated that while the outline history is fairly well known[28] details are sparse; and this thesis has attempted to provide the details in the case of selenium.

There is a need for an extensive, detailed study of the development of theories of solid state electrical conduction between 1873 and 1919.[29] For the whole of this period the problems presented by solids were treated as appendages of other areas; they were set aside as difficulties to be overcome by developments of the more or less established theories. Thus up to the introduction of electron theories in the closing years of the nineteenth century Maxwell's electro-dynamics was expected to provide the answers to the problems; a view taken confidently by Lodge.[30] Similarly during the twentieth century the Drude-Lorentz formulation of the electron theory formed the basis for explaining the conduction of electricity through solids. There was, however, a contrast; for the simple electron theory was never more than an approximation to a total explanation; it was never able to account for all the phenomena of metallic conduction let alone the rather more complex situations pertaining in semiconductors. Maxwell's theory was never put to the test with respect to the conduction of electricity through solids for the theorems of electromagnetism were recoverable within a structure in which the presence of mobile charges was assumed.[31] With the discovery of the electron the properties of solids were explicable, in principle, in straightforward terms.[32] Consequently a great amount of theoretical activity was devoted to the electron theory; directed towards modifications that would fit more accurately to experimental results.

The study reported in these pages, that is the history of selenium, will be complemented when the work put into other materials has been researched. Even the brief consideration devoted to these substances in this thesis has uncovered a vast amount of source material concerned with other solids. There is a pressing need to examine the history of materials akin to selenium, particularly the researches carried out by the German workers who have been mentioned here and there. Their work led them to a classification of semiconductors by 1920 and deserves considerable examination.

A confluence of research eventually occurred, outside the time period we have considered; although hints of an intersection between various lines of work were evident as early as 1914. Some of the work carried out for this thesis, although not discussed in the substantive chapters, suggests that Gudden and Pohl were mainly responsible for the colligation of the diverse results and substances.

We can summarise the areas in which much fruitful historical research can be done thus:-

1. Theories of electricity and the solid state before the electron theory; electrolysis, Volta forces, contact forces and conduction.
2. The introduction of the electron theory; its influence on descriptions of solid state conduction and the modifications that were suggested to produce an accurate picture of the phenomena.
3. Experimental and theoretical work on other semiconductors; particularly those researches that culminated in the threefold classification of solid electrical conductors into electrolytic, pure metallic and variable conductors.
4. The confluence of results in the 1920's; particularly to assess the significance of the work of Gudden and Pohl who devoted much of their effort to electrical conduction in nom-metallic crystals and published a considerable number of papers.[33]

If this research programme is ever completed the history will be written up to the introduction of the band theory of solids in 1931.[34,35] Then will the path be open to examinations of the ultra-fine structure of the history of semiconductors.

## 2. EPILOGUE.

At the moment of conception of this thesis the end of the research was anticipated to be a study of semiconductors from 1833 to 1948; from the discovery of the positive temperature coefficient of conductivity to the invention of the transistor. Like many plans, perhaps like all plans, this hope was not to be realised. The original expectations were based on historical information in review articles and textbooks, which, although presumably not intentionally, are misleading in their treatment of the early period. For however good such writings may be they are concerned not with developments in and as history but with discoveries, adumbrations and 'fruitful' lines of research; their content and method is 'Whiggish'. As research progressed it became increasingly evident that far too much material existed for detailed treatment in one thesis; and that the problems and investigations in the fifty years between 1870 and 1920 presented sufficient interest and import to demand a study in their own right. Eventually a history of selenium between 1873 and 1919 was written.

Yet the story lacks 'human interest'; the main characters, Adams, Bidwell, Brown, remain shadowy figures. For beyond published works, obituaries and short biographies, there is little to connect us with the men themselves. Some letters of Bidwell's exist in the library of the Royal Society in London, but of Adams and Brown there seems to be nothing. We can only guess at the motivations and minds that lie behind the facade of the formal papers. Surprisingly Pohl was still living when the research for this thesis began and was kind enough to consent to an interview;[36] during which he provided some fascinating glimpses into his work during the 1920's and into his methods and motivations.

Pohl straddled the old and the new. He began his researches just as the quantum theory of heat radiation was emerging and before Einstein's theories of relativity and the photoelectric effect were widely known; and his active work continued until what we class as 'modern physics' was completely established. Particularly, in the thirties, he saw his experimental work, and that of others, in which many of the properties of semiconductors were established rendered clear, if not obsolete, by the band theory of semiconductors.

The word 'obsolete' has been chosen with care, for, in a sense, all experimental work that predates a comprehensive theory is obsolete; but in the case of the band theory it seems as if previous experimental work had little or no effect on its invention. Yet after its formulation a vast proportion of obscure experimental details fell into place, even though Wilson, the proposer of the band theory, had almost no knowledge of the work in semiconductors. This is Wilson's own opinion given to me in a delightful interview in 1974.[37] Sir Alan Wilson exuded a confidence in his memory of the events of the late 1920's and early 1930's that added colour to the researches; the accuracy of his memory and interpretation requires more independent confirmation than it has so far received. (Partial confirmation came in an interview with Sir Nevill Mott of Cambridge

University and by letter from Sir Rudolf Peierls of Oxford).

This epilogue represents my thanks to these gentlemen, particularly Robert Pohl and Alan Wilson, who kindly spared time to answer my questions concerning their work, motivations and successes. What follows is a precis of their vision of the past and their own early associations with semiconductors.

Neither Pohl nor Wilson intended to contribute to the solid state in the manner that they eventually did. Pohl's researches stimulated many others[38] and Wilson's laid the foundations of the modern theory of the solid state; but their entries into this field possessed those elements of chance that applied in the early history of selenium.[39]

Pohl had begun his postgraduate work in 1906, investigating the external photoelectric effect[40] while at the University of Berlin, and carried out researches on X-ray diffraction during his vacations in Hamburg. He published a number of papers before the First World War[41] and while on military service was called to the chair of Experimental Physics at Göttingen; a post he held from 1919 until his retirement in 1943. He had intended to extend his work on the external photoelectric effect, but found the austerities of post-war life precluded this aim. Peace time shortages were not limited to the necessities of life, but affected Physics Departments, and, according to Pohl, turned his thoughts towards solids. Successfully to prosecute a research programme into the photoelectric effect required the production and maintenance of extremely high vacua; to which end liquid air was essential; but liquid air was unobtainable in Göttingen in 1919. In Pohl's words, 'I was half annoyed, and suggested, half jokingly, that we should take the exact opposite of a vacuum, that is a solid body! ' Thus he began his researches into the solid state.

His aim was to reproduce in solids the effects he had noted during his early research into the photoelectric effect; that the emission of electrons from the alkali metals was markedly dependent on the cleanliness of the surface. He suspected that the presence of small amounts of impurity in a 'carrier' material would, on irradiation by light, emit electrons and display the result as an increase in the dielectric constant of the 'carrier' material.

Pohl's suspicions were correct; the dielectric constant of zinc sulphide in which a small amount of copper had been introduced was increased by the action of light. Pohl had demonstrated that electrons were liberated by the action of light within solid materials. As Pohl's ideas for research stemmed from his pre-war interests, so did his wartime work present him with measurement techniques that were adaptable to his work at Göttingen. His main task during the First World War was to produce continuous radio waves; no doubt for communication purposes. At Göttingen he employed continuous electromagnetic waves as the measuring tool to detect the shifting dielectric constants by a beat frequency method.[42]

Other phosphors did not possess the same properties as zinc sulphide. Pohl realised, as had Brown ten years earlier, that the properties of phosphors were dependent on their physical form; in particular their existence as powders. It appeared essential that single crystals be used and to that end a diamond was selected as their working substance. Pohl, joined now by Gudden, soon showed that 'a battery of a few hundred volts and a single match were sufficient to show photoconductivity.'

A notable peculiarity of the experimental work of the Göttingen researchers in the 1920's is the lack of use of the Hall effect by then a fairly well established technique[43] and the abrupt end to the researches on diamond for the majority of the work carried out by Pohl and others was concerned with the alkali-halogens.[44] Now, while as Pohl pointed out the alkali-halogens could be made artificially in a very pure state, and were cheap, there was, in fact, nothing scientific about the decision to use alkali-halogens and to make little use of the Hall effect; and the two decisions were linked.

The work on the single diamond possessed by the laboratory at Göttingen promised to be extremely fruitful but required confirmation with other specimens. However, after much searching around the diamond merchants of Germany the Göttingen diamond proved unique. So work continued with it. Gudden suggested that the Hall effect in diamond should be measured using their one useful specimen. The Hall measurement with the diamond ruined both the specimen and Pohl's opinion of the Hall effect as a measuring technique.

> 'We positioned the diamond between the poles of a large electromagnet. However we forgot to fasten down the poles of the magnet; they were attracted together and, immediately, our one useable diamond had been pulverised.'

This experience appears to have had a considerable effect on Pohl, for he accompanied the story with a smack of fist upon palm when saying 'Diamenten pulver!' After that result he wished, 'To hear no more of the Hall effect.' A decision, which in view of his opinion of later American work, he considered to have been mistaken.

From the experimenters in Pohl's laboratory there issued a stream of papers concerned with the electrical and optical properties of solids. Between them they established the significance of the impurities in these properties and the work done in Göttingen attracted the attention first of Mott[45] and then of a group of American workers among whom Pohl referred to Shockley, ('With his fast cars!'), Bardeen and Brattain. These men, with the aid of Wilson's band theory were to extend Pohl's work greatly. Yet while Pohl influenced the field of the solid state, either directly, or through his pupils many of whom became Professors of Physics, he, himself, did not essay any theoretical interpretations. In 1974 Pohl's view of himself was as an experimenter interested in facts, for as he told me:-

> 'It has become very common, nowadays, to represent all these developments starting from a particular theory, I always proceeded in a different way. I

> was always more interested in the facts. Facts, after all remain, but theories explaining them come and go.'

Indeed Pohl is right. All modern textbooks concerned with solids begin with a statement of Wilson's band theory of semiconductors and its subsequent modifications; for the theory is general. The genesis of his theory and its immediate reception is only rarely considered; and seems never to have been examined within a historical framework. This part of the epilogue, while making no attempt to provide an historical analysis, will record a few of Wilson's own memories of the conception of his ideas, and the effect they engendered.

In January 1931 Wilson was in Leipzig on a Rockefeller Foundation Scholarship. He had chosen Leipzig in preference to Copenhagen primarily because of the presence of Heisenberg and Bloch. Wilson had graduated from Cambridge in 1926 and, like many theoreticians there, had done a little work in nuclear physics. By 1929, when a research fellow at Emmanuel, Sommerfeld's theory and Kapitza's work[46] turned his interest, and that of a few others, towards the solid state. He saw his Rockefeller Scholarship as an 'escape' from Cambridge 'which was highly concerned with nuclear physics', and his choice of Leipzig reflected his desire to extend his work in the solid state.[47] He did not expect to investigate the properties of semiconductors at all, for as he said:-

> 'So I went there in January 1931. Without any specific problem to deal with, for one dealt with a number of problems, would try anything. You worked for a month or two, if you got a lead on

> it you went on, if not then . . . . I was trying to get an explanation of Kapitza's results, as were many people at the time too. Now the specific way in which I came to discover the theory of semiconductors was, of course, not working on semiconductors at all. Not many were at that time. Most that was known were variable current conductors'.[48]

Research workers at Leipzig were expected to read seminar papers and Wilson was asked by Heisenberg to present an appreciation of some work by Peierls[49] who had arrived at puzzling results concerned with the motion of electrons within certain types of solid; they appeared to move in the wrong direction. Wilson was concerned to understand the papers fully for, 'to give a seminar in German at which I would be cross-examined back and forth would be a bit of an ordeal, and therefore one had to understand someone else's work more thoroughly than if one was talking about one's own'. It was this effort and Heisenberg's demand that explanations should be made physically intuitive that led him to his band theory of semiconductors. Wilson realised that if bound electrons and energy gaps were used as the starting point of the explanation then the anomalous results were explicable in terms of vacancies in the valence bands of crystals and elements. It was this physical picture that gave him his theory.

Thus Wilson, who had intended to examine magnetoresistance, instead illuminated a much more general field. After some initial resistance from Bloch the ideas were accepted and discussed at a colloquium in Leipzig. This event, according to Wilson, was when he began to acquire some knowledge of semiconductors, and was the explanation for his two papers to the Royal Society.[50] It was evident that the theory was intuitively attractive, but there remained many areas of disagreement between experimentalists.[51] There was a need for new experiments and for the confirmation or denial of earlier knowledge. Yet, apparently, Wilson found it almost impossible to persuade any of his Cambridge contemporaries to carry out the necessary work.[52] Thus by 1936, Wilson ceased doing work in the solid state 'because of the complete indifference of anybody in Cambridge to the subject.' The development of his theory, for which he was awarded the Adams Prize 'was to be largely in the hands of Mott when he went to Bristol University.'[53]

Thus there is a final irony in the fact that Mott left Cambridge and effectively founded a school of solid state physics, while Wilson, the man mainly responsible for the gigantic developments in the field in the last forty years turned away from the subject. As he remarked:-

> 'There was no school; and, this is rather odd, Mott started off working on collisions. Then he left and went to Bristol and then took up my subject, solid state physics. I stayed in Cambridge and took up his subject, collisions. Because it is very difficult working in a vacuum and the only way to go is to talk about things that you work on. So I turned over to deal with mesons and so on, there were people you could talk to.'

Further historical research may substantiate

Wilson's claim, in which he was not being arrogant, that

> 'It couldn't have been done without me, because it was such a mucky subject you could never see your way through. Once you'd got the band theory and the acceptor and donors the need for pure material was demonstrated. The way to go was clear.'

# REFERENCES

# and

# NOTES

References and Notes. CHAPTER 1.

1. See, for example, Mott, N.F. in 'Theory and Experiment since Schrödinger's Equation', Inst. Phys. Bulletin, 25,(1974), pp 448-451. The article is largely concerned with the author's experience and interest in the solid state and in the later paragraphs makes the point that glassy solids have become a subject of study. Sir Nevill Mott made similar statements in an interview on the 1st November 1974 at the Cavendish Laboratories.

2. It is a little difficult to determine when a branch of science becomes part of the 'establishment', or, indeed, what the 'establishment' is, but without entering into a controversy on this point it is interesting to note that the Institute of Physics set up a 'Solid State Sub-Committee' in May - June 1965 and in Inst. Phys. Bulletin, 13, (1962), pp. 235-237 a report on a 'Conference on "The Teaching of Solid State Physics" ', can be found. Of particular interest in that report is the following paragraph.

> 'Both Mr. Gibbs and Mr. Jones drew attention to the rate at which semiconducting devices were superseding vacuum electronic devices in most fields of application, and predicted the time was not far distant when vacuum devices would be obsolete except for a few special applications. This change would radically alter the nature of a course on 'Electronics' whether taught as a small part of a degree course in pure physics, or a rather larger part of a course in applied physics. The likely development of the 'solid circuit' will bring about even more profound changes in these branches, although the basic circuit theory will, of course, still be applicable. These changes may well have repercussions in H.N.C. and 'A' level teaching. Even if thermionic emission, as such retains its place in the syllabus, it will be difficult to justify the inclusion of thermionic diodes and triodes. Already some schoolteachers are pointing out that the kind of question which really interests their pupils is how a pocket transistor works.'

Thus by 1965 the subject of solid state physics had become sufficiently well 'established' to be incorporated in the sub-committee structure of the Institute of Physics and to have been the subject of at least one Teaching conference in which the inclusion of the study of solid state devices in 'A' level courses was considered to be a possibility.

3. Tilton, J.E., Diffusion of Semiconductor Technology, (Washington, D.C. 1971).

4. Referring to Britain only, many firms concerned with electronics and vacuum tube devices began to expand their activities in the solid state by setting up factories whose main concern was with research, development and production in the field of solid state devices. Thus from 1952-1958 companies such as STC, (c1953), Mullards (c1955), Texas Instruments (c1956), and G.E.C. (c1952) all made special efforts to move into the market that was beginning to emerge with the improvement in transistor technology.

5. Tilton, J.E., op.cit., (3),(1971),Chapter 4.

6. Aston University has recently set up, under the direction of Professor Ernest Braun, a Technology Policy Unit, and in a letter Dr. Stuart Macdonald of that unit wrote,

   'The Technology Policy Unit at Aston has recently embarked on a study of some of the socio-economic implications of semiconductor innovation, basically since the introduction of the transistor. We are really concerned with the main developments, comparing the opinions of those most concerned with the main developments at that time with what eventually transpired.'

   Dated 23.1.74.

7. The firm referred to is Hawker Siddeley Dynamics, then De Havilland Propellors, which was engaged in the design and development of an air-to-air guided missile activated by the infra-red emission from the exhausts of jet engines. Thus to the common environmental problems of air-to-air missiles, vibration, high acceleration forces and great extremes of temperature were added those of low signal levels, necessitating, at that time, extremely sensitive detectors and high gain low noise amplifiers. Transistors appeared to solve many of these problems. They are robust, need little current for their operation, have a low noise, yet a lack of understanding in the manner of their operation gave rise to design problems that were difficult and expensive to solve. For example, see ref. 11, below, there was a tendency to use them in common base configuration which was ill suited to accepting the high output impedances of the sensitive cells then in use, (the author remembers a suggestion that a cathode follower should be used between the high resistance sensitive cells and the first stage of the transistor amplifiers!). The adoption of an indium antimonide cell solved the problems of impedance matching but raised new ones of sensitivity and temperature control of the cells, problems that were overcome but only at the expense of much time and money.

8. The adoption of silicon transistors by De Havilland Propellors' engineers in 1956 highlighted the fact that the 'state of the transistor art' was at a fairly primitive stage. It was imperative that low noise, high gain elements be used in the amplifiers and it was obvious that although some commercial transistors satisfied the stringent specifications demanded most did not and a rather complicated agreement was entered into between the development laboratories of De Havillands and its main supplier, then Texas Instruments of Bedford, that resulted in satisfactory yet expensive transistors. At least one reject batch is believed to have formed part of the foundations of the Texas Instrument factory at Bedford.
(I am indebted to John Lee, Managing Director of Hawker Siddeley Engineering and Lionel Thompson, Chief Systems Engineer of the same company, for confirmation of the points made in footnotes 7,8 and 11).

9. Vacroux, A.G., 'Microcomputers', <u>Sci. Amer.</u>, <u>232</u>, (1975), pp 32-40.

10. Diffusion and masked etching were techniques that were introduced into the manufacture of solid state devices in the early 60's, and allowed the construction of reliable and complex devices. Diffusion is the production of a junction in a substrate of a particular type of semiconductor by the process of thermal diffusion. Junctions produced in this manner are reliable geometrically and electrically. Masked etching is the production of a particular shape on the surface of a crystal by the generation and controlled removal of oxide layers thereby allowing several junctions to be produced in the same device. The twin methods allowed very much better quality control and very much more versatile elements to be manufactured.

11. An interview with Lionel Thompson of Hawker Siddeley Engineering, who during the 1950's was one of the engineers responsible for the introduction of transistor circuitry into the then missile electronics, confirmed an impression that at this time the behaviour of transistors was not well understood. He detailed a case when he had 'discovered' a new transistor effect. A circuit was producing pulses of a regular sort and all efforts to locate the source of these unwanted signals proved fruitless, although they were all based on well tried methods. Eventually the interference was traced to an external airfield radar transmitter the signals of which were being 'detected' in an altogether unexpected fashion. In Thompson's opinion their failure to make an early diagnosis of the problem was entirely connected with their lack of appreciation of the behaviour of circuits using transistor in place of valves.

However a lot of confusion seemed to arise from the fact that transistors, in contrast to vacuum tubes, operated at low voltages and comparatively high currents. From this stemmed the notion that transistors were 'current operated' while vacuum tubes were 'voltage operated' although Ohm's law would seem to imply definite relationship between current and voltage. Yet from the early days transistor characteristics have been expressed in terms of operating currents and this seems to have caused initial difficulties.

12. The following are the numbers of papers quoted in Physics Abstracts referring to semiconduction. They are a guide only for there were several alterations to the publication, for example a change in indexing system in 1958 and 1965 and the introduction of semiconductor abstracts in 1959. However the few years quoted indicate a trend.

| | | | |
|---|---|---|---|
| 1944 | 3 | 1954 | 257 |
| 1946 | 8 | 1956 | 427 |
| 1948 | 19 | 1958 | 569 |
| 1950 | 126 | 1960 | 1350 |
| 1952 | 105 | 1962 | 1840 |

In the same period the total number of papers cited rose from 2688 to 24,000.

13. See the work of the Technology Policy Unit at Aston University, Ref. (6), above.

14. Wilson, A.H., 'The Theory of Electronic Semi-Conductors - I', Proc. Roy. Soc., (A), 133,(1931) pp 458-491 and 'II' Proc. Roy. Soc., (A), 134,(1931) pp 377-387.

15. Smith, R.A., Semiconductors, (Cambridge, 1959 and later editions).

16. Pearson, G.L. and Brattain, W.H., 'History of Semiconductor research', Proc. I.R.E., 43, (1955),pp 1794-1806.

17. Wilson, A.H., 'Theory and Experiment in Solid State Physics', Inst. Phys. Bulletin, 14, (1963), p 173.

18. Pearson, G.L. and Brattain, W.H., op.cit.,(16), (1955), p1794.

19. Wilson, A.H., op.cit.,(17), (1963), p 174.

20. Ibid., p 174.

21. See note (6).

22. Wilson, A.H., op. cit., (17), (1963).

23. Gudden, B. 'Elektrische Leitfäghigkeit elektonischer Halbleiter.' Erg. Exat. Nat., 13, (1934), p 223.

24. Wilson, A.H., op.cit., (17), (1963).

25. Baedeker, K., 'Über die elektrische Leitfähigkeit und die thermoelektrische Kraft einiger Schwermetallverbindungen.' Ann.d.Phys., 22, (1909), pp 749-766.

26. Baedeker, K., 'Künstliche metallische Leiter', Phys. Zeits., 13, (1912), pp 1080-1082.

27. See for example Thomson, J.J., 'Recent Researches in Electricity and Magnetism' (Oxford, 1893). This work makes mention, in passing of the wayward conduction characteristics of carbon, and refers to the Hall effect once on p 486.

28. Lodge, O., 'Electrons', (London, 1906), pays little attention to the conduction properties of solids in general or semiconductors in particular.

29. Fournier d'Albe, best known for his biography of Crookes, became interested in the photoconductivity of selenium and published several papers concerned with this question. Fournier d'Albe appears to have been fully in touch with the science of electricity during the latter years of the 19th century and the early years of the 20th, for he was a regular contributor to 'The Electrician'. He also published several books on the fringes of science concerned with matters more spiritual than physical. He retained an interest in the properties of selenium and published The Moon Element in 1918, primarily to publicise the Optophone a device intended to aid the blind in reading.

30. Wick, F.G., wrote a series of papers in Phys.Rev.,27, (1908), concerned with the electrical properties of silicon; further reference to this work will be made in a later chapter.

31. Pohl, R., interview at Krefeld, 25th July, 1974.

32. The quality of the theoreticians at Göttingen is indicated by the presence of Born and Hilbert, for example, yet it appeared from the interview with Professor Pohl, (31) that there was scant interest in his work on the electrical properties of crystals. In Pohl's opinion this was a result of the over-riding influence of the interest in atomic and nuclear physics and the development of quantum theory, which at that time was not applicable to the problems he was investigating.

33. Wilson, A.H., op.cit., (14), (1931).

34. Wilson, A.H., Interview at the Athenaeum 9th November 1974 and Private communication.

35. See, for example, Tilton, J.E., op.cit.,(3), (1971).

36. Mott, N.F., see Ref. (1).

37. Faraday, M., Experimental Researches in Electricity Series IV, (April, 1833), paras. 432-433 (pp 122-124, Dover edition, New York, 1965).

38. Smith, W., 'The Action of Light on Selenium', Soc. Tel. Eng. J., 2, (1873), pp 31-33.

39. The Electrician was mainly concerned with topics of interest to practising electrical engineers, yet included in its pages articles concerned with up to date researches in electricity.

40. The significance of this sentence revolves around the definition of 'eminence'. Attempting to clarify this results in a circular argument.

41. Ref. (31) above.

42. Ref. (34) above.

43. Gudden, B., op.cit., (23), (1934).

44. Lark-Horovitz, K., The New Electronics in The Present State of Physics, (AAAS 1954).

45. Wilson, A.H., op.cit., (17), (1963).

46. Pearson and Brattain, op.cit., (16), (1955).

47. Lark-Horovitz, K., op.cit., (44), (1954).

## References and Notes. CHAPTER 2.

1. See for example Thomson, J.J., Recent Researches in Electricity and Magnetism, (Oxford, 1893).
2. Faraday, M., Experimental Researches in Electricity, Series IV, (April 1833), Paras. 432-433.
3. Ibid., Series IV, (April 1833), Para. 434.
4. Ibid., Series IV, (April 1833), Para. 435.
5. Ibid., Series IV, (April 1833), Para. 436.
6. Ibid., Series IV, (April 1833), Para. 439.
7. Ibid., Series XII, (Jan. 1838), Para. 1340.
8. See Ref. (7).
9. Ibid., Series XII, (Jan. 1838), Para. 1341.
10. Ibid., Series XII, (Jan. 1838), Para. 1342.
11. Lodge, O., Electrons, (London, 1906).
12. Ibid., Introduction p xiii.
13. Maxwell, J.C., Treatise on Electricity and Magnetism, (London, 1873).
14. See for example Topper, D.R., J.J. Thomson and Maxwell's Electromagnetic Theory, Case Western Reserve University, Ph.D., (1970), or Thomson, J.J., Report on Electrical Theories, B.A. Report, (1885).
15. The origins of quantum theory are discussed in detail in Jammer, M., The Conceptual Development of Quantum Mechanics, (New York, 1966).
16. Smith, W., 'The Action of Light on Selenium'., Soc.Tel. Eng.J., 2, (1873), pp 31-33.
17. Braun, F., 'Über die Stromleitung durch Schwefelmetalle', Ann.d.Phys. (Pogg.), 153, (1874), pp 556-563.
18. Adams, W.G., and Day, R.E., 'The Action of Light on Selenium', Phil. Trans., 167, (1877), pp 313-349.
19. Smith, W., op. cit., (16), (1873), pp 31-32.

20. The nature of selenium, i.e. metal or non-metal, was not established in 1873. Siemens, C.W., (ref. (35), below), was not prepared to place selenium in either category with certainty. For he wrote:- '(Selenium) is fusible, combustible, and similar in many other respects to sulphur, phosphorous, and tellurium. It is in fact one of those substances which are placed by chemists upon the border between metals and metalloids, and, like a true borderer, selenium refuses to be amenable to the laws governing either of these natural groups.'

21. Smith, W., 'Selenium, its Electrical Properties and the Effect of Light thereon', Soc.Tel.Eng.J., 6, (1877), pp 423-448.

22. Smith, W., op.cit., (16), (1873), p 33.

23. It is unlikely that 'group' is being used here in its modern sense; that is referring to the periodic table. Of course, in this sense, selenium is not in the same group as all the other elements mentioned. Probably an earlier criterion was being used, for although Mendeleef had produced his idea by 1873 it was not being used as a means of classifying the elements.

24. No reference was supplied by the Chairman and none has been found in which an effect of light on plumbago, (i.e. graphite), was shown.

25. That is amorphous and crystalline. This had been known for a number of years.

26. That Smith should have used rock salt to stop heat rays reaching his selenium is remarkable. The fact that rock salt transmitted heat was well known.

27. Maxwell, J.C., 'A Dynamical Theory of the Electromagnetic Field', Phil. Trans., 155, (1865), pp 459-512. Introduction reprinted in A Source Book in Physics, (Cambridge, Mass. 1965), edited by Magie, W.

28. Tyndall, J., On the Identity of Light and Radiant Heat, a lecture delivered at the Royal Institution on Friday, February 2, (1872). Printed in Royal Institution Library of Science, (Physical Sciences), 2, pp 330-334, (London, 1970).

29. Ibid., p 331.

30. Hertz's experiments of 1887-1890 may be considered to have 'clinched' the issue.

31. Sale, W., 'The Action of Light on the Electrical Resistance of Selenium', Proc.Roy.Soc., 21, (1873), pp 283-285.

32. Rosse, the Earl of, 'On the Electric Resistance of Selenium', Phil. Mag., (4th Series), 47, (1874), pp 161-164.

33. Sale, W., op.cit., (31), (1873), p 285.

Sale appears to have moved swiftly off the mark. Willoughby-Smith presented his letter to the Society of Telegraph Engineers on 4th February 1873, the reading taking place on the 12th of the same month. A week later Nature carried a precis of the letter. The issue of Nature for March 6, 1873 carried a request from Lieut. Sale, R.E. asking for methods of measuring high resistances. He received no reply through the columns of Nature but must have managed for his report, reached the Royal Society on March 28th, 1873. Evidently the Royal Engineers did not believe in a slow approach!

34. Rosse, the Earl of, (1874), op.cit., (32), p 163.

35. Siemens, C.W., 'The Action of Light on Selenium', Proc.Roy.Inst., 8, (1875-1878), pp 68-79. Also in The Royal Institution Library of Science, 2, pp 466-477.

36. Siemens waxed almost poetic. 'Amongst the powers of nature, light seems to be the one which enters least into the composition of matter. The beam of light falling upon the landscape, or upon a work of art, reveals instantly its form to our minds, but with the disappearance of the light its effects seem to vanish entirely: .... there seems to be no permanent effect produced in the material condition of the objects before us. Shall we wonder, then, that the true nature of light has remained a mystery more profound than that of the other forces of nature, and that Newton himself exclaimed, in desponding mood, the memorable words, "Nil luce obscurius." ' Siemens was impressed by Smith's discovery indicating his feelings in a question later in the lecture. 'Could it be possible that the mere superficial action of light upon a solid substance could so change instantaneously its internal condition as to open amongst its particles flood-gates for the passage of the electric current, to close again upon the removal of the light?'.

37. Siemens, C.W., op.cit., (1876), (35), pp 75-76.

38. Adams, W.G., 'The Action of Light on Selenium', Proc.Roy.Soc., 24, (1875), pp 535-539.

39. Siemens, C.W., op.cit., (1876), (35), p 76.

40. Allen, H.S., Photo-electricity. The Liberation of Electrons by Light, 2nd Ed. (London, 1925).

41. Siemens, C.W., op.cit., (1876), (35), p 70.

42. Ibid., p 72.

43. Later workers, Saunders for example (see bibliography), showed that the heat evolved was easily measurable.

44. Ibid., p 75.

45. Ibid., p 75.

46. Ibid., p 76.

47. Adams, W.G. and Day, R.E., op.cit., (18), (1877).

48. Lark-Horovitz in his review The New Electronics in The Present State of Physics, AAAS, 1954, credits E. Becquerel with the discovery of the photovoltaic effect. Certainly in a paper entitled Sur Les Effets Electriques qui se Produisent sous les Influences Solaire it is shown that a voltage is produced when light is incident on electrodes in an electrolyte. Adams and Day were the first to notice and report the effect in solids. Becquerel's paper appeared in Comp. Rend., 9, (1839), pp 711-714.

49. Adams, W.G. and Day, R.E., op.cit. (18), (1877), p 313.

50. Ibid., p 348.

51. Ibid., p 322.

52. Smith, W., op.cit., (16), (1873).

53. Sale, W., op.cit., (31), (1873).

54. Adams, W.G. and Day, R.E., op.cit. (18), (1877), p 319.

55. Ibid., p 328.

56. See Smith, R.A., Semiconductors, (Cambridge, 1959), for example.

57. Henisch, H.K., Metal Rectifiers, (Oxford, 1949).
On pages 8 - 13 Henisch describes the manufacture of selenium rectifiers where after the production of a layer of selenium on a metal substrate has been achieved he outlines the 'forming' process necessary to achieve a satisfactory rectifier. 'At the conclusion of the processes described above the electrical characteristics of the disks are still unsatisfactory, and in particular the reverse resistance is low. In order to improve the characteristics the disks are subjected to an electrical 'forming' process, ....

The details of this process can differ considerably for rectifiers of different manufacture. Sometimes a current of 50 mA/cm$^2$ is passed through the disk in the reverse direction for a few minutes. In other cases between 10 and 20 volts are applied for 24 hours, the voltage being increased as the reverse resistance rises.

. . . . . .

Before the forming process very considerable variations are observed between individual disks. After forming, the disks are much more comparable. Between 25 and 30 per cent of the unformed disks do not show any asymmetric conduction at all. This is thought to be due to short circuits between the electrodes. The fault can usually be remedied by passing a heavy current through the disk and thus "burning the weak spot out".'

58. Braun, F., 'Über unipolare Elektricitätsleitung', Ann.d.Phys. (Wied), 4, (1875), pp 476-484.

59. Thomson, J.J. and Thomson, G.P., Conduction of Electricity through Gases, 2, (3rd edition), (Cambridge, 1933), p 429.

60. Adams, W.G., and Day, R.E., op.cit., (18), (1877), p 328.

61. Lark-Horovitz, K., op.cit., (48), (1954), On p 58 of his paper he puts the situation succinctly and well.

'The first step in the investigation of the electrical properties of any non-metallic substance must be the clarification of the type of conductivity, whether electrolytic or metallic. One usually concludes that electrolytic conductivity exists if Faraday's law of electrolysis is fulfilled and the transport number, the fraction of the total charge carried by any one ion corresponds to the value expected for electrolytic conductivity. One must also compare the measured conductivity with the maximum conductivity which can be expected for an electrolyte.'

62. Lodge, O., On Electrolysis, B.A. Report, (1885), p 723-772.
This report is a masterly summary of the state of knowledge in 1885 and is completed with a set of problems that, in Lodge's opinion, demanded solutions. This paper will be used in the next chapter when a discussion of various theories will be made.

63. Ibid., p 727.

64. Adams, W.G., and Day, R.E., <u>op.cit</u>., (18), (1877), p 329. 'That this is not due to a current arising from thermoelectric action in consequence of the junctions where the current enters and leaves the selenium being unequally heated is evident, since a current may be obtained from the selenium a considerable time after the battery-current has been interrupted, so long as the selenium electrodes have not been connected in the interval.'

65. It is interesting to note that Adams and Day do not explicitly conclude that an electrolytic interpretation is the correct one. We are left with an unfinished syllogism. If the conduction is electrolytic, then there will be polarisation. There is polarisation, hence . . . .

66. Lark-Horovitz, K., <u>op.cit</u>., (48), (1954), p 58.

67. The value for the conductivity of silver chloride was obtained from Mott, N.F. and Gurney, R.W., <u>Electronic Processes in Ionic Crystals</u>, (Oxford, 1940).

68. Adams, W.G. and Day, R.E., <u>op.cit</u>., (18), (1877), p 332.

69. Ibid., p 333.

70. Note (48) above refers to the work of E. Becquerel who, in the opinion of Lark-Horovitz discovered a photo-voltaic effect in electrolytes, or rather at the electrodes in electrolytes. But this was by no means unequivocally an example of the direct conversion of light into electricity nor was it accepted as such; the effect could have been due, for example, to chemical reactions initiated by the action of light. However, if priority of publication is thought important Adams and Day have that honour in the case of the photo-voltaic effect in semiconducting materials.

71. Adams, W.G. and Day, R.E., <u>op.cit</u>. (18), (1877), p 333.

72. Quoted in Lark-Horovitz, K., <u>op.cit</u>., (48), (1954), p 72.

73. Adams, W.G. and Day R.E., <u>op.cit</u>., (18), (1877), p 335.

74. Adams, W.G. and Day, R.E., <u>op.cit</u>., (18), (1877), p 320. A description of two methods of preparation is given. One of these is identical to that developed by W. Siemens and reported by C.W. Siemens in <u>op.cit</u>.,(35), (1876).

75. Adams, W.G. and Day, R.E., op.cit., (18), (1877), p 338.

76. The full results are published on pp 333-342 of Adams W.G., and Day, R.E., op.cit., (18). They are wholly discursive; my tabular reproduction is considerably more clear and unambiguous. One other sample was tested but showed no photo-current whatsoever.

77. As an example of their style of reporting results they gave the observations obtained with one sample in this form. (p 337, op.cit., (18)) 'No. 14, which had been used both for direction and also for polarisation experiments, was examined in the same way with the limelight.

When the light was brought to bear upon one face, there was a current to the left of zero, and when, by means of a reflector and a lens, the light was directed on to the rear face of the selenium, there was a current of 100 in the same direction as before.'

78. Adams, W.G. and Day, R.E., op.cit., (18), (1877), pp 338-341.
The purpose of this experiment was not made clear. It appears to have been a purely 'Baconian' venture, except that having isolated two effects of light they proceeded to investigate the possibility of some unforseen interaction between them. They in fact found that the two effects were independent.

79. Matthiessen, A., 'On the Thermo-electric Series', Phil. Trans., 148, (1858), pp 369-381.

80. Adams, W.G., and Day, R.E., op.cit., (18), (1877), p 342.
The manufacture of reliable thermoelements was not very easy if non metals were used; since the specimens used were not prepared with thermoelectricity in mind, it is not surprising, among all the other possibilities, that little weight can be given either to Adams' and Day's results or to Matthiessen's (see note (77) ).

81. This statement is not very meaningful, for there was no independent way to check the process of annealing; perhaps the statement can be considered more as an insight than a useful empirical conclusion.

82. Adams, W.G. and Day, R.E., op.cit., (18), (1877), p 341.

83. Interview with Sir Nevill Mott, Cambridge, November 1st, 1974.

84. Gudden and Pohl realised the need for very pure materials in the 1920's, and the point was brought home forcefully by Wilson in his 1931 theory and its subsequent extensions.

85. See, for example, Smith, R.A., Semiconductors, (Cambridge, 1959), Chap. 5.

86. Ibid., pp 381-383. On the subject of the resistivity of selenium Smith writes 'The situation is complicated by the fact that the resistivity is found to be dependent on the applied field ~ 5 V/cm; the resistivity generally decreases as the field is increased but this is not always so and the phenomenon is far from being completely understood.' It is interesting that Adams and Day applied fields of up to 15 V/cm when they noticed the decrease of the resistance of their samples. They may therefore have met the property to which Smith refers and an explanation would be inappropriate then and now. Also on p 157.

87. Ref. (36) this chapter.

88. Lark-Horovitz, K., op. cit., (48), (1954), p 72.

89. Martin, M.J., 'Selenium', Wireless World, 3, (1915), pp 681-685.

90. Adams, W.G. and Day, R.E., 'The Action of Light on Selenium', Proc.Roy.Soc., 25, (1876), p 117.

91. For a short biography see Proc. Phys. Soc., 6, (1885), (Report of Annual Meeting), pp 10-11.

92. Sabine, R., 'Some Electrical Experiments with Crystalline Selenium', Phil. Mag., 5, (5th Series), (1878), pp 401-415.

93. Ibid., p 401.

94. Ibid., p 414.

95. Ibid., p 414. He wrote 'So far, the experiments seem to suggest the suspicion that light causes a modification of the surface tension of selenium, possibly an expansion of the crystalline surface.' Later parts of this paragraph indicate that he was postulating a mechanism that visualised differential expansions and contractions that altered the resistance between the crystals of the selenium hence modifying the electrical properties of the material. He did not suggest that the modification of the properties was due to heat, for the instantaneous effects that were obtained would have precluded this interpretation; as Adams and Day had clearly recognised.

96. Ibid., p 414. A suggestion is given in the following terms. 'I apprehend that the superficial atoms of any body, which are bounded on one side only by similar atoms, and on the other side by the medium in which the body is immersed may be capable of assuming vibrations of different periods to those which the atoms underneath the surface can assume.

It may also be that the luminous rays striking upon the superficial molecules of selenium, impart a vibration to them of a slower period than those of the exciting waves, and which correspond nearer to the period of the heat rays.' This vague statement takes on a clearer meaning if the notes in (95), above are read in conjunction with it. Sabine seems to want to appeal to the effect of heat, but cannot do so directly; he therefore appeals to some kind of sympathetic resonance phenomenon allowing the rays of light to produce the effect of heat. Apart from showing that under suitable conditions the effects of heat and light could be the same his ground was not very strong.

97. It is difficult to be positive of the exact date at which the resistance of carbon was known to vary with pressure. Bidwell's admittedly later, assumes this to be well known.

98. Sabine, R., op.cit., (92), (1878), p 403.

99. Ibid., p 404.

100. The results he gave for one cell were:-

| Junction number | Resistance of junction | Resistance of selenium between junctions |
|---|---|---|
| 2 | .0333 M | 0.1914 M |
| 3 | .0553 M | 0.1045 M |
| 4 | .0328 M | 0.1233 M |
| 5 | .0199 M | 0.1084 M |
| 6 | .0285 M | |

101. Ibid., p 405.

102. Ibid., p 407. Using currents of 2.9 and 0.42 μwebers he found a maximum of 8% variation in the resistance of the junction regions one specimen, and a difference of less than 0.1% in the body of the material.

103. Ibid., p 407.

104. Ibid., pp 409-410.

105. Ibid., p 412.

106. Ibid., pp 412, 413.

107. Ibid., p 413.

108. Using three cells Sabine measured the following values of x and y,

| x | | y | |
|---|---|---|---|
| I | III | II | IV |
| 5.68 MΩ | 5.56 MΩ | 4.89 V | 3.57 V |
| 6.39 MΩ | 6.43 MΩ | 5.76 V | 3.86 V |
| 55.2 MΩ | 53.0 MΩ | 0.75 V | 0.53 V |

These results, though somewhat circumstantial, seemed to Sabine, conclusive enough.

109. Braun, F., <u>op.cit</u>., (17), (1874).

110. Schuster, A., 'On Unilateral Conductivity', <u>Phil. Mag.</u>, (4th Series), <u>48</u>, (1874) pp 251-278.
Schuster had discovered, purely by chance, that poor contacts between copper wire and brass terminals possessed the property of conducting currents differently in opposite directions. He suggested that oxide films were responsible for the property.

111. A short biography of Bidwell can be found in <u>World's Who's Who in Science</u> p 173; and his obituary appeared in <u>Nature</u>, <u>82</u>, (1909), pp 252-253.

112. Bidwell, S., 'Selenium and its Application to the Photophone and Telephotography.' Royal Institution Friday Evening Discourse, March 11, (1881). Published in <u>Roy. Inst. Lib. Sci. (Phys</u>.), <u>3</u>, (1970), London, pp 138-149.

113. Ibid., p 144.

114. Adams, W.G., and Day, R.E., <u>op.cit</u>., (18), (1877).

115. Draper, H.N., and Moss, R.J., 'On Some Forms of Selenium and on the Influence of Light on the Electrical Conductivity of this Element', <u>Proc.Roy. Irish Acad</u>., <u>1</u>, (1873-74), pp 529-533.

116. Bidwell, S., <u>op.cit</u>., (112), (1881), p 144.

117. Bidwell, S., 'The Electrical Resistance of Selenium Cells', <u>Phil.Mag</u>., (5th Series), <u>15</u>, (1883), pp 31-35.

118. Bidwell, S., 'The Electrical Properties of Selenium', <u>Phil.Mag</u>., (<u>40</u>), (1895), p 242.

119. It is interesting to record that when photoconductive cells were manufactured for various uses in the years during and following the second world war, if these were of the microcrystalline type, protection against contamination was vital if they were to function at

all well. Moisture and oxygen both produced deleterious effects. We will show later that some of the effects described by Bidwell and others may be ascribed to the effects of moisture and other forms of contamination.

120. Bidwell, S., 'On the Sensitiveness of Selenium to Light, and the Development of a Similar Property in Sulphur', Proc. Phys. Soc., 7, (1885), pp 129-145.

121. Ibid., p 130.

122. Ibid.,

123. Ibid.

124. Fritts, C.E., 'On a New Form of Selenium Cell, and some Electrical Discoveries made by its use', Amer.J.Sci., 26, (1883), pp 465-472.

125. ____________., 'On the Fritts Selenium Cells and Batteries', Electrical Review, 16, (1885), pp 208-211.

126. Ibid., p 208.

127. These are not included in the body of the thesis for no other worker seems to have reported them, and they have no direct bearing on the semiconductor story, however they are worth the attention of a footnote. Fritts reported that the kind of battery employed affected the light sensitiveness of selenium cells. He discovered that while some cells operated perfectly satisfactorily with Leclanche cells they refused to react to the action of light when bichromate batteries were used in the circuit. This is a most extraordinary result. He found that an alternating current passing through one of the selenium cells he had made rewarded him with a 'singing' tone, he offered no explanation of this effect, which is indeed difficult to understand. The rectification could produce an unbalanced force on one or other of the electrodes which might then provide the source of sound; but it is hard to imagine how such a motion would gain sufficient energy to transmit a readily heard sound to the ear.

128. Fritts, C.E., op.cit., (125), (1885), p 210.

'This (photo-) current is continuous, constant and of considerable electromotive force. A number of cells can be arranged in multiple arc, or in series, like any other battery. The current appears instantly when the light is thrown upon the cell, and ceases instantly when the light is shut off. If the light is varied properly by any suitable means, a telephonic or other corresponding current is produced, which can be utilised by any suitable apparatus, thus requiring no battery but the selenium cell itself.'

This represented a considerable technological improvement over the type of cell used by Adams and Day; the currents from their cells were quite small, and unable to affect a microphone.

129. The features of construction that contributed to the superior performance of Fritts' cells were the thin selenium layer, thicknesses of 1 to 5 thousandths of an inch were given by Fritts; the large area of the electrodes, his 'standard' size was 2 x 2½ inches; and possibly, a relatively good 'ohmic' contact at one face, the opaque one, and a rectifying contact at the other, where gold foil was merely pressed against the selenium.

130. He did comment on the possibilities of investigations into selenium; he had noted, as had others, that the resistance and sensitivity of his cells depended occasionally, on the electrical treatment they received. He was particularly impressed that a few devices altered their resistance remarkably under the influence of alternating currents. He wrote:-

> 'The spectacle of a little selenium being stimulated, by a few interruptions of the current through it, into changing its resistance from a fraction of an ohm up to a million or several millions of ohms, and repeatedly and instantly changing back and forth, . . . . is one which suggests some very far-reaching inquiries to the electrician and the physicist. What is nature of electrical conductivity or resistance, and how is it so greatly and so suddenly changed?'.

131. Bidwell, S., op.cit., (120), (1885), p 131.

132. Ibid., p 132.

133. Ibid., p 132.

134. Bidwell, S., 'The Effect of Temperature on the Electrical Resistance of Mixtures of Sulphur and Carbon'. Phil. Mag., (5th Series), 13, (1882), pp 347-353.

135. Bidwell, S., op.cit., (120), (1885), p 133, and op.cit., (134), (1882), p 351.

136. See, for example, a paper read to the National Academy of Sciences by Alexander Graham Bell on April 21, 1881.

137. Many selenides do conduct electricity, possibly with a very small electrolytic contribution, but they act mainly as semiconductors.

138. Bidwell, S., op.cit., (120), (1885), p 134, where he wrote:-

> '. . . . as the result of a single rough experiment . . . . it appears that the conductivity of selenium which has been annealed in contact with copper is nearly 3000 times greater than that of selenium which has undergone similar treatment without the presence of a metal.'

139. The full statement can be found in op.cit., (120), pp 134-136.

140. Bidwell's words, on this point, were:-

> 'The fact observed by Adams and Day that there is generally a "dimunition of resistance in selenium as the battery power is increased." The same phenomenon occurs in the mixtures of sulphur and carbon before referred to. It points to the existence of imperfect contact between conducting particles, the conduction partaking of the nature of a disruptive discharge, and is consistent with the supposition that the particles of conducting selenide are imbedded in the selenium.'

141. Bidwell, S., op.cit., (120), (1885), p 136.

142. Ibid., p 136.

143. Ibid., p 137.

144. Selenium could be annealed from a temperature of about 217°C cooling through the melting point of the vitreous form, around 104°C, allowing the crystalline variety to appear. Sulphur, of course, does not behave like this, and annealing of this sort was not possible. For Bidwell this process was not one of true annealing, indeed in the passage always in parentheses, but a stage in which the selenides could form around the selenium, and perhaps grow in extent.

145. See note (144).

146. Again Bidwell appeared to be searching for indirect evidence.

147. Bidwell, S. op.cit., (120), (1885), p 137.

148. Ibid.

149. Ibid., pp 137-138.

150. It was later shown that sulphur was affected by light exhibiting the property of photoconductivity. However, its resistivity was far too high for Bidwell to have detected this phenomena. Unilluminated the resistivity of sulphur is about $10^{18}$ ohm-cms, decreasing by up to six orders of magnitude on illumination by suitable sources.

151. See Bidwell, S., op.cit., (120), (1885), p 142.

152. Ibid., p 142.

153. The resistance of the galvanometer used as a current meter was much lower than the lowest resistance of the sulphur - silver sulphide cell at its minimum.

154. Bidwell, S., op.cit., (120), (1885), p 143.

155. Note that it had not been established whether silver sulphide was an electrolytic conductor.

156. Bidwell, S., op.cit., (120), (1885), p 145.

157. In spite of his apparent close reading of the literature the work of Braun, (17), (1884), seems to have escaped his attention, as it did that of most workers in the late 19th century.

158. Moser, J., 'The Microphonic Action of Selenium Cells' Proc. Phys. Soc., 4, (1880-1881), pp 348-360.

159. Ibid., p 357, for example.

160. Microphones operating on the varying contact resistance of carbon granules with changing pressure had been introduced by Bell in the late 1870's.

161. Bidwell, S., 'On the Generation of Electric Currents by Sulphur Cells', Phil. Mag., (5th Series), 20, (1885) pp 328-336.

162. Moser, J., op.cit., (158), (1880-1881), p 348.

163. The two kinds of photophone were the mechanically operated variety that might have operated by temperature effects, and the purely electrically operated variety. The three forms of light rays, were, chemical, visible and heat.

164. Moser, J., op.cit., (158), (1880-1881), p 348.

165. The full description of this method of preparation of selenium cells is given in Moser, J., op.cit., (158), (1880-1881), pp 351-352.

166. Moser, J., op.cit., (158), (1880-1881), p 352.

167. Ibid., p 357.

168. Moser's footnote on this point was;

'On melting selenium, a grey film formed on the surface. This being removed by a platinum spatula, the amorphous selenium showed a brilliant surface; and only such selenium was employed, in order to get congruent results.'

169. It is questionable whether the allotropic modifications can be considered as chemical modifications, a reservation fully shared by Moser.

170. Moser, J., op.cit., (158), (1880-1881), p 360.

171. Bidwell, S., op. cit., (120), (1885).

172. Adams, W.G., and Day, R.E., op. cit., (18),(1877).

173. Flowers, A.E., 'Crystal and Solid Contact Rectifiers' Phys. Rev., 29, (1909), pp 445-460.

174. Bidwell, S., 'The Electrical Resistance of Selenium Cells', Phil. Mag., (5th Series), 15, (1883), pp 31-35.

175. Adams, W.G., and Day, R.E., op. cit., (18), (1876), p 329.

176. Bidwell, S., op. cit., (174), (1883), p 31.

177. Ibid.

178. Ibid.

179. His words, to be found in op. cit.,(174), (1883), p 31, were:-

'This theory can evidently be submitted to a very simple and conclusive test. If it is true that the observed effects are due merely to a rise of temperature, then it is clearly immaterial whether such a rise of temperature is brought about by the heating action of light or by the direct application of heat in the ordinary way.'

180. That is while in many cases the resistance increased with temperature, often the reverse was true.

181. See, for example, Bidwell, S., 'The Effect of Temperature upon the Electrical Resistance of Selenium', Phil. Mag., (5th Series), 11, (1881), p 302.

182. Adams, W.G., and Day, R.E., op. cit., (18), (1877).

183. Sabine, R., op. cit., (92), (1878).

184. Bidwell, S., op. cit., (174), (1883), p 35.

185. Bidwell, S., op. cit., (120).

186. Bidwell, S., 'On the Generation of Electric Currents by Sulphur Cells', Phil. Mag., (5th Series), 20, (1885), pp 328-336.

187. The most important 'suitable' circumstance was that the free sulphur, presumably liberated by electrolysis from the sulphide, would combine with the anode. Hence the general use of silver.

188. Bidwell, S., 'A Voltaic Cell with a Solid Electrolyte' Nature, 32, (1885), p 345.

189. Ibid.

190. The presence of an E.M.F. could be taken as 'proof' of chemical action producing electricity; the reverse process of electrolysis might then be expected.

191. Bidwell, S., <u>op.cit</u>., (118), (1895), pp 233-256.

192. Bidwell, S., <u>op.cit.</u>, (120), footnote p 144.
'It is especially desirable to ascertain experimentally whether the combination of selenium with metals use as electrodes in selenium cells is assisted by light.'

193. Adams, W.G., and Day, R.E., <u>op.cit</u>., (18), (1877), pp 328-332.

194. Bidwell, S., <u>op.cit</u>., (118), (1895), p 245.

195. Ibid., p 245. Bidwell claimed that a current 'not greater than 1/300 part of that which occurred in ordinary air would not have escaped detection.' He did not give the magnitude of this current.

196. Bidwell, S., <u>op.cit</u>., (118), (1895), p 247.

197. Bidwell's definitions of metallic and electrolytic conduction were the commonly accepted ones; in metallic conduction there was no transport of material and the temperature coefficient of resistance was positive; electrolytes behaved in the contrary sense.

198. Bidwell could only demonstrate that in the presence of moisture was essential to the assumed electrolytic action in cuprous selenide; also the weight changes that accompanied this action were larger than was expected. The full experimental details can be found in Bidwell, S., <u>op.cit</u>., (184), pp 247-251.

199. Bidwell, S., <u>op.cit</u>., (118), (1895), p 241.

200. Ibid., pp 254-256.

201. 17 conclusions were quoted in his summary.

202. Bidwell, S., <u>op.cit</u>., (118), (1895), pp 254-256.

203. Henisch, H.K., <u>Rectifying Semiconductor Contacts</u> (Oxford, 1957).

204. Ibid., p 265. The concept of 'forming' expressed here is not dissimilar to the idea of 'set' proposed by Adams and Day to describe the effect of an initial current passed through their cells.

205. Ibid., pp 340-341.

206. Reyval, J., 'Les Propriétés Electriques du Sélénium', Ecl. Elec., 17, (1898), pp 311-316.

207. Ibid., p 316.

## References and Notes. CHAPTER 3.

1. A value of $10^5$ ohm-cm is given in Moss, T., *Photoconductivity in the Elements*, (London, 1952), p 192.

2. In Moser, J., 'The Microphonic Action of Selenium Cells', *Proc.Phys.Soc.*,*4*, (1880-81), pp 348-360, we find the following comment on the opinions of Sabine and Bidwell:-

   > 'Both authors assume the selenium to possess a special sensitiveness, and this quality to be damaged by the high resistance of the junctions. Therefore they aim at annihilating this resistance at the surfaces of contact. Aiming at this annihilation, they enlarge the surfaces of contact and thus diminish the resistance.
   > The surfaces of contact should indeed be enlarged. The reasons, however, for which this must be done are, in my opinion, just the opposite to those influencing these two observers. It is the high resistance at the junctions which is the variable, and which is necessary for the microphonic action.'

3. Siemens, W., 'On the Influence of Light upon the Conductivity of Crystalline Selenium', *Phil. Mag.*, (4th Series), *50*, (1875), p 416.

4. Siemens, W., *op.cit.*, ( 3 ), (1875).

5. Moss, T., *op.cit.*, ( 1 ), (1952).

6. Moss, T., *op.cit.*, ( 1 ), (1952), p 192, states that the resistivity of the third, or red, form of selenium has a resistivity of the order of $10^{15}$ ohm-cm, to be compared with the $10^{18}$ ohm-cm of sulphur.

7. Siemens, C.W., 'The Action of Light on Selenium', *Proc.Roy.Inst.*, *8*, (1875-1878), p 72.

8. Adams, W.G., and Day, R.E., 'The Action of Light on Selenium', *Phil.Trans.*, *167*, (1877), p 320.

9. Henisch, H.K., *Rectifying Semiconductor Contacts*, (Oxford, 1957), p 78.

10. Bidwell's method outlined first in 'Selenium and its Application to the Photophone and Telephotography', *Royal Institution Library of Science*, *(Physical Sciences)*, *3*, (London, 1970), p 141, was that of Bell's detailed in the previous year to the Royal Institution. The major difference being that while Bell had found only a short period of annealing to be necessary, Bidwell discovered that a long period of crystallisation and cooling produced the most sensitive cells.

11. Bidwell, S., 'The Electrical Properties of Selenium', Phil.Mag., (5th Series), 40, (1895), p 234-235.

12. Siemens, W., op.cit., (3), (1875).

13. Siemens, C.W., op.cit., (7) (1875-1878).

14. Of the relative ease of constructing the cells Bidwell said in op.cit., (10), p 140, 'Dr. Werner Siemens therefore adopted the device (among others) of coiling up the wires so as to form a double spiral, and thus made a convenient and portable cell of great sensitiveness. But it is very difficult indeed, as I know by experience, to produce these double spirals of any size without the two wires touching one another at some point'. Bidwell cut a set of notches on a mica slip and wound a double helix around these notches, thus keeping the two electrodes apart.

15. Draper, H.N., Letter on the 'Effect of Light on the Electrical Conductivity of Selenium', Nature, 7, (1873), p 340.
Draper had tried to repeat the findings of Smith but had been unable to find any effect due to illumination, indeed he found it impossible to pass a current even through very thin specimens. This led him to ask for information about the selenium:-

'What was the molecular condition of the "metal" employed, - vitreous or crystalline?
'Where can "bars" of selenium be obtained which will afford the results stated?
'Are there any unstated conditions essential to the successful production of the phenomena?'

16. Fritts, C.E., 'On the Fritts Selenium Cells and Batteries', Electrical Review, 16, (1885), pp 208-211.

17. Fritts, C.E., op.cit., (16), (1885), p 208, gives the value of 14.8 times reduction of resistance for the most sensitive cell made by Werner Siemens, his own cells showed factors between 82.3 and 337.5. He expressed the significance of the latter factor in the words:-

'The tremendous change of resistance involved in the expression "337.5 times" may perhaps be more fully realised by saying that 99.704 per cent of the resistance had disappeared temporarily, under the joint action of light and electricity, so that there remained less than 3/10 of 1 per cent of the original resistance of the selenium in dark.'

18. Bidwell, S., op.cit., (11), (1895), p 235.

19. Ibid., pp 238-240.

20. Fritts, C.E., 'On a New Form of Selenium Cell, and some Electrical Discoveries made by its use', Amer.J.Sci., 26, (1883), p 465.

21. Smith, W., 'The Action of Light on Selenium', Soc.Tel.Eng.J., 2, (1873), p 33. Latimer Clark was chairman at the meeting where Smith's letter was read.

22. Siemens, W., op.cit., (3), (1875), p 416.

23. Siemens, C.W., op.cit., (7), (1876), p 77.

24. Bidwell, S., op.cit., (10), (1881), pp 145-149.

25. Nipkow, P., (1884).

26. A comparison photometer using selenium cells and its concomitant circuitry might well be more complicated, less accurate and more expensive than a simple visual photometer.

27. Bidwell, S., Letter to Nature, 78, (1908), pp 105-106.

28. Bell, A.G., Lecture to the Royal Institution May 17, 1878.

29. Bell, A.G., and Tainter, S., 'Photophone Transmitter', U.S. Patent, 235,496, 25/9/1880.

    ______________, U.S. Patent, 235,497, 25/9/1880.

    Berliner, E., 'Photophonic Transmitter', U.S.Patent, 235,120, 3/9/1880.

30. Nature, 21, (1880), p 576.

31. Ibid., p 589.

32. Bell had found that thin sheets of various materials emitted sounds when illuminated by light of varying intensity. He discovered many substances that behaved in this fashion, glass, worsted, fibres and so on. He reported a large number of investigations into these phenomena in Nature, 24, (1881), pp 42-44. His original observations were discussed by other researchers and seem to have influenced Moser in his work. Lord Rayleigh provided some calculations in Nature, 23, (1881), pp 274-275.

33. Thompson, S.P., 'The Photophone', Nature, 22, (1880), p 481.

34. Ibid.

35. Ibid.,

36. Ibid.

37. Bell, A.G., 'Selenium and the Photophone', Nature, 22, (1880), pp 500-503. Abstract of Lecture delivered to the American Association for the Advancement of Science.

38. Ibid., p 503.

39. Nature, 23, (1881), pp 15-19. Article unsigned.

40. Bidwell, S., Nature, 'The Photophone', 23, (1881), pp 58-59.

41. Nature, 23, (1881), pp 423-424. Report of a paper delivered to The Physical Society, February 26, 1881, by Ayrton and Perry.

42. Lodge, O., 'Modern Views of Electricity', Nature, 36 - 39, (1887-1889). Serialised in four parts. Later published in book form 1889; 2nd Ed., 1892.

43. ________., 'On Electrolysis', B.A.A.S. Report, (1885), pp

44. Thomson, J.J., Notes on Recent Researches in Electricity and Magnetism, (Oxford, 1893).

45. Whittaker, E.T., History of the Theories of Aether and Electricity, (Dublin, 1910).

46. That is, of course, with the publication of A.H. Wilson's seminal papers in Proc.Roy.Soc., (A), 133 and 134, (1931).

47. This is a necessary injunction, for it is important to bear in mind that the publication of Maxwell's work on electrodynamics did not immediately allow even electro-magnetism to be completely explained; and electrochemical problems had been the seat of almost continuous debate and discovery since the initial work in the opening years of the 19th century.

48. That is Adams and Day, Siemens, Sabine, Bidwell, Fritts, Braun, Earl of Rosse, Moser.

49. Thomson, J.J., op.cit., (44), (1893), p.v, Preface.

50. Several letters were published in Nature, for example; including one in June 1875 from J.E.H. Gordon a student at The Cavendish under Maxwell.

51. Thomson, J.J., op.cit., ( 44 ), (1893), pp 1-52.

52. Ibid., p 2.

53. See, for example, Topper, D.R., J.J. Thomson and Maxwell's Electromagnetic Theory, Case Western Reserve University, Ph.D., (1970).

54. To define 'fundamentals of electrical theory' is somewhat difficult without meeting some circularity of argument. Perhaps to define 'fundamental' research as being that which aims to confirm or change the bases of existing theories; while non-fundamental is that research which takes existing theories as given and then attempts to describe new phenomena in those terms, may be a passable approach to the problem. Maybe the term is only definable with hindsight.

55. Thomson, J.J., op.cit., (44), (1893), p 50.

56. Ibid., p 52.

57. Ibid.

58. Arrhenius, S.A., 'On the Dissociation of Substances in Aqueous Solution', Zeits.f.Phys.Chem., 1, (1887), pp 631-648.
Translated paper published in Hurd, D.L., and Kipling, J.J., (eds.), The Origins and Growth of Physical Science, 2, pp 294-306, (London, 1964), (Pelican Edition).

59. Some hints of the problems raised, and solved, by Arrhenius' theory are indicated in Pledge, H.T., Science since 1500, 2nd. ed., (London, 1966), pp 208-212.

60. That is in Recent Researches. It may be arguable whether a compilation of up-to-date work is didactic; but it has been suggested to me, (by Dr. D.M. Knight), that all non-fiction books serve such a purpose.

61. Thomson, J.J., op.cit., (44), pp 43-52. Some interesting diagrams are given illustrating the interaction between tubes of force; showing them strained, growing, breaking, shrinking and so on. Thomson develops a mainly qualitative description of various electrical phenomena.

62. Hall, E.H., 'On a New Action of the Magnet on Electric Currents', Amer.J.Math., 2, (1879). pp 287-292, and Phil.Mag., (5), 9, (1880), pp 225-230, reprinted in Magie, W.F., Source Book in Physics, Harvard, (1965), pp 542-547. Future reference will be to this version; abbreviation will be Hall, E.H., (Magie), (62).

63. Hall, E.H., (Magie), (62), p 542.

64. Ibid., pp 543, 544. Hall's words were:-
'The statement seemed to me to be contrary to the most natural supposition in the case considered, taking into account the fact that a wire not bearing a current is in general not affected by a magnet,

and that a wire bearing a current is affected exactly in proportion to the strength of the current, while the size and, in general, the material of the wire are matters of indifference. Moreover, in explaining the phenomena of statical electricity, it is customary to say that charged bodies are attracted toward each other or the contrary solely by the attraction or repulsion of the charges for each other.

'Soon after reading the above statement in Maxwell I read an article by Prof. Edlund, entitled "Unipolar Induction" (Phil. Mag., Oct. 1878, or Annales de Chimie et de Physique, Jan. 1879), in which the author evidently assumes that a magnet acts upon a current in a fixed conductor just as it acts upon the conductor itself when free to move.'

65. Hall, E.H., (Magie), (62), pp 543-544. The resistance measurements were made on a flat spiral of German-silver wire that could be placed between the poles of an electromagnet; the magnet could produce a field of about 3000 Gauss. Hall detected no resistance change greater than one part in one hundred and fifty thousand.

66. He was content merely to indicate the direction of the transverse e.m.f.; in this first paper, at least, he did not ascribe a sign to the current itself.

67. Hall, E.H., (Magie), (62), p 545.

68. Thomson, J.J., op.cit., (44), pp 484-509. Hall's effect is given the equivalent of a page's discussion in a more general treatment of the interaction between polarised light and its reflection form magnetic pole pieces. It is interesting to note that in the Index of Recent Researches the Hall effect is referred to on pp 484 and 486; in fact two 'Hall' effects are referenced. The first refers to a measurement Hall (presumably the same one) made on the rotation of the plane of polarisation when light is reflected from nickel and cobalt; the second refers to our 'Hall' effect; i.e. the production of a transverse e.m.f. across a thin conductor carrying a current and intersected by a magnetic field.

69. Rowland, H.A. 'Preliminary Notes on Mr. Hall's Recent Discovery', Proc. Roy. Soc., 4, (1880-81), pp 10-13.

70. Ibid., p 11.

71. Ibid.

72. See for example Papers Listed in McKay, T., 'The Hall Effect:- a bibliography', Proc. Amer. Acad., 41, (1906), pp 385-395.

73. Thomson, (see Ref.(74),below), wrote 'Prof. Rowland has lately published in the <u>Amer.J.Math</u>., (<u>2</u>., No.4; <u>3</u>., Nos. 1 and 2) a series of papers on "The General Equations of Electromagnetic Action with Application to a New Theory of Magnetic Attractions, and to the Theory of Light." The papers, in addition to what is stated in their title, contain the mathematical consideration of that action of magnetism on electric currents which was lately discovered by Mr. Hall, and it is proved in them that, if Maxwell's theory of light be true, this action will explain the magnetic rotation of the plane of polarisation of light.'

74. Thomson, J.J., 'Prof. Rowland's New Theory of Magnetic Action', <u>Nature</u>, <u>24</u>, (1881), pp 204-206.

75. Bidwell, S., 'On an Explanation of Hall's Phenomenon', <u>Proc.Roy.Soc</u>., <u>36</u>, (1884), pp 341-348.

76. __________., 'On some Experiments illustrating an Explanation of Hall's Phenomenon', <u>Proc. Phys. Soc</u>., <u>6</u>, (1885), pp 29-47.

77. <u>Nature</u>, <u>29</u>, (1884), p 467.

78. Bidwell, S., 'The Reversal of Hall's Phenomenon', <u>Nature</u>, <u>29</u>, (1884), p 514.

79. Bidwell, S., <u>op.cit</u>., (76), (1884).

80. The Hall effect would be rewarding to study, both as a phenomenon in its own right, and as a measuring 'tool'. It is interesting to note that an elementary explanation of this effect involves no more (!) than an acceptance of the electron and a knowledge of the force between magnetic fields and moving charges. It is remarkable how the introduction of the elementary electrical charge allowed the long mathematical 'unsuccessful' treatment by Thomson in <u>Recent Researches</u> to be replaced by a few lines of algebra.

81. Bidwell, S., <u>op.cit</u>., (76), (1884), p 29.

82. Ibid.

83. Ibid.

84. Ibid., p 30.

85. Ibid., p 34.

86. Ibid., pp 35-36. Bidwell described his early tests in these words:-

> 'The idea of mechanical strain occurred to me; . . . I attached a string by means of sealing-wax across the middle of a thin sheet of iron, which was cemented to glass and connected with the battery and the galvanometer as usual. On pulling the string in a transverse direction I found unmistakable

indications of a galavanometer-deflection in the same direction as if the sheet of iron had been acted upon, not by a mechanical pull, but by the electromagnetic force. The effect was small, but I have since greatly increased by the following device:- A strip of thin iron was cemented between two thin slips of deal about 20 cms long, forming a kind of sandwich. The sandwich was attached to a board by means of four screws, the distance between the middle screws being about 7 cm. The two ends of the iron were connected with a battery, and the middle points of its opposite edges with a galavanometer. On pressing with the finger the middle of one edge of the sandwich in a direction perpendicular to its length and in the plane of the metal, though no appreciable distortion was produced, the galvanometer was immediately deflected the direction of the current from the strip to the galvanometer being always the same as the direction of the force.'
Similar results were obtained with platinum foil although in the opposite sense.

87. Bidwell, S., <u>op.cit</u>., (76), (1884), p 36.

88. Ibid., pp 39-41. The whole of these pages is reproduced. The text must be read in conjunction with the diagrams drawn below; the figure numbers are Bidwell's.

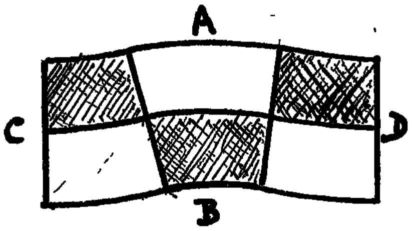
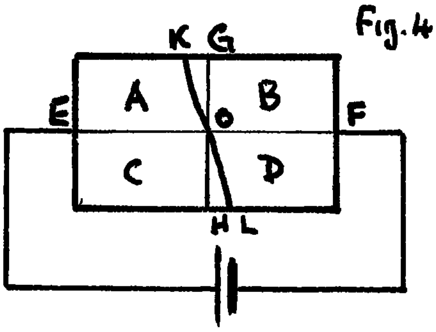


Fig 3.

Fig.4.



'Suppose that a current is passing through the plate from C to D, and that A and B are two points on the opposite edges, which, when the metal is unstrained, are at the same potential. Then the ratio of the resistances between the points C and A, and the points A and D, is equal to that between the points, C, B and the points B,D. And so far as mechanical strain alone is concerned, this equality will not be disturbed by placing the plate in a magnetic field, the strain produced symmetrically distributed on both sides of the middle line. At all events, no strain could occur which would in itself affect the resistance of gold and iron in opposite ways, for the resistance of both is increased by extension, and (presumably) diminished by compression. But the currents from C to A and from B to D pass from regions which are compressed to regions which are stretched, while the opposite is the case with currents passing from C to B and from A to D. And here the thermoelectric effect comes into play.

It has already been mentioned that a thermoelectric current will pass from a stretched copper wire to an unstretched copper wire in contact with it, if the junction is heated. From this it might be inferred, that a current would flow through the heated junction from an unstretched or free copper wire to a longitudinally compressed copper wire. And I have proved by actual experiment that this is the case. A fortiori, therefore, a current would pass through the heated junction from a stretched copper wire to a compressed copper wire. For similar reasons the current would, if the wires were of iron, flow in the opposite direction, from the compressed wire to the stretched wire, across the hot junction. And the same effects, so far as regards currents between stretched and unstretched portions, occur, as I have proved experimentally, if strips of foil are used instead of wires. If, therefore, a battery-current is passed from a stretched portion of a wire or foil to a compressed portion, heat will (according to the laws of the Peltier effect) be absorbed at the junction if the metal is copper and be developed at the junction if the metal is iron. In passing from compressed to stretched regions the converse will occur.

Let us imagine the metal plate to be divided into four equal regions A,B,C,D, as shown in figure 4. Let a current pass through the plate from E to F, and let a force (produced electromagnetically or otherwise) be applied in the direction HG. First, suppose that the plate is of copper, then the current travelling from E to the line OG passes from a compressed to a stretched portion of the metal; heat will therefore be developed in the region A. Between the line OG and the point F, the current passes from a stretched to a compressed portion of the metal; heat will therefore be absorbed in the region B. For like reasons, heat will be absorbed in C and developed in D. The temperature of the copper plate will therefore not be uniform, the portions A and D being on the whole hotter than the portions B and C. But the resistance of A and D will therefore be greater, and the resistance of B and C smaller, than before the plate was strained. If therefore GH were originally an equipotential line, it is clear that it will be so no longer. An equipotential line through the point O will now be inclined to GH in the direction KL, as shown in the figure.'

89. Bidwell, S., op.cit., (76), (1884), p 42.

Where there was no correlation, in the case of aluminium and one specimen of gold, Bidwell suggested that impurities or irregularities could be the cause of differences.

90. Ibid., p 47.

91. Ibid., p 47. Bidwell refers to a paper by William Thomson published in Phil. Trans. in which the thermoelectric effect between differently treated copper wire is announced.

In *op.cit.*, (75), (1884), p 344, Bidwell references Thomson's Bakerian lecture of 1856 *Phil. Trans.* (1856), p 711.

92. See Ref. (88).

93. Whetham, W.C.D., *A Treatise on the Theory of Solution including the Phenomena of Electrolysis*, (Cambridge, 1902), pp 367-368.

94. Bidwell, S., *op.cit.*, (11), (1895).

95. Ibid., p 236.

96. Berkson, W., *Fields of Force: The Development of a World View from Faraday to Einstein*, (London, 1974).

97. Nye, M.J., *Molecular Reality: A Perspective on the Scientific Work of Jean Perrin*,(London, 1972).

98. Berkson, W., *op.cit.*, (96), (1974), p 161.

99. The 'point' Berkson is referring to was Maxwell's successful incorporation of displacement current into his expression for the magnetic field generated by a current; showing that both 'conduction' and 'displacement' components had to be included. The equation given by Berkson is:-

$$4\pi j + \frac{\partial D}{\partial t} = \mathrm{curl}\ \underset{\sim}{H}$$

100. See, for example, Berkson, W., *op.cit.*, (96), p 145, p 271. On the latter page Berkson writes:-

> 'Thus Lorentz combined the old theories of Weber, etc., which assume that all electricity is due to small charged particles acting at a distance, with Maxwell's theory which rejected action at a distance and considered the hypothesis of 'electrons' foreign to it. Maxwell had kept to Faraday's idea that charge was an effect ofthe medium between bodies, and not a fluid. This marriage of the different schools was not comfortable, because the electron was hard to incorporate into Maxwell's theory'.

101. Nye, M.J., *op.cit.*, (97), Introduction, p ix.

102. Helmholtz, H., The Modern Development of Faraday's Conception of Electricity, *J.Chem.Soc.*, *39*, (1881), pp 277-304.

103. The term 'review type' is, I recognise, somewhat vague. The works I refer to here and in subsequent pages were rather more than the normal review paper where the 'state of the art' is reviewed with little polemic and less history. Rather, they were concerned with a detailed analysis of a particular subject in which comparisons and contrasts were drawn between various theories and experiments which were aimed at defining a line of development rather than outlining the route to the then held

opinion. Like all review papers they included not only the work of the writer but that of major contributors to the field; also the material included for discussion was inevitably selected and pre-digested. However although it is impossible to be sure it is probably this sort of information that would filter through to those who were not primarily concerned with understanding the processes of electricity per se. Whether these are primary or secondary material is rather difficult to say; they are secondary in that they represent not original work on the subject but glosses and discussions of that work; they are primary in that the gloss they give is contemporary with the work that was still being actively pursued and that they were written by a physicist of undoubted eminence whose opinions were taken seriously, (at least in physics!)

104. Lodge, O., op.cit., (42), (1887-89).

105. ________., op.cit., (43), (1885).

106. ________., 'On the Seat of the EMF's in a Voltaic Cell', J.IEE, 14, (1885), pp 187-223.

Lodge's paper engendered considerable discussion reported in the same volume on pp 224-298.

107. ________., 'On the Controversy Surrounding Volta's Contact Force, Phil. Mag., (5th Series), 49, (1900), pp 351-383.

108. Kelvin, Lord, 'Contact Electricity of Metals', Phil. Mag., (5th Series), 46, (1898), pp 82-120.

109. Quoted in Berkson, W., op.cit., (96), p 155. Cites source as Duhem, P., The Aim and Structure of Physical Theory, translated by P.P. Wiener, (New York, 1962), p 71.

110. Lodge, O., op.cit., (42), (1887-89), p 533.

111. Ibid., Lodge is referring to the phenomenon of charging bodies with electricity.

112. Ibid., p 533.

113. It is almost impossible to understand what this analogy meant precisely, for Lodge made no use of the picture. He introduced it to overcome the very real difficulties that existed when the properties of a mechanical ether were used to explain electrical phenomena, and at the same time to allow for the well known mechanical movement of the planets, for example. In any case the structure of jellies was no clearer than the structure of the ether; such an analogy only serves to confuse further and can be taken as another illustration that the etherial theory of electricity was not at its best when mechanical analogies were introduced.

114. Twenty years later takes us to the year 1908 by which time the dominant electrical theory was that of Lorentz and Drude. The fundamental basis had shifted from an ether whose modifications produced observable electric and magnetic phenomena to the assumption of an atomic electricity represented by the electron. Furthermore Lorentz's theory which resulted in an unobservable etherial fluid was being replaced by Einstein's relativistic concepts when an ether was unnecessary.

115. This point, I confess, is not made explicit in Berkson's work; but I suggest that it is one of the threads in the first chapters of the book where Berkson leads us through the build up to Maxwell's theory of the electromagnetic field. Berkson views the work of Faraday and Maxwell as being, in a sense, anti-Newtonian and in Chapter 3 of his Fields of Force, (Ref. (96) above pp 74-103), the opinion can be clearly seen that electrostatics and the models used to develop the associated theories of stationary electricity, could not be used to examine the relative truths of rival theories.

116. This is not a purely trivial point; for while it is evident that given a formal analogy between systems that obey the same equations a model of one may be made with the other it is, of course, not true that the performance of an analogy may be used to predict the action of the system it is modelling. There may be unknown effects that the model does not represent. In the case of electrical systems we may evidence the Hall effect which could not be modelled on Lodge's systems of pulleys, wires and beads.

117. Particularly Chapter VI in Lodge, O., Modern Views of Electricity 2nd Ed., (London, 1892).

118. Lodge, O., op.cit., (42), Nature, 36, (1887), pp 582-583.

119. Ibid., p 583.

120. Ibid.

121. Lodge, O., op.cit., (42), Nature, 37, (1887), p 12.

122. Ibid., pp 12-13.

123. See, for example, Refs. (43), (106), (107).

124. In the book version of Modern Views, for example, half the writing is devoted to subjects that fall within the scope of electrodynamics and magnetism.

125. Lodge, O., op.cit., (42), Nature, 39, (1888), pp 320-322.

126. Ibid., p 13.

127. Ibid.

128. Ibid.

129. Ibid.

130. Ibid., p 321.

131. Lodge, O., op.cit., (117), (1892), Preface p vii.

132. Ibid., p ix. Lodge wrote:

> 'Some of the details of my explanations may be wrong (though I hope not), and all must be capable of ultimate improvement, but as to the main doctrine concerning the nature of electricity, though I call it a "view", it is to me no view but a conviction. Few things in physical science appear to me more certain than that has so long been called electricity is a form, or rather a mode of manifestation, of the ether. Such words as "electric", may remain; "electrification" may gradually have to go.'

133. Ibid., p x.

134. Particularly see Bidwell's reply to Moser in Bidwell, S., 'The Electrical Resistance of Selenium Cells,' Phil. Mag., (5th Series), 15, (1883), pp 31-35.

135. Adams, W.G., and Day, R.E., 'The Action of Light on Selenium', Phil. Trans., 167, (1877), pp 313-349.

136. Braun, F., 'Über Unipolare Elektricitätsleitung', Ann.Phys.(Wied.), 4, (1878), pp 478-479.

137. That is, of course, Faraday's laws of electrolysis, and the fact of chemical action.

138. That in an electrolyte there were at least some molecules dissociated in solution.

139. Helmholtz had suggested, ref. (102), that electricity might, in fact be actually atomic.

140. Lodge, O., op.cit., (43), (1885).

141. Ibid., p 723.

142. Ibid., p 723.

143. Ibid., p 725. Lodge, when discussing the possibility of detecting very small amounts of polarisation with very delicate galvanometers, pointed out that 'this test may also fail by reason of secondary actions. It is the merest commonplace that an ordinary voltameter behaves as a very leaky condensor. A continual drain

of electricity goes through it, however small the E.M.F. applied; and when charged, and left, the charge is found very rapidly to diminish. It is facts like these which have so often suggested slight metallic conductivity, and which at one time tempted Faraday to postulate this.'

144. Ibid., p 727.

145. Ibid., p 727.

146. Ibid.

147. Ibid., pp 749-762.

148. Ibid., pp 749-750.

149. Ibid., p 750. Lodge's description of the problem puts the difficulty very neatly.

'The only objection that may be plainly stated against the theory is that it seems to require some small force able to effect the necessary initial decomposition, and it suggests that conductivity and tenacity of composition are related to one another in some opposing manner. Facts, however, fail to bear out any such idea; conductivity and chemical tenacity seem independent of one another; and, as has been just said . . . ., no finite force, however small, has ever been found necessary to decompose an electrolyte when really applied to it.

In other words, no polarisation exists inside a homogeneous electrolyte; <u>there is no chemical cling of the atoms there, but only a frictional rub.</u>'

150. Ibid., p 750.

151. Ibid., p 751.

152. Ibid., p 750.

153. Ibid., p 751.

154. Ibid., p 751.

155. Ibid.

156.
157.
158.
159. Ibid., pp 751-757. Lodge describes Wiedemann's theory thus:-

'He supposes the atoms charged by contact with each other, and the molecule charged by contact with the vessel; and, having thus obtained the needful electrifications, decomposition and endosmose naturally follow. . . . the atoms in a molecule, if they electrify each other by contact, necessarily do so with equal quantities; .... Wiedemann explains the unequal rate of travel. . . . by a difference in the resistance met with . . . . a hydrogen atom slips through the liquid more easily than an oxygen atom, and so gets along faster.

Wiedemann's theory thus chimes in beautifully with that of Kohrausch, who postulates a specific velocity for every ion; a velocity which depends only on the nature of the liquid in which it has to travel, and the dV/dx which drives it.'

Introducing Kohlrausch's picture Lodge wrote:-

'The fundamental assumptions underlying the beautiful theory of Kohlrausch are the same as those adopted by Wiedemann. He considers electrolytic conduction performed by dissociated atoms, each of which carries the same numerical charge of electricity, one set positive the other negative.'

160. Ibid., pp 754-757.

According to Lodge Kohlrausch considered that absolute ionic velocities could be determined from conductivity data, (at least at low concentrations). Lodge argued that this may be true if current was conveyed by the dissociated salt only, if the solvent took part in conduction then only the product of concentration and velocity could be determined.

161. Ibid., p 757.

162. Helmholtz, H., op.cit., (102), (1881).

163. Lodge, O., op.cit., (43), (1885), p 759.

164. ________., op.cit., (106), (1885), Lodge's extensive study of contact forces in this publication showed that he had thought long and hard about this problem.

165. ________., op.cit., (43), (1885), p 759.

166. ________., (132).

167. ________., op.cit., (43), (1885), pp 765-772.

168. The known thermoelectric effects were the Seebeck effect - the development of an E.M.F. between junctions heated to different temperatures; the Peltier effect - the heating or cooling produced when a steady current passed through a junction; and the Thomson effect - the generation of a current in a conductor in which there existed a temperature gradient. These effects were very small in magnitude - of the order of a few millivolts.

169. Lodge, O., op.cit., (106), (1885).

170. I am using the term 'Volta' force in a difference sense to that which seems to be employed by Lodge;

although he was not always direct in its use. By Volta force here I mean that E.M.F. force whose presence is typified by the action of batteries in which chemical changes are used to produce electrical energy. Some writers of this period (1880's) used the term 'Voltaic' force to designate the contact potential that could be developed between metals and other substances, between which there was no electrolyte. For Lodge, of course, with his chemical view of the nature of the contact force the two usages were the same.

171. Reflecting the acceptance of the law of conservation of energy.

172. See, for example, the opening paragraphs in Lodge, O., <u>op.cit</u>., (106), pp 186-187.

173. Ibid., p 187.

174. Ibid., pp 187-190.

175. Ibid., p 190.

176. Ibid., p 192.

177. See, for example, Ibid., pp 218-219.

178. Ibid., pp 224-226.

179. That is William Thomson later Lord Kelvin.

180. Lodge, O., <u>op.cit</u>., (106), (1885), p 235.

181. Ibid., pp 236-237. Fleming suggested that the potentials developed between perfectly clean metallic surfaces 'immersed wholly in a neutral non-conducting liquid such as paraffin, and endeavour to ascertain if the phenomena are affected.'

Such experiments were carried out in 1898 and reported in Erskine-Murray, J., On Contact Electricity of Metals, <u>Proc.Roy.Soc</u>., <u>63</u>, (1898), pp 113-146. This worker showed that 'When two metals are coated with the same non-conductor, such as wax or glass, their potentials are not sensibly different from that of the bare metals in air; . . . . These results seem to prove that gaseous films play no <u>essential</u> part in the phenomenon.'

However the debate lingered on into the twentieth century; for example in Lodge, O., On the Controversy Concerning Volta's contact Force, <u>Phil. Mag</u>., (5th Series), <u>49</u>, (1900), pp 351-383, the argument was continued.

182. Lodge, O., <u>op.cit</u>., (106), (1885), p 237.

183. Ibid., p 238.

184. Ibid., p 247. Swinburne also remarked that neither theory, contact or chemical explained all the facts of electrolysis.

185. Ibid., pp 254-267.

186. Considerably more research concerning Lodge's picture of junction phenomena would be required before being categoric on this point; but it seems likely that since Lodge seemed so enamoured of an 'etherial' approach to the problems of electricity - compare, for example, the comments that have been made earlier on his 'Modern Views' - that he would prefer to seek for an explanation that would lend itself to a field interpretation. It is evident that a theory of strain and chemical action would more easily be so adapted; alternative theories would seem to presuppose a 'new' electrical effect at boundaries, that was not catered for by Maxwell's electrodynamics.

187. That is, if no real question existed Lodge's arguments could have been ignored or defeated readily. In fact they were not; see note (181).

188. Berkson, W., *op.cit.*, (96), (1974), particularly Chapter 8.

189. Thomson, J.J., 'Report on Electrical Theories', *B.A. Report*, (1885), pp 97-155.

190. Thomson, J.J., *op.cit.*, (44), (1893).

191. That is Thomson in *Recent Researches*, Ref. (44), and Lodge in *Modern Views*, ref. (117).

192. See, for example, the treatment of field theories in Born, M., *Einstein's Theory of Relativity*, (Dover edition), (New York, 1962).

193. See, for example, the accounts given in *Recent Researches* ref. (44) and in Whittaker's *History of the Theories . .* ref. (45).

194. Thomson, J.J., *op.cit.*, (74), (1881).

195. Lodge, O., *op. cit.*, (42), (1887-89).

196. ________., *op. cit.*, (43), (1885), and *op.cit.*, (106), (1885).

197. Here I am not suggesting that Maxwell's theory and its development was intellectually simple but that in circuits containing chemicals, and various metals all which might develop potential differences one to the other the *physical* situation was inherently a complex one. With respect to gases at least here

the interactions between atoms and molecules could be more closely controlled allowing an easier experimental situation.

198. The judgement 'major' is a retrospective one. It is difficult to award the appellation without running the risk of being ahistorical. In their time men such as Adams and Day, Siemens and Braun were not minor figures in the scientific world and we must remember that Bidwell was a President of the Physical Society and a council member of the Royal Society; but by comparison with Kelvin, Maxwell and Thomson their impact was not lasting and their work has not entered the general corpus of scientific history.

199. These other substances were, sulphur, tellurium, various sulphides, carbon and some oxides. In spite of the variety their study added little weight to either the experimental evidence or the theoretical interpretations.

200. Of course Bidwell measured currents and deflections, but he did not measure reaction rates, or amount of matter transported. By this I mean his work was largely qualitative.

201. See, for example the discussion in Chapter 2, pp 90-91.

## *References and Notes.* *CHAPTER 4.*

1. See Chapter 5 pp 259-264.

2. For short biography see *World's Who's Who in Science*, pp 252-253.

3. Guilleminot, H., 'Sur la Variation de Résistance Electrique du Sélénium irradié par les Rayons X et les Rayons du Radium', *CR*, *156*, (1913), pp 1155-1157.

4. Athanasiades, G., 'Wirkung der Röntgenstrahlung auf den Elektrische Widerstand Selens', *Ann.d.Physik*, *27*, (1908), pp 890-896.

5. Guilleminot, H., 'Les Rayons N. Ne paraissent pas influencer la Résistivité du Sélénium', *Archives d'Electricité Medicale*, *13*, (1905), pp 243-246.

   It is pleasing to note that the author of this paper could not detect any effect of N rays on selenium. He was not bold enough to wonder whether there were any such entities, however, noticing only that they appeared not to modify the electrical properties of selenium!

6. Brown, F.C., 'Effect of Abrasion on the Conductivity of Selenium', *Sci.Abs.*, (Phys.) *16* , (1913), p 77.

7. __________., 'The Action of Mercury Vapour on Selenium', *Phys. Rev.*, (2nd Series), *2*, (1913), pp 153-160.

8. Brown, F.C., and Stebbins, J., 'The Variation of the Light Sensitiveness of the Selenium Cell with Pressure', *Phys. Rev.*, *25*, (1907), pp 501-502.

9. ____________________________., 'Some Studies on the Change of Electrical Resistance of Selenium Cells', *Phys. Rev.*, *26*, (1908), pp 273-298.

10. McDowell, L.S., 'Some Electrical Properties of Selenium, I.', *Phys. Rev.*, *29*, (1909), pp 1-36.

11. _____________., 'Some Electrical Properties of Selenium, II,' The Recovery from Excitation by X-Rays', *Phys. Rev.*, *30*, (1910), pp 474-481.

12. _____________., 'Some Electrical Properties of Selenium, III. The Influence of Temperature upon the Recovery.', *Phys. Rev.*, *31*, (1910), pp 524-535.

13. Pfund, A.H., 'A Study of the Selenium Cell', *Phil.Mag.*, (6th Series), *7*, (1904), pp 26-39.

14. __________., 'The Electrical and Optical Properties of Selenium, *Phys. Rev.*, *28*, (1909), pp 324-336.

15. See Chapters 2 and 3 above.

16. Martin, M.J., 'Selenium', Wireless World, 3, (1915), pp 681-685.

17. Ibid., p 685.

18. Lorentz's account of the theory is given in Lorentz, H.A., The Theory of Electrons and its Application to the Phenomena of Light and Radiant Heat, (Leipzig, 1909), (New York, (Dover reprint), 1952).

19. Thomson, J.J., The Corpuscular Theory of Matter, (New York, 1907).

20. Brown, F.C., 'Theory of the Action of Selenium', Phys. Rev., 33, (1911), pp 403-420.

21. Siemens, C.W., 'The Action of Light on Selenium', Proc. Roy. Inst., 8, (1875-78), pp 68-79, and in Roy.Inst. Lib. Sci.,(Phys.), 1, pp 466-477.

22. We can see, of course, that as in the case of specific heat at low temperatures, no completely 'classical' theory could account for the electrical properties of solids; the quantum theory proved essential.

23. Pfund, A.H., op.cit., (14), (1909), p 331. Pfund wrote:-

    > 'At the present time it is quite generally acknowledged that the conduction in selenium is electronic and not electrolytic in character.'

24. It is evident from Henisch, H.K., Rectifying Semiconductor Contacts, (Oxford, 1955), that even twenty years after the introduction of Wilson's theory of materials no satisfactory account of the properties of selenium could be given; and from an interview with Sir Nevill Mott, (Cambridge, 1974), it appears that serious inroads into the problems of complex crystalline or glassy substance have only been made within the last decade.

25. Superficially elemental selenium is a relatively simple material, but as we now know, simplicity, in the semiconducting sense, is a combination of chemical and structural perfection and not one solely of purity. Thus while metal contacts on galena, for example, appear more complex than selenium cells, they are, in fact, more straightforward in their behaviour. Also the interpretation of their properties in terms of barriers, (i.e. differences in energy levels) was more obvious than a similar approach to selenium might have been.

26. Chapter 2 of this thesis p 86 et seq.

27. Ibid., p 42 et seq.

28. Bidwell, S., 'The Electrical Properties of Selenium' *Phil. Mag.*, (5th Series), *40*, (1895), pp 233-256.

29. Brown, F.C., 'The Nature of Light Action in Selenium', *Phys. Rev.*, *33* (1911), pp 1-26.

30. Ibid., p 2.

31. Brown had discovered that certain of his cells had a property such that their resistance would increase on illumination; these he called 'light negative'; the more usual experience he ascribed to 'light positive' selenium.

32. Pfund, A.H., *op.cit.*, (13), (1904), pp 26-39.

33. Berndt, G., 'Einige Beobachtungen an Selenzellen', *Phys. Zeits.*, *5*, (1904), pp 121-124.

34. Pfund certainly took great care in the preparation of this selenium, as did Berndt. Neither, however, stated levels of impurities referring only to their sources, in Pfund's case to a paper by Lehner, V., in *J. Am. Chem. Soc.*, *20*, and in Berndt's to the *Handbuch d. anorg. Chem.*, *1*.

35. Pfund, A.H., *op.cit.*, (13),(1904), p 26.

36. Ibid.

37. Ibid., p 27.

38. Ibid., p 28.

39. Berndt, G., *op.cit.*, (33), (1904).

40. Pfund, A.H., *op.cit.*, (13), (1904), p 29.

41. Ibid., pp 29-31.

42. Adams, W.G. and Day, R.E., 'The Action of Light on Selenium', *Phil. Trans.*, *167*, (1877), pp 313-349.

43. Pfund, A.H., *op.cit.*, (13), (1904), p 31.

44. Ibid.

45. Ibid., pp 32-33.

46. Ibid., p 34.

47. Ibid.

48. In Bidwell, S., 'The Electrical Properties of Selenium', *Phil. Mag.*, (5th Series), *40*, (1895), p 240, the quantity of selenide in the selenium cells used by Bidwell varies around 3%. Bidwell did not go so far as to claim that this is the ideal quantity, but it was implied.

49. Brown, F.C., op.cit., (33), (1911), p 1.

50. Pfund, A.H., op.cit., (13), (1904), p 34.

51. Bidwell, S., 'On the Sensitiveness of Selenium to Light', Phil. Mag., (5th Series), 20, (1885), pp 178-191.

52. Pfund, A.H., op.cit., (13), (1904), p 37.

53. Ibid.

54. Ref. (48), above.

55. Pfund, A.H., op.cit., (13), (1904), p 29.

56. Ibid., pp 37-38.

57. The existence of three allotropic forms of selenium had been known since the middle of the 19th century. Saunders, A.P., in 'The Allotropic Forms of Selenium', J. Phys. Chem., 4, (1899-1900), pp 424-513, had demonstrated the presence of a fourth modification.

58. Siemens had hinted at the idea in his 'The Action of Light on Selenium', (1877), Ref. (35), Chapter 2.

59. Pfund, A.H., op.cit., (14), (1909), p 331.

60. This point will be taken up in Chapter 5.

61. Berndt, G., op.cit., (33), (1904).

62. This is expressing the situation rather more strongly than did Berndt; see, for example the quotation from his conclusion, pp 174-175.

63. Ref. (34), above.

64. Berndt, G., op.cit., (33), (1904), p 121.

65. Berndt referred to Bidwell's 1895 paper.

66. Berndt, G., op.cit., (33), (1904), p 121.

67. Ibid.

68. Ibid.

69. Ibid., p 122.

70. Ibid., p 122-124.

71. Ibid., p 122. Berndt wrote:-

> 'Es war nicht völlig ausgeschlossen, dass bei der Belichtung doch chemische Prozesse auftraten (ich denke hier vor allen Oxydationen), die bei Verdunkelung wider zurückgingen.'

72. Ibid., p 124.

73. Ref. (16), above.

74. Ref. (2), above.

75. Brown, F.C., and Stebbins, J., op.cit., (9), (1908).

76. Brown, F.C.,

77. It was not, indeed is not, unusual for priority of publication to be an important issue in academic scientific circles, yet Brown's plan does sometimes seem to have been rather obvious. As I have said his 1908 paper, for example, was a summation of work he carried out over a period of some three four years. For instance he included the effect of pressure on the resistance of selenium cells a piece of work which he first reported to the (American) Physical Society in February 1904. A year later this preliminary note was followed by a paper of which an abstract appeared in Physical Review, 20, (1905), pp 185-186. Insofar as an abstract of a paper can give a clue to motivation one paragraph of that abstract (p 186), contained the following:

> 'So far as I have been able to find out, in looking through Science Abstracts and Beiblätter there has been no work done on the conductivity of selenium under pressure'.

Whether he was merely filling in an unexplored region or was driven by a theoretical question is not discussed.

78. Ref. (57), above.

79. Ref. (58), above.

80. Berndt, G., op.cit., (33), (1904).

81. Marc, R., 'Uber das Verhalten des Selens gegen Licht und Temperatur', Zeits.f.Anorg.Chem.,(37),(1903), pp 459-474. Also two further works, see bibliography.

82. Ref. (77), above.

83. Brown, F.C., and Stebbins, J., op.cit., (9), (1908), pp 273-298.

84. Ibid., pp 294-295.

85. Ibid., p 295.

86. Ibid., p 297.

87. Brown, F.C., op.cit., (29), (1911), p 1.

88. Brown, F.C., and Stebbins, J., op.cit., (9), (1908).

89. See Note (31), above.

90. Even the extensive work of Saunders (ref.(57)) or Marc (ref. (81)) had not provided the necessary direct evidence.

91. Brown, F.C., op.cit., (29), (1911), p 2.

92. Ibid., p 2.

93. Ibid.

94. Ibid., p 5. Brown pointed out that this implied that the amount of C always increased during illumination while of the amount of A decreased. The quantity of B would evidently depend on the relative rates of change of A and C.

95. Ibid., p 3.

96. Ibid., p 5.

97. The constants were rather complex, for example.

$$c_1 = \left[\frac{C_0}{\beta_1} + \left(\frac{L}{N} - B_0\right)\frac{1}{\beta_2 + m_2} - \frac{L}{N\beta_2}\right]\frac{(\beta_2 + m_2)(\beta_1 + m_2)}{m_2 - m_1}$$

Where $L = \beta_2\alpha_1(A + B + C)$
$N = \alpha_1\beta_1 + \alpha_1\beta_2 + \alpha_2\beta_2$

and $m_1$ and $m_2$ were given by

$$m_1 m_2 = N = \alpha_1\beta_1 + \alpha_1\beta_2 + \alpha_2\beta_2$$

$$m_1 + m_2 = -(\alpha_1 + \alpha_2 + \beta_1 + \beta_2)$$

and $B_0$ is the initial value of B.

N.B. There is a small error, probably a printing mistake, on p 3; $(\alpha_1 - \beta_1)$ being written for $(\alpha_1 - \beta_2)$ : The error was not propagated through the paper and was not, therefore significant.

98. Brown, F.C., op.cit., (76), (1911), p 5.

99. Unfortunately Brown does not give us the method of approximations he used to obtain his results. One must suspect that 'guesses' were more the order of the day.

100. Brown, F.C., op.cit., (76), (1911), p 5.

101. His words were:

> 'Case 2 is regarded as a highly improbable one in that the rates of change between B and C compared to the reverse changes between C and B are greater before illumination than afterwards.'

He does not elaborate this point further, which is disappointing for there does not seem to be any compelling reason why this claim should have been made.

102. On p 4 Brown lists all the factors that enter into his equations. They were:-

$\alpha_1, \alpha_2, \beta_1, \beta_2$ ; before and after illumination, $m_1$, $m_2$, $A_0$, $B_0$, $C_0$, the initial quantities, $A_1$, $B_1$, $C_1$ the steady state values of the quantites, K the total and L/N. Not all these factors were independent of each other. The values he chose were such as to in some case shift the equilibrium on illumination in the favour of B to produce light positive selenium; and in other cases to arrange things such that light negative selenium could be produced. He was careful to reach values that seemed to him to be of reasonable physical magnitudes and ratios.

103. Brown, F.C., op.cit., (76), (1911), p 6.

104. Ibid., p 7.

105. Ibid.

106. Ibid.

107. Ibid.

108. Ibid., p 6.

109. Ibid.

110. Ibid., p 7.

111. Ibid., p 7.

112. Ibid., p 9.

113. Ibid. Brown quoted the following; where sensibility is defined as the ratio of the conductivity in the light to that in the dark.

| Resistance. | Sensibility. |
|---:|---:|
| $10^9$ | 200/1 |
| 400,000 | 30/1 |
| 90,000 | 10/1 |
| 100,000 | 10/1 |
| 160,000 | 4/1 |
| 30,000 | 2/1 |
| 17,000 | 1.1/1 |
| 12,000 | 1.0/1 |
| 3,500 | 1.0/1 |
| 400 | -1.002/1 |
| 20 | -1.15/1 |
| 1 | -1.5/1 |

In view of the variability of selenium these results and the accuracies quoted at the low end of the sensibility scale are almost too good to be true!

114. Ibid., p 9.

115. Ibid., p 10. The results he gave were a few empirical relationships between light intensity and the conductivity variations. E.g.,

$i = cm^2$, $i = cm^3$, $i = m\ (m - a)\ b$, $i = b^m - 1$,

$R_a/R_b = (\ b/a\ )^a$, $i = cm$. Where 'i' is the light intensity, 'm' the change of conductivity, 'R' the resistance and 'a', 'b', and 'c' are constants.

It is of interest to note that while working with photoconductive cells in the late 1950's I found that the change of resistance of a wide variety of materials under the influence of infra-red was dependent on the cube of the resistance of a particular cell, no matter how that resistance was varied; irradiation by an intense constant source of light, by temperature etc., and that this discovery did not have a theoretical explanation at that time. This was provided in 1960 by a theoretician at the Royal Radar Establishment. Even at that date there was no correlation between different cells, even made of the same material.

116. Ibid.

117. Ibid., p 11.

118. Brown, F.C., 'The Effective Depth of Penetration of Selenium by Light.' <u>Phys. Rev</u>., <u>34</u>, (1912), pp 201-204.

119. See note (115), above.

120. Brown, F.C., <u>op.cit</u>., (23), (1911), p 10.

121. Ibid.

122. Ibid., p 23.

123. Ibid., p 24.

124. Ibid., pp 24-25.

125. Ibid., p 25.

126. Ibid.

127. p 176, above.

128. Brown, F.C., <u>op.cit</u>., (76), (1911), p 23.

129. See discussion of Bidwell's work in Chapter 3.

130. Brown, F.C., op.cit., (23), (1911), p 13.

131. Ibid.

132. Ibid., p 14.

133. Ibid., p 15.

134. See this Chapter p 164 f.

135. Brown, F.C., 'The Recovery of the Giltay Selenium Cell and the Nature of Light Action in Selenium', Phys. Rev., 33, (1911), pp 403-420.

136. Ibid., p 420.

137. Ibid., pp 412-414.

138. By positive direction Brown meant A→B, B→C.

139. See above, p 188.

140. Brown, F.C., op.cit., (135), (1911), p 419.

141. __________., op.cit., (118), (1912).

142. __________., op.cit., (135), (1911).

143. Pfund, A.H., op.cit., (14), (1909).

144. __________., op.cit., (13), (1904).

145. Brown, F.C., and Seig, L.P., 'Wavelength Sensibility Curves for Light Sensitive Selenium and Their Significance'. Phys. Rev., (2nd Series), 4, (1914), pp 48-61. On page 61 they wrote:-

> 'Previous results on the effect of abrasion and on the pressure effect on the electrical conductivity indicated in a very marked degree that the slow changes accompanying the light action were the results of crystal changes.'

146. Brown, F.C., 'The Nature of Electric Conduction as Required to Explain the Recovery of Resistance of Metallic Selenium Following Illumination'. Phys.Rev. (2nd Series), 5, (1915), pp 395-403.

147. Brown collaborated with Richardson to investigate the emission of electrons from hot surfaces. See Richardson, O.W., The Electron Theory of Matter, (Cambridge, 1916), p 6.

148. See p 213, below.

149. These points will be discussed in the next Chapter.

150. As a model the theory had a use in that the action of the mathematical theory matched the performance of cells; as the action of rubber sheets can mirror the action of a radio valve.

As a learning device it had a use in that it pointed to tests, whose results, negative or positive could be useful in the search for an understanding.

151. p 190, above.

152. Brown, F.C., and Sieg, L.P., 'The Sensibility Curves for Selenium; A New Sensibility-Wavelength Maximum and a New Principle', Phys. Rev., (2nd Series), 2, (1913), pp 487-494.

153. ________________________., op.cit., (145), (1914).

154. Ibid., Fig.3, p 53.

155. Nicholson, P.J., 'Physical Properties of Selenium' Phys. Rev., (2nd Series), 3, (1914), pp 1-24.

156. See discussion of Brown's 1911 papers above.

157. Brown, F.C., and Seig, L.P., op.cit., (145), p 61.

158. Ibid., p 60.

159. Ibid.

160. Ibid., p 61.

161. Ibid.

162. Ibid.

163. There had been some recognition of this in the work of Bidwell and later in the researches of Baedeker, (of which a little later), but Brown deserves the credit for stating the fact clearly.

164. See the epilogue for a short assessment of the work of Gudden and Pohl and also the Bibliography where a short list of their work is included.

165. Brown, F.C., and Seig., L.P., 'The Seat of Light Action in Certain Crystals of Metallic Selenium, and some New Properties in Matter.' Phil. Mag., (6th Series), 28, (1914), pp 497-508.

166. Brown, F.C., 'The Electrical, The Photo-electrical and the Electromechanical Properties of Certain Crystals of Metallic Selenium, with certain Applications to Crystal Structure.' Phys. Rev., (2nd Series), 5, (1915), pp 167-175.

167. __________., 'The Nature of Electric Conduction as required to explain the Recovery of Resistance of Metallic Selenium following Illumination', Phys.Rev., (2nd Series), 5, (1915), pp 395-403.

168. Brown, F.C., 'Some Experiments on the Nature of Transmitted Light-action in Crystals of Metallic Selenium', <u>Phys. Rev</u>., (2nd Series), <u>5</u>, (1915), pp 404-411.

169. Brown, F.C., 'The Crystal Forms of Metallic Selenium and some of its Properties', <u>Phys.Rev</u>., (2nd Series), <u>4</u>, (1914), pp 85-98. Description of the method of preparing single crystals of selenium is given on pp 86-87. Also see a short note, Brown, F.C., 'Isolated Crystals of Selenium of the Second and Fifth Systems, and the Physical Conditions determining their Production', <u>Phys.Rev</u>., (2nd Series), <u>5</u>, (1915), pp 236-237.

170. Brown, F.C., and Seig, L.P., <u>op.cit</u>., (165), (1914), p 497.

171. Ibid., p 500.

172. Ibid., pp 501-502.

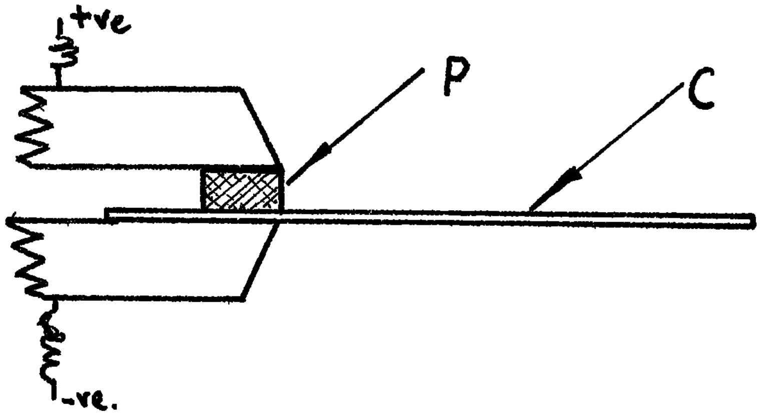
173. Ibid.

174. Ibid.

175. Ibid., p 504.

176. Ibid., p 505.

177. As an example of Brown's techniques I give without editing his description of the method he employed to demonstrate that the effect of light was transmitted along the crystal. Ibid., pp 505-506.



'The above result led directly to a peculiar experiment with the amazing result that light action may be transmitted laterally to a longer distance than 10 mm. in an acicular hexagonal crystal of metallic selenium without any, at present known, apparent mechanism to carry the action. First a crystal of dimensions 10 x .12 x .13 mm was placed with one end between silver electrodes, as shown in Fig. 3. The conductance in the dark was 110. A beam of light was focused first near the electrodes and then moved out to the end step by step, and the following readings of the conductance were observed.

| Location of light | Conductance C | Change in Conductance $\Delta C$ |
|---|---|---|
| Off crystal | 110 | - |
| Near electrodes | 144 | 34 |
| On step 1 | 137 | 27 |
| " " 2 | 117 | 7 |
| " " 3 | 111 | 1 |
| " " 4 | 124 | 14 |
| " " 5 | 146 | 36 |
| " " 6 | 150 | 40 |
| On end of crystal | 151 | 41 |

This shows, as did also similar experiments with other crystals, that along the crystals there are light sensitive parts which control the conductivity mechanism of the selenium. For, strangely enough, the greatest effect was produced in the crystal above when the illumination was at the end of the crystal farthest from the electrodes, a distance out of some 6 mm. If the current had travelled the entire distance around by way of the illuminated end it would have gone about 100 times the distance between the electrodes, and so if the effect of the light had been confined to the neighbourhood of the tip of the crystal, this great change in the conductance could surely not have taken place.

178. Ibid., p 507.

179. Ibid.

180. Ibid.

181. See for example introduction in Brown, F.C., op.cit., (203), (1915), p 167.

182. Ibid.

183. Brown, F.C., op. cit., (168), (1915).

184. Ibid., p 407.

185. Ibid.

186. Ibid., section headed 'The Action at a Distance is Propagated Mechanically.'

187. Ibid., p 407.

188. Ibid., p 408.

189. Ibid.

190. Ibid.

191. The meaning of 'electrical potential effect had been empirically defined in Brown, F.C., op.cit., (203), (1915), pp 170-173.

192. Brown, F.C., <u>op. cit</u>., (268), (1915), p 408.

193. Ibid., p 409.

194. Ibid., p 410.

195. Ibid.

196. Ibid.

197. Ibid.

198. Ibid., p 408.

199. See discussion in Chapter 3, Section 7.

200. Marc, R., <u>op.cit</u>., (81), (1904).

201. Kruyt, H.R., 'Die Dynamische Allotropie des Selens', <u>Zeits.f.anorg.Chem</u>., <u>64</u>, (1909), pp 305-326.

202. Brown collaborated with Richardson see note (147) above; it can be presumed, therefore, that this would be one source, particularly as Brown acknowledged his debt to Richardson.

203. See Ref. (155), above.

204. For example Koenigsberger produced an extensive review article 'Das Elektrische Verhalten der Variablen Leiter und deren Beziehungen zur Elektronen Theorie', <u>Jahr.d.Rad.u.Elek</u>., <u>11</u>, (1914), pp 84-142.

205. See, for example, Baedeker, K., <u>Die Elektrischen Ershiegungen in Metallischen Leitern</u>, (Braunschweig, 1911).

206. Richardson, O.W., <u>The Electron Theory of Matter</u>, (Cambridge, 1916).

207. Marc, R., <u>op. cit</u>., (81), (1903).

208. ________., 'Über der Verhalten des Selens gegen Licht und Temperatur, II', <u>Zeits.f.anorg.Chem</u>., <u>48</u>, (1906), pp 393-426.

209. ________., 'Über der Verhalten des Selens gegen Licht und Temperatur, III', <u>Zeits.f.anorg.Chem</u>., <u>50</u>, (1906), pp 446-464.

210. Saunders, A.P., <u>op.cit</u>., (57), (1899-1900).

211. Schrott, P. von., 'Das Elektrische Verhalten der Alltropen Selenmodifikationen unter dem Einflusse von Wärme und Licht.' <u>Akad.Wiss.Wien</u>., <u>115</u>, (1906), pp 1081-1170.

212. Ibid., p 1169.

213. Translating this phrase as 'The light effect is produced by ionisation of the B type selenium, which continues up to a saturation. The increase of resistance following saturation is perhaps due to an opposing simultaneous photopolymerisation.'

214. McDowell, L., *op.cit.*, (10), (11), (12), (1909), (1910), (1910).

215. Crum, L.B., 'Certain Characteristics of Light Negative Selenium', *Phys. Rev.*, *33*, (1911), pp 538-548.

216. White, G.W., 'The Properties of Selenium Blocks', *Phil. Mag.*, (6th Series), *29*, (1914), pp 370-382

217. Ibid., p 381.

218. See discussion of Brown's work, above.

219. Pfund, A.H., *op.cit.*, (14), (1909).

220. Ries, C., 'Engegengesetztes Verhalten des Selens' *Phys. Zeits.*, *9*, (1908), pp 228-233, is one example of his works.

221. Nicholson, P.J., 'The Physical Properties of Selenium', *op. cit.*, (155), (1914), pp 1-24.

222. Brown, F.C., and Sieg., L.P., 'Wavelength Sensibility Curves for Selenium', *Phys. Rev.*, *4*, (2nd Series), (1914), pp 48-61. On p 57 Brown wrote:-

> 'Quite recently Nicholson has made a very able analysis of certain phenomena in selenium on the basis of electron theory'.

223. ______________________., 'The Sensibility Curves for Selenium; A New Sensibility-wavelength maximum and a New Principle', *Phys. Rev.*, *2*, (2nd Series), (1913), pp 487-494. On p 493 we find:-

> 'Dr. Pfund had had the kindness to communicate some very interesting and as yet unpublished results by Mr. P.J. Nicholson which are directly in agreement with out results.'

Brown made no mention of Nicholson's theory at this stage. Maybe that information was not included.

224. That is his interest in the depth of penetration may have been suggested by Pfund's work (see p 197 above).

225. Brown made many references to the effects of impurities in various papers, some of which have been noted previously.

226. Brown, F.C., op.cit., (206), (1914), pp 97-98.

'The action of light seems to be in centers inside the crystals and does not necessarily involve the existence of more than one complete crystalline form. These centers inside the crystal resemble the so-called active centers in zinc-sulphide as described by Rutherford.'

227. Wick, F.G., 'Some Electrical Properties of Silicon, I. Thermoelectric Behaviour', Phys.Rev., 25, (1907), pp 382-390.

228. __________, 'Some Electrical Properties of Silicon, II. The Electrical Resistance of Silicon at Various Temperatures', Phys. Rev., 27, (1908), pp 11-17.

229. __________.,'Some Electrical Properties of Silicon, III. The Hall Effect at Ordinary and Low Temperatures', Phys. Rev., 27, (1908), pp 76-86.

230. __________.,'Some Electrical Properties of Silicon, IV. The Electro-motice Force of Cells in which Silicon forms one Electrode', Phys. Rev., 27, (1908), pp 238-249.

231. Audubert, R., 'Contribution a l'Etude des Contacts Solides - Sulfure de Plomb et Sulfure d'Argent', J.de Phys., 7, (1917), pp 209-223.

232. Wold, P.I., 'The Hall Effect and Allied Phenomena in Tellurium', Phys. Rev., 7, (2nd Series), (1916), pp 169-193.

233. Morris - Airey, H., and Spencer, E.D., 'On the Temperature Coefficient of Electrical Resistance of Carbon at Low Temperatures', Mem.Man.Lit. and Phil.Soc., 49, (1905), pp 1-8.

234. Baedeker, K., 'Über eine eigentümliche Form elektrischen Leitvermögens bei festen Körpern.' Ann.d.Phys., 29, (1909), pp 566-584.

235. See discussion in Chapter 3, sections 8 & 9.

236. Lark-Horovitz, K., The New Electronics in The Present State of Physics, (AAAS), (1954), p 59.

237. Ibid., p 69.

238. Ibid., p 66.

239. See bibliography.

240. I make this observation from the lack of acknowledgements in the papers referred to later.

241. Braun, F., 'Über Unipolare Elektricitätsleitung', *Ann.d.Phys.*, *4*, (1878), pp 476-484.

242. Pierce, G.W., 'Crystal Rectifiers for Electric Currents and Electric Oscillations, I, Carborundum.', *Phys. Rev.*, *25*, (1907), pp 31-60.

243. ___________., 'Crystal Rectifiers for Electric Currents and Electric Oscillations, II, Carborundum, Molybdenite, Ana tase, Brookite,' *Phys. Rev.*, *28*, (1909), pp 153-187.

244. Pierce, G.W., 'Crystal Rectifiers for Electric Currents and Electric Oscillations, III, Iron Pyrites', *Phys. Rev.*, *29*, (1909), pp 478-484.

245. ___________., *op.cit.*, (242), (1907), p 50. '. . . . . a lighted match held under the piece so as to heat it chiefly at one electrode does not much change the rectified current. These facts seem to be inconsistent with the assumption that the direct electromotive force obtained with an alternating current is thermoelectric in origin.'

246. Ibid., p 56.

247. Pierce, G.W., *op.cit.*, (243), (1909), p 186.

248. Austin, L.W., 'Some Contact Rectifiers of Electric Currents', *Bull.Bur.Stan.*, *5*, (1908), pp 133-147.

249. Pierce, G.W., *op.cit.*, (286), (1909), p 484.

250. Flowers, A.E., 'Crystal and Solid Contact Rectifiers', *Phys. Rev.*, *29*, (1909), pp 445-460.

251. That is, of course, only with the modern concepts of holes and electrons, and donor and acceptor levels does his observations on artificially induced rectification take on full significance.

252. Flowers, A.E., *op.cit.*, (292), (1909), p 459.

253. Ibid., p 457.

254. 'Unfortunately' used in the Whiggish sense.

255. Flowers, A.E., 'Characteristics of Crystal Rectification', *Phys. Rev.*, *3*, (2nd Series), (1914), pp 25-46.

256. Goddard, R.H., 'On the Conduction of Electricity at Contacts of Dissimilar Solids', Phys. Rev., 34, pp 423-451.

257. Lark-Horovitz, K., op.cit., (238), (1954), p 66.

258. Ibid., p 68.

259. Interview with Pohl, Krefeld, 1974.

260. Not only did they produce a large number of original papers (see bibliography) Gudden, in particular, wrote two or three extensive review articles.

261. Case, T.W., 'Notes on the Change of Resistance of Certain Crystals Substances in Light', Phys. Rev., (2nd Series), 9, (1917), pp 305-310.

262. See Chapter 3, pp 119-129.

263. Smith, A.W., 'On the Hall Effect and Allied Phenomena', Phil. Mag., (6th Series), 31, (1916), pp 367-368.

264. Koenigsberger, J., op.cit., (204), (1914), pp 85-142.

265. Baedeker, K., op.cit., (234), (1909), pp 566-584.

266. See Lark-Horovitz, K., op.cit., (238), p 64.

267. Baedeker, K., op.cit., (234), (1909).

268. Case, T.W., op.cit., (261), (1917), and Pfund, A.H., 'Light Sensitivity of Copper Oxide', Science, 42, (1915), pp 805-806.

269. Brown was not cited by Gudden in his review papers for example.

270. See above, p 158 and Chapter 5 pp 259-264.

271. See Koengisberger, J., op.cit., (204), (1914).

272. Ibid.

273. For example the Hall Effect; but also Pohl's work during World War I on radio presented him with some highly sophisticated measurement techniques (See Epilogue).

## References and Notes. CHAPTER 5.

1. Hirosige, T., 'Origins of Lorentz' Theory of Electrons and the Concept of the Electromagnetic Field', *Hist. Stud. Phys. Sci.*, 1, (1969), pp 151-209.
2. Pfund, A.H., 'The Electrical - Optical Properties of Selenium', *Phys. Rev.*, 28, (1909), pp 324-336.
3. Brown, F.C., 'The Nature of Electric Conduction as Required to Explain the Recovery of Resistance of Metallic Selenium following Illumination.' *Phys.Rev.*, (2nd Series), 5, (1915), pp 395-411.
4. Sommerfeld, A., 'Zur Elektronentheorie der Metalle auf Grund der Fermischen Statistik', *Zeits.Phys.*, 47, (1928), pp 1 - 32.
5. Wilson, A.H., 'The Theory of Electronic Semiconductors - II', *Proc. Roy. Soc.*, (A), 133, (1931), pp 458-491.
6. ———————., 'The Theory of Electronic Semi-Conductors - II', *Proc. Roy. Soc.*, (A), 134, (1931), pp 377-387.
7. Richardson, O.W., *The Electron Theory of Matter*, (Cambridge, 1916).
8. Thomson, J.J., *The Corpuscular Theory of Matter*, (New York, 1907).
9. See discussion in Chapter 3, Section 2.
10. Whittaker, E.T., *A History of the Theories of Aether and Electricity*, Vol. II, (London, 1953).
11. Hume-Rothery, W., *The Metallic State. Electrical Properties and Theories*, (Oxford, 1931).
12. Lindemann, F.A., 'Note on the Theory of the Metallic State', *Phil. Mag.*, (6th Series), 29, (1915), pp 127-140.
13. Thomson, J.J., 'Conduction of Electricity through Metals', *Phil. Mag.*, (6th Series), 30, pp 192-202.
14. Livens, G.H., 'The Electron Theory of Metallic Conduction', *Phil. Mag.*, (6th Series), 29, (1915), pp 105-112, 112-124, 173-183, 425-432.
15. ———————., 'The Electron Theory of Metallic Conduction', *Phil. Mag.*, (6th Series) 30, (1915), pp 287-295, 549-559.
16. ———————., 'Electron Theory of the Hall Effect and Allied Phenomena', *Phil. Mag.*, (6th Series), 30, (1915), pp 526-548.

17. Lodge, O., 'On the Controversy concerning Volta's Force', *Phil. Mag.*, (5th Series), *49*, (1900), pp 351-383, 454-475.

18. Hirosige, T., *op.cit.*, (1), (1969) pp 196-202.

19. See discussion in Chapter 3, for example p 130.

20. Ibid.

21. The Wiedemann-Franz law was announced in *Pogg.Ann.*, *89*, (1853), p 531.

22. See, for example, Swann, G., 'The Expression for the Electrical Conductivity of Metals as deduced from the Electron Theory', *Phil. Mag.*, (6th Series), *27*, (1915). pp 441-445. Swann wished to decide between Drude's formula $\sigma = \frac{ne^2\lambda v}{4\alpha\theta}$ and his own $\frac{ne^2\lambda v}{3\alpha\theta}$

    He concluded that his was correct, Drude's being the result of a mathematical error.

23. M'Whan, J., 'On the Electron Theory of Thermoelectricity', *Proc. Roy. Soc. Edin.*, *23*, (1912-1913), p 169.

24. Baedeker, K., 'Zur Elektronentheorie der Thermoelektrizität', *Phys. Zeits.*, *11*, (1910), pp 809-811.

25. M'Whan refers to Krüger, *Phys. Zeits.*, *11* (1910), p 800.

26. M'Whan, J., *op.cit.*, (20), (1915), p 175.

27. Ibid.

28. Jammer, M., *The Conceptual Development of Quantum Mechanics*, (New York, 1966), pp 1 - 10.

29. Ibid., Chapters 1 - 4.

30. Sommerfeld, A., *op.cit.*, (4), (1928).

31. See Chapter 4 and later this chapter.

32. Lindemann, F.A., *op.cit.*, (12), (1915), pp 127-140.

33. Ibid., p 127.

34. Ibid., p 128.

35. Ibid., p 129.

36. Ibid., p 140.

37. See Jammer, M., *op.cit.*, (25).

38. Hall, E.H., 'On Electric Conduction and Thermoelectric Action in Metals', *Proc. Amer.Acad.*, *50*, (1914), pp 67-103.

39. Ibid., p 68.

40. Ibid., p 67.

41. Lindemann, F.A., *op.cit.*, (12), (1915), p 129, for example.

42. Hall, E.H., *op.cit.*, (35), (1914), p 96.

43. Thomson, J.J., 'Conduction of Electricity through Metals', *Phil. Mag.*, (6th Series), *30*, (1915), p 192.

44. Ibid., p 193.

45. Ibid.

46. Koenigsberger, J., and Kilching, K., 'Über das Verhalten gebundener und "freier" Elektronendgegen elektro-magnetische Strahlung', *Ann.d.Phys.*, *28*, (1909), pp 889-924.

47. Houston, R.A., 'Electrons and the Absorption of Light', *Nat.*, *80*, (1909), pp 338-339.

48. Pfund, A.H., *op.cit.*, (2), (1909).

49. Livens, G.H., *op.cit.*, (11), (1915), p 173.

50. Ibid., pp 173 - 174.

51. Ibid., p 174.

52. Pfund, A.H., *op.cit.*, (2), (1909), p 331.

53. ____________., 'A Study of The Selenium Cell' *Phil.Mag.*, (6th Series), *7*, (1904), pp 26-39.

54. ____________., *op.cit.*, (2), (1909), p 332.

55. Ibid., p 332.

56. Ibid., p 336.

57. Ibid., p 334.

58. Ibid., p 332.

59. Ibid.

60. Ibid., p 334.

61. Barnard, G.P., *The Selenium Cell*, (London, 1930), p 167.

62. Vonwiller, O.U., 'Observations of the Effect of Light on Selenium', *Roy. Soc. (N.S.W.) J. and Proc.*, *43*, (1910), pp 361-380.

63. Barnard, G.P., *op.cit.*, (61), (1931), p 167.

64. Ibid., p 169.

65. Brown, F.C., 'The Effective Depth of Penetration of Selenium by Light', *Phys. Rev.*, *34*, (1912), pp 201-214.

66. Brown's method used the slight difference between the action of heat and light on selenium.

Vonwiller by irradiating a selenium on either side or both sides together made a direct determination of the depth of penetration.

67. Vonwiller, O.U., <u>op.cit</u>., (62), (1910), p 377.

68. Ibid., pp 370-371.

69. See, for example, Brown, F.C., 'The Recovery of the Giltay Cell and the Nature of Light Action in Selenium', <u>Phys. Rev</u>., <u>33</u>, (1911), pp 403-420.

70. Attempts to determine the relationship between conductivity and intensity had been started by Adams and Day in the 1870's. The exact form of the dependence was still a matter for discussion in this period.

71. Vonwiller, O.U., <u>op.cit</u>., (62), (1910), p 379.

72. Ibid., p 380.

73. Einstein, A., 'On a Heuristic Point of View about the Creation and Conversion of Light', <u>Ann.Phys</u>., <u>132</u>, (1905), p 132. Translation in <u>The Old Quantum Theory</u>, Haar, D. ter, (London, 1967), pp 91-107.

74. See for example Jammer, M., <u>op.cit</u>., p 44.

A quotation is given concerning the occasion of Einstein's election to the Prussian Academy on June 12, 1913. Jammer gives several sources for the passage the primary one being a document discussed by Kahan, T., 'Un Document Historique de l'Academie des Sciences de Berlin sur l'activité d'Albert Einstein' <u>Archive Internationale d'Histoire des Sciences</u>, <u>15</u>, (1962), pp 337 - 342.

'Summing up, we may say that there is hardly one among the great problems in which modern physics is so rich, to which Einstein has not made an important contribution. That he may sometimes have missed the target in his speculations, as, for example, in his hypothesis of light quanta, cannot really be held against him, for it is not possible to introduce fundamentally new ideas, even in the most exact sciences without occasionally taking a risk.'

75. Barnard, G.P., <u>op.cit</u>., (61), (1930), p 175.

76. Chapter 2, Ref. (57).

77. Barnard, G.P., (61), wrote, (pp 168-169), that 'Nicholson (1914) has offered an explanation of most of the observed phenomena by means of a somewhat involved internal photoelectric hypothesis. The modern theory of Piersol (1927) differs but little from the older hypothesis of Vonwiller'.

78. Ibid.

79. Nicholson, P.J., 'The Physical Properties of Selenium', Phys. Rev., 3, (2nd Series), (1914), p 12.

80. Ibid., pp 12-13.

81. Ibid., p 13.

82. Ibid.

83. Ibid. Possibly referring to the possibility that Ohm's law did not hold for very thin films; an effect attributed to an electron mean free path greater than the size of the film, a point already considered by Pfund.

84. Ibid., p 13. Nicholson referred to the published work of Amaduzzi and to the unpublished work of Pfund.

85. Note that the photo-electric effect, as normally defined today, is most pronounced for the alkali metals irradiated with ultra-violet light.

86. See this Chapter, p 259.

87. Nicholson, P.J., op.cit., (79), (1914), p 13.

88. Barnard, G.P., op.cit., (61), (1930), pp 158-160.

89. McDowell, L.S., 'Some Electrical Properties of Selenium, III. The Influence of Temperature on the Recovery', Phys. Rev., 31, (1910), pp 524-535.

    In point 3 of the summary, McDowell wrote:-

    'Change in conductivity due to excitation by light of the same intensity takes place more slowly at low temperatures than at ordinary temperatures, but the final change produced by saturation is enormously greater.'

90. His basic assumptions were:-

    1. That electrons are responsible for current flow.
    2. That light can liberate electrons from selenium.
    3. That other non-competing agencies can produce extra electrons.
    4. That the absorption of light follows an exponential law.
    5. That continuous recombination takes place.

91. By series expansion and approximation. Nicholson, P.J., op.cit., (79), (1914), p 15.

92. Equation (1) was reduced to

$$\begin{aligned}\frac{dn}{dt} &= M^2 + kI \cdot \exp(-kx) - \alpha^2 n^2 \\ &= M^2 + c^2 \cdot \exp(-kx) - \alpha^2 n^2 \\ &= \underline{q^2 - \alpha^2 n^2}\end{aligned}$$

The solution of this equation was given as

$$n = \frac{q}{\alpha}\left[1 - \frac{2}{\frac{q+M}{q-M}\exp(2\alpha qt) + 1}\right]$$

and the integral with which he was faced was

$$m = \int_{(c^2+M^2)^{1/2}}^{(c^2\exp(-Kx)+M^2)^{1/2}} \frac{q}{\alpha}\left[1 - \frac{2}{\frac{q+M}{q-M}\exp(2\alpha qt) + 1.}\right]\frac{2q \times dq}{q^2 - M^2}$$

By considering a large 't' he expanded the denominator within the square bracket and considered only the first term.

93. The full expression for m was

$$m = \frac{2A}{\alpha k}\left\{(c^2+M^2)^{\frac{1}{2}} - M + \frac{M}{2}\log_4\frac{c^2}{M^2} \cdot \frac{M + (c^2+M^2)^{\frac{1}{2}}}{M - (c^2+M^2)^{1/2}} + \frac{M}{2}ks\right\}$$

$$- \frac{2A}{\alpha k} \cdot \frac{1}{\alpha t}\left\{\frac{1}{4}\exp(-2\alpha Mt) \times \frac{c^2 + M^2}{\left\{(c^2+M^2)^{\frac{1}{2}} + M\right\}^2}\exp(-2\, t(c^2+M^2)^{\frac{1}{2}}\right\}$$

94. For example to obtain equation (3) he considered a steady state and removed the term in $\frac{M}{2}ks$, for that represented the dark current, writing this as $m_0$.

Hence the change in conductivity is represented by the first three terms in the first curly bracket. If $M \ll c$ only the first term need be considered. Hence the equation (3) is obtained.

His justification for this assumption was to argue that the number of electrons ejected by light was of the same order of magnitude as the number produced spontaneously i.e. $M^2 = c^2/k$, but, said Nicholson, k is a very large number, ($6 \times 10^4$) hence $c \gg M$.

95. Barnard, G.P., in 1930 quoted dependences varying from linear to one-fourth power. <u>op.cit</u>., (61), p 87.

96. Nicholson, P.J., <u>op.cit</u>., (79), (1914), p 16.

97. Ibid., p 16.

98. Ibid., p 17.

99. Ibid., p 18.

100. Ibid.,

101. Ibid., p 19.

102. Ibid., p 20.

103. Ibid., pp 21-23.

104. Some already had, for example the absorption coefficients, others, such as recombination coefficients were to be measured in the 20's by Pohl and Gudden and later in the 50's. See, for example, Moss, T.S., <u>Photoconductivity in the Elements</u>, (London, 1952).

105. Nicholson, P.J., <u>op.cit</u>., (79), (1914), p 24.

106. Ibid.

107. Brown, F.C., 'The Nature of Electric Conduction as Required to Explain the Recovery of Resistance of Metallic Selenium following Illumination', <u>Phys. Rev</u>., <u>5</u>, (2nd Series), (1915), pp 395-403.

108. Brown refers to J.W. Nicholson, but the paper to which he gives '<u>Phys. Rev</u>., (2nd Series), <u>3</u>, p 1, was, according to Phys. Rev., authored by P.J. Nicholson.

An error was made although whether by Brown or by the editors of <u>Physical Review</u> has not been determined. There was a J.W. Nicholson but he worked in England and was a mathematician and was never concerned with selenium.

109. Brown, F.C., <u>op.cit</u>., (96), (1915), p 395.

110. Ibid.

111. Ibid.

112. Ibid.

113. Ibid.

114. Ibid.

115. Hume-Rothery, W., <u>op.cit</u>., (11), (1931).

116. Ibid., p 206.

117. Ibid.

118. Thomson, J.J., *op.cit.*, (8), (1907).

119. Ibid., p 86.

120. Hall, E.H., 'A Possible Function of the Ions in the Electric Conductivity of Metals', *Proc.Nat. Acad. Sci.*, *3*, (1917), pp 163-171.

121. Brown, F.C., *op.cit.*, (107), (1915), pp 395-396.

122. Ibid., p 396.

123. Ibid., p 396.

124. Ibid.,pp 396-397.

125. Ibid., p 397.

126. Ibid.

127. Ibid.

128. Ibid., p 398.

129. See the discussion in Chapter 4, above.

130. In Brown, F.C., The Nature of Light Action in Selenium, *Phys. Rev.*, *33*, (1911), p 2, Brown cited the work of Biltz and Peuneur, *Zeits.f. anorg.Chem.*, *64*, p 305. Brown wrote:-

    'This paper will not attempt to define the three components whose existence is supposed nor will it consider the particular reason why the components have different rates of change under the same external conditions. But since Biltz and Preuneur have found three components in sulphur changing under the influence of pressure and temperature according to the reaction,

    $$S_8 \rightleftharpoons S_4 \rightleftharpoons S_2$$

    it would not be surprising to find later that the three components of light-sensitive selenium may be identified and studied as separate allotropic forms.'

131. See Chapter 2.

132. Ibid., p

133. Brown, F.C., *op. cit.*, (107), (1915), p 399.

134. Ibid.

135. Ibid.

136. Ibid.

137. See, for example, Smith, R.A., Semiconductors, (Cambridge, 1959), Chapter 5.

138. Ibid.

139. Ibid., p 157. But note that variations in carrier concentrations can give rise to departures from Ohm's law, and Brown had pointed out the possible effects of this.

140. See Chapter 4, for example.

141. See Chapter 2.

142. In Chapter 4 it was noted that he moved towards the use of single crystals to avoid the problems, that had been found by another researcher, to be attendant on surface and junction properties.

143. Koenigsberger, J., 'Das Elektrische Verhalten der Variablen Leiter und deren Beziehungen zur Elektronentheorie', Jahr.d.Rad.u.Elek., 11, (1914), pp 84-142.

144. Both original and review papers written by Gudden and Pohl from 1924-1934 include many references to the work of Koenigsberger, and also to Baedeker.

145. Koenigsberger, J., op.cit., (143), (1914), p 127.

One paragraph of five and one half lines was devoted to selenium.

146. Four works were cited, with particular attention being directed to, Marc, R., Die Physikalisch - chemischen Eigenschaften des Metallischen Selens., (Leipzig, (1907).

147. Koenigsberger, J., op.cit., (143), p 85.

148. Reference was made to a review paper published by Baedeker in 1907, but not identified clearly, and to Baedeker, K., Die Elektrischen Ersheinungen in Metallischen Leitern, (Braunshweig, 1911).

149. Koenigsberger, J., op.cit., (131), (1914), p 84.

150. Ibid., p 85.

151. Ibid.

152. Ibid.

153. Chapter 4 and this Chapter.

154. Koenigsberger, J., op.cit., (143), (1914), p 85.

155. Ibid.

156. More than two thirds of Koenigsberger's discussion was devoted to these subjects.

157. Koenigsberger, J., op.cit., (143), (1914), p 96. The relationship, $e = \frac{R}{F} \ln \frac{N'}{N''}$ is quoted and is credited to Baedeker.

158. In all the word makes some half a dozen appearances.

159. The modern meaning is backed up by a substantial theory and a large body of knowledge that Koenigsberger did not possess. The word 'semiconductor' appeared in the late 18th century in English, and was used sporadically in the 19th century. Koenigsberger did not specifically define 'halbleiter' but his meaning is fairly clear from his writings. It has been assumed by many English writers that the word 'semiconductor' and the word 'halbleiter' have had parallel meanings in the two languages; but, in my opinion, this was not true until the end of the 1920's, as evidenced by Gudden's careful definition of the term in 1931.

160. Smith, R.A., op.cit., (137), (1961), p 4.

161. See, for example, Koenigsberger, J., op.cit.,(143), p 121.

162. Gudden, B., 'Uber die Elektrizitätsleitung in Halbleitern', Erlangen Ber., 62., (1931), pp 289-302.

163. Ibid., pp 289-290.

164. Ibid., p 290.

165. Pfund, A.H., 'Light Sensibility of Copper Oxide', Science, 42, (1915), pp 805-806.

166. Koenigsberger, (143), did not consider rectification in his 1914 paper but Coblentz, as has been remarked, recognised the group of properties that are typical of semiconductors.

167. Wilson, A.H., 'The Theory of Electronic Semiconductors', Part I, Proc. Roy. Soc.,(A), 133, (1931), pp 458-491, Part II, Proc. Roy. Soc., (A), 134, (1931), pp 377-387.

168. Even very recently it was not always possible to be absolutely certain. For example, Smith, R.A., op.cit., (137), (1961), p 390, contains the phrase 'No elements other than those discussed above are semiconductors in their normal form. In some cases, however, allotropic forms exist which may be semiconductors; the main evidence for this has been obtained through a study of electrical conduction and photo-conduction in thin films.'

169. See for example a series of papers written by Drude and published in *Ann. d. Phys.*, **1**, (1900), pp 566-613, and **3**, (1900), pp 384-385. Abstracted in *Sci. Abs.*, (Phys.), **3**, (1900), p 473 and **4**, (1901), pp 384-385.

170. Thomson, J.J., *op.cit.*, (8), (1907).

171. Ibid., p 69.

172. Ibid.

173. Ibid., p 70.

174. Ibid.

175. Ibid., p 70.

176. At least that was Hall's gloss of 1914, for in 'On Electric Conduction and Thermoelectric Action in Metals', *op. cit.*, (35), (1914), p 67 he wrote 'Sir J.J. Thomson suggested in his *Corpuscular Theory of Matter* and action somewhat like that which I imagine for the (A) electrons, though he seems presently to have abandoned this idea as unnecessary'. Hall was a little premature, for as we have noted, Thomson returned to the theory in 1915. See Note (13) above.

177. See Notes (11), (12), and (13) above.

178. See Note (151) above.

179. Richardson, O.W., *op. cit.*, (7), (1916).

180. For example in Wick, F.G., 'Some Electrical Properties of Silicon, III, The Hall Effect at Ordinary and low Temperatures', *Phys. Rev.*, **27**, (1908) p 85 a table gives the Hall Coefficient and the Thermoelectric Power for a variety of materials. She gave as her source Beattie, J.C., *Proc.Roy.Soc. Edin.*, 1895-96.

181. In Ibid., p 85, we find that for metals the Hall coefficient ≈ .001 in most cases; for silicon & tellurium the values given were 120.2 and 532. Thermoelectric power for metals was in the range 0.68 — 17; for silicon, 400, tellurium 502.

182. Richardson, O.W., *op.cit.*, (7), (1916), p 439.

183. Ibid., p 438.

## References and Notes. CHAPTER 6.

1. For example in Pearson, G.L., and Brattain, W.H., 'History of Semiconductor Research', Proc. I.R.E., 43, (1955), pp 1794-1806.
2. Chapter 2, above, pp 28-29.
3. Ibid., pp 42-63.
4. See list of papers in bibliography.
5. Chapter 2, above, pp 68-95.
6. Ibid.,
7., See Ref. (48), Chapter 2, above.
8. That is with a positive temperature coefficient of conductivity.
9. Siemens, C.W., 'The Action of Light on Selenium', Proc.Roy.Inst., 8, (1875-1878), pp 68-79.
10. See the discussion of the work of Pfund, Marc, Berndt and others in Chapter 4.
11. Chapter 4, above, pp 180-188.
12. Ibid., pp 201-209.
13. The purity of the selenium was unknown, it often being heated in the presence of metals with which it would form selenides. The differential expansion between the selenium, the substrate and the electrodes introduced unknown factors, thereby complicating the experimental results.
14. Barnard, G.P., The Selenium Cell, (London, 1930), p 11.
15. The word 'internal' is used in the usual sense, i.e. denoting a study of the purely scientific work on selenium excluding technical and personal factors.
16. See the discussion of Faraday's work in Chapter 2, above.
17. Bidwell, S., 'On the Sensitiveness of Selenium to Light and the Development of a Similar Property in Sulphur', Proc. Phys. Soc., 7, (1885), pp 129-145.
18. Braun, F., 'Über Unipolare Elektricitätsleitung' Ann.d.Phys., 4, (1878), pp 476-484.
19. Chapter 5, above, pp 259-264.
20. Koenigsberger had a transparency criterion for electrolytic solids.
21. See discussion Chapter 5, above, pp 259-264.

22. Ibid.

23. Of these Day is the most obscure although given some space in Pogg.biog.lit.Handwörterbuch. Adams was Professor of Natural Philosophy and Astronomy at King's College, London, for 30 years; Bidwell, a lawyer, became a Council member of the Royal Society, (1904-06) and was President of the Physical Society, (1897-99). Pfund, from 1927, was Professor of Physics at Baltimore and is best known for the series named after him in the hydrogen spectrum. Brown became a Professor of Physics at Indiana University, served on scientific committees in World War I and was Assistant acting Director of the National Bureau of Standards, (1917-27).

24. Their biographies can be found in World's Who's Who in Science, ~~and~~ in Pogg.biog.lit.Handwörterbuch.

25. Chapter 2, above, pp 68-95.

26. Chapter 3, above, pp 97-110.

27. For example the possibility that selenides were of doubtful value in explaining the properties of selenium cells, (1904), the electronic theory of photoconductivity, (1909), the depth of penetration of selenium by light, (1909), the light sensitive properties of copper oxide, (1916).

28. Ref. (1) above.

29. That is between the discovery of the photoconductivity of selenium and the time at which this thesis closes.

30. Chapter 3, above, pp 134-141.

31. Maxwell's theory did not assume the presence of charges, electricity was a result of the action of fields on conductors, and manifested in 'tubes of force'. Lorentz showed that Maxwell's equations were derivable in a theory in which the presence of charged particles was a basic assumption.

32. I.e. the motion of charged particles, represented as electrons.

33. See restricted list in the bibliography of this thesis.

34. Wilson, A.H., 'The Theory of Electronic Semiconductors - I'. Proc. Roy. Soc., (A), 133, (1931), pp 458-491.

35. ___________., 'The Theory of Electric Semiconductors - II', Proc. Roy. Soc., (A), 134, (1931), pp 377-387.

36. In Krefeld, 25th July 1974. All quotations of Pohl's are from that interview.

37. At the Athenaeum 9th November 1974.

38. For example Mott, Shockley, see p 282.

39. For example the discovery of photoconductivity by Smith, rectification by Adams and Day and so on. .

40. That is the emission of electrons from surfaces; today known simply as the photoelectric effect.

41. See Pogg.biog.lit.Handwörterbuch.

42. That is the crystals formed part of a tuned circuit; the resonant frequency of which would depend on the capacitance of the circuit and hence would vary with the dielectric constant of the crystals. The modified frequencies could be mixed with an unmodified wave resulting in beats. This can be a very accurate method of determining dielectric constants.

43. It had been used by Baedeker, for example, as early as 1907, to investigate the properties of non-metallic conductors.

44. See bibliography.

45. Given by Pohl in the interview and confirmed by Mott in an interview at Cambridge, 2nd November 1974.

46. That is Sommerfeld's introduction of a simple band theory of solids in 1928 and Kapitza's investigations into the magnetic properties of materials at very low temperatures.

47. Bloch was something of an expert in solid state at that time, and was associated with developments of Sommerfeld's theory.

48. That is Koenigsberger's 'variablen leiter'.

49. That is Sir Rudolf Peirls of Oxford; Wilson's memories were partially confirmed by him in a letter.

50. See notes (34) and (35) above.

51. That is about the role of impurities; whether there was any substantial difference between insulators and metals; what substances were semiconductors and so on. Some of these problems may have been the result of no suitable definition of semiconductors until Wilson's theory. See for example the discussion in Chapter 5.

52. Wilson was quite firm on this point. Bernal promised some work, but apparently did none; a G.E.C. employee, Riemann, 'was interested but the only way he could get any work done was to leave G.E.C., so he got some sort of Fellowship and joined the Mond laboratory at

Cambridge, and did some work there completely cold-shouldered by everybody and he put in enough time to get a job and then was off.'

53. It is interesting how the paths of Wilson and Mott seem to have crossed. They were both candidates for the Adams prize, which went to Wilson; according to Mott they were the contenders for the Chair at Bristol which he got.

## PUBLISHED SOURCES.

ADAMS, E.P., 'Effects Related to the Hall Effect', *Phil. Mag.*, *27*, (6th Series), (1914), pp 244-252.

———., 'The Hall and Corbino Effects', *Proc. Am. Phil. Soc.*, *53*, (1915), pp 47-51.

ADAMS, W.G., 'On the Action of Light on Tellurium and Selenium', *Proc. Roy. Soc.*, 24, (1875-1876), pp 163-164.
Also *Nature*, *13*, (1876), p 238.

———., 'The Action of Light on Selenium', *Proc. Roy. Soc.*, *24*, (1875), pp 535-539.

ADAMS, W.G., and DAY, R.E., 'The Action of Light on Selenium', *Proc. Roy. Soc.*, *25*, (1876), pp 113-117.

———., 'The Action of Light on Selenium', *Phil. Trans.*, *167*, (1877), pp 313-349.

ADDENBROOKE, G.L., 'Selenium', *The Electrician*, *67*, (1911), pp 591-592.

AICHI, K., and TANAKADATE, T., 'Effect of Temperature on The Conductivity of Selenium', *Sci. Abs.*, (Phys.), *8*, (1905), No. 398, p 126.
*Math. & Phys. Soc., Tokyo*, *2*, (1904), pp 217-221.

ALLEGRETTI, M., 'Photoelectric Currents', *Sci. Abs.*, (Phys.), *4*, (1901), No. 1681, p 760.
(*Phys. Zeits.*, *2*, (1901), pp 317-319).

ALLEN, H.S., *Photo-Electricity*, (2nd Edition), (London, 1925).

AMADUZZI, L., and LEONE, L., 'Hall Effect in Liquids', *Sci. Abs.*, (Phys.), *3*, (1900), No.1850, p 713.
(*Acad.Lincei*, *9*, (1900), pp 252-255).

———., 'Hall Effect in Liquids', *Sci. Abs.*, (Phys.), *3*, (1900), No. 1850,pp 713-714.

ANDERSON, D.L., *The Discovery of the Electron*, (Princeton, 1964).

ANON., 'Report on C.W. Siemen's Lecture to Royal Institution, Friday 18th February, 1876', *Nature*, *13*, (1876), pp 407-408.

ANON., 'Bell's Photophone', *Nature*, *23*, (1881), pp 15-19.

ANON., 'Seeing by Electricity', *Nature*, *23*, (1881), pp 423-424.

ANON., 'The Selenium Cell', *Elec. World*, *59*, (1912), p 251.

ANON., 'The Genesis of the Transistor', Case 38139-8, *Bell Memo for Record*, (Dec. 27, 1949), in Niels Bohr Library, *Amer. Inst. of Phys.*,(Cat.No.1100 WSG-XB).

ANGELLO, S.J., et al. 'Semiconductor Rectifiers', *Electrical Eng*., *68*, (1949), pp 865-872.

ARRHENIUS, S.A., 'On the Dissociation of Substances in Aqueous Solution', *Zeits. Phys. Chem*,,*I*, (1887), pp 631-648, in Hurd & Kipling J.J., *The Origins and Growth of Physical Science*, *2*, (*London, 1964 - Pelican*), pp 294-306.

ATHANASIADIS, G., 'Conductivity of Selenium', *Sci. Abs*., (Phys.), *11*, (1908), p 245, No. 671. *Ann.d.Phys*., *25*, (1908), pp 92-98.

______________., 'Wirkung der Röntgenstrahlung auf der Elektrischen Widerstand Selens', *Ann.d.Phys*., *27*, (1908), pp 890-896.

AUBEL, E. van., 'Sur la Résistance électrique des corps peu conducteurs aux très basses temperatures', *Comp. Rend*., *135*, (1902), pp 456-457.

____________., 'Sur la Résistance électrique du sulfure de plomb aux très basses temperatures', *Comp. Rend*., *135*, (1902), pp 734-736.

_____________.,'Sur la phénomène de Hall et le pouvoir thermo-electrique', *Comp. Rend*., *135*, (1902), pp 786-788.

AUDUBERT, R., 'Contribution a l'étude des contacts solides-sulfure de plomb et sulfure d'argent', *J.de Phys*., *7*, (1917), pp 209-223.

AUSTIN, L.W., 'Some Contact Rectifiers of Electric Currents', *Bull. Bur. Standards*, *5*, (1908), pp 133-147.

___________., 'A New Method of using Contact Detectors in Radio Measurements', *Proc. I.R.E*., *7*,(1919), pp 257-259.

BAEDEKER, K., 'Metallic Conduction of Electricity', *Sci. Abs*., (Phys.), *14*, (1911), No. 270, p 91.

___________., 'Über eine eigentümliche Form elektrischen Leitvermögens bei festen Körpen', *Ann.d.Phys*., *29*, (1909), pp 566-584.

___________., 'Über die elektrische Leitfähigkeit und die thermoelektrische Kraft einiger Schwermetallverbingungen', *Ann.d.Phys*., *22*, (1909), pp 749-766.

___________., 'Zur Elektronentheorie der Thermoelektrizität', *Phys. Zeits*., *11*, (1910), pp 809-811.

___________., *Die Elektrischen Erschiegungen in Metallischen Leitern*, (Braunschweig, 1911).

___________., 'Künstliche metallische Leiter', *Phys. Zeits*., *13*, (1912), pp 1080-1082.

BAGARD, M.H., 'Phénomène de Hall dans les Liquides', *J.de Phys*., (3rd Series), *5*, (1896), pp 449-505.

BARDEEN, J., and BRATTAIN, W.H., 'The Transistor, a Semi-Conductor Triode', *Phys. Rev.*, (2nd Series), **74**, (1948), pp 230-231.

BARNARD, G.P., *The Selenium Cell, its Properties and Applications*, (London, 1930).

BAUERMAN, H., 'An Experiment for Showing the Electric Conductivity of various forms of Carbon', *Phil. Mag.*, (4th Series), **50**, (1875), pp 24-27.

BECKMAN, B., 'Influence of Pressure on the Electric Conductivity of Metallic Alloys', *Sci.Abs.*, (Phys.), **16**, (1913), p 78. (*Ark.f.Mat.Astron.o.Fysik.*, (*Stockholm*), **7**, (1912), pp 1-18).

BECQUEREL, E., 'Sur les effets électriques qui se produisent sous l'influence solaire', *Comp.Rend.*, **9**, (1839), pp 711-714.

————., 'Inversion du Phénomène de Hall dans le Bismuth. Superposition de deux Effets Galvano-magnetiques de Sens opposés'. *Comp.Rend.*, **154**, (1912), pp 1795-1798.

BELL, A.G., 'Researches in Electric Telephony', *J.of Soc. Tel.Eng.*, **6**, (1877), pp 385-421.

————., 'Selenium and the Photophone', *Nature*, **22**, (1880), pp 500-503.

————., 'The Production of Sound by Radiant Energy',(Abs.), *Nature*, **24**, (1881), pp 42-44.

BELL, A.G., and TAINTER, S., 'Selenium Cell', *U.S.Pat.* No. 235,497, 25/9/1880.

————————., 'Photophone Transmitter', *U.S. Pat.* No. 235,496, 25/9/1880.

BERLINER, E., 'Photophonic Transmitter', *U.S. Pat.*, No. 235,120, 3/9/1880.

BERKSON, W., *Fields of Force: The Development of a World View from Faraday to Einstein*. (London, 1974).

BERNDT, G., 'Einige Beobachtungen an Selenzellen', *Phys. Zeits.*, **5**, (1904), pp 121-124.

BEUTNER, R., 'Über Neue Galvanische Elemente', *Zeits.f.Elektrochem.*, **12**, (1909), pp 433-439.

BIDWELL, C.C., 'Resistance and Thermoelectric Relations in Iron Oxide', *Phys. Rev.*, (2nd Series), **8**, (1916), pp 12-19.

BIDWELL, S., 'The Photophone', *Nature*, **23**, (1881),pp 58-59.

————., 'The Effect of Temperature on the Electrical Resistance of Selenium', *Phil. Mag.*, (5th Series), **11**, (1881), p 302.

BIDWELL, S., 'Selenium and its Applications to the Photophone and Telephotography', (Discourse, Royal Institution; Friday March 11, 1881), in *Roy. Inst. Lib. Sci.*, (Phys.Sci.), *3*, (London, 1970), pp 138-149.

__________., 'The Effect of Temperature on the Electrical Resistance of Mixtures of Sulphur and Carbon', *Phil. Mag.*, (5th Series), *13*, (1882), pp 347-353.

__________., 'On the Electrical Resistance of Carbon Contacts', *Proc. Roy. Soc.*, *35*, (1883), pp 1 - 18.

__________., 'The Electrical Resistance of Selenium Cells', *Phil. Mag.*, (5th Series), *15*, (1883), pp 31-35.

__________., 'The Reversal of Hall's Phenomenon', *Nature*, *29*, (1884), p 514.

__________., 'On an Explanation of Hall's Phenomenon', *Proc. Roy. Soc.*, *36*, (1884), pp 341-348.

__________., 'On Some Experiments Illustrating an Explanation of Hall's Phenomenon', *Proc. Phys. Soc.*, *6*, (1885), pp 29-47.

__________., 'A Voltaic Cell with a Solid Electrolyte', *Nature*, *32*, (1885), p 345.

__________., 'Solid Electrolytes', *Nature*, 32, (1885), p 391.

__________., 'The Action of Light in Diminishing the Resistance of Selenium', *Chem. News*, *51*, (1885), p 261.

__________., 'On the Generation of a Voltaic Current by a Sulphur Cell with a Solid Electrolyte', *Chem.News*, *52*, (1885), pp 219-220.

__________., 'On the Sensitiveness to Light of Selenium and Sulphur Cells', *Chem. News*, *52*, (1885), pp 191-193.

__________., 'On the Generation of Electric Currents by Sulphur Cells', *Phil. Mag.*, (5th Series), *20*, (1885), pp 328-336.

__________., 'On the Sensitiveness of Selenium to Light and the Generation of a Similar Property in Sulphur', *Proc. Phys. Soc.*, *7*, (1885), pp 129-145.

__________., 'Some Experiments with Selenium Cells', *Phil. Mag.*, (5th Series), *31*, (1891), pp 250-256.

__________., 'The Electrical Properties of Selenium', *Phil. Mag.*, (5th Series), *40*, (1895), pp 233-256.

__________., 'Telegraphic Photography and Electric Vision', *Nature*, *78*, (1908), pp 105-106.

BLEANEY, B., RYDE, J.W., and KINMAN, T.H., 'Crystal Valves', *Jour.I.E.E.*, *93*, (1946), pp 847-854.

BLOCH, E., 'Sur l'emploi des Cellules Photoélectriques commes Photophones', *Comp. Rend.*, *154*, (1912), pp 427-428.

BLOCH., F., 'Über die Quantummechanik der Elektronen in Kristallgittern', *Zeits.f.Phys.*, *52*, (1912), pp 555-600.

BLONDIN, J., 'Electrolytic Rectifiers', *Sci. Abs.*, *1*, (1898), No. 328, p 169. *Ecl.Elec.*,*14*, (1898), p 293-298).

BORELIUS, G., 'Zur Elektronentheorie der Thermoelektrizität', *Ann.d.Phys.*, *57*, (1918), pp 231-243.

——————., 'Zur Elektronentheorie der Metallische Leitung', *Ann.d.Phys.*, *57*, (1918), pp 278-286.

——————., 'Zur Elektronentheorie des Magnetismus und der Halleffektes', *Ann.d.Phys.*, *58*, (1919), pp 489-504.

BORN, M., *Einstein's Theory of Relativity*, (Dover reprint), (New York, 1962).

BOTTOM, V.E., 'Invention of the Solid-State Amplifier', *Physics Today*, *17*, (1964), pp 24-26.

BOTTOMLEY, J.T., 'On Contact Electricity in Common Air, Vacuum and Different Gases', *B.A. Report*, (1885), pp 901-903.

BRADSHAW, S.E., 'Semi-Conductors: (1) Materials', *Research Review*, (*G.E.C. Labs. House Journal*), Winter, (1954).

BRAGG, W.L.,and PORTER, G.,(eds.), *The Royal Institution Library of Science, Physical Sciences*, (10 vols.), (London, 1970).

BRANDES, H., 'Über Abweichungen von Ohmschen Gesetz Gleichrichter - Wirkung and Wellenzeiger der drahtlosen Telegraphie', *Elektrotech. Zeits.*, *27*, (1906), pp 1015-1017.

BRANTHAM, G.E., 'The Time Factor in Selenium Resistance', *Phys. Rev.*, (2nd Series), *4*, (1914), pp 259-266.

BRATTAIN, W.H., 'Historical Development of Concepts basic to the Understanding of Semiconductors', *IEEE Paper*, No. 3072E, (1960).

BRAUN, F., 'Über die Stromleitung durch Schwefelmetalle', *Ann.d.Phys., (Pogg.)*, *153*, (1874), pp 556-563.

——————., 'Über unipolare Elektricitätsleitung', *Ann.d.Phys., (Wied.)*, *4*, (1878), pp 476-484.

BREWER, R., 'When is a Transistor Dead?', Research Review, (G.E.C. Labs. House Journal), Spring, (1960), pp 2-4.

BRODIE, B.C., 'On the Allotropic Changes of Certain Elements', (Discourse, Royal Institution: Friday, May 21, 1852), in Roy. Inst. Lib. Sci., (Phys.Sci.), 1, (London, 1970), pp 55-58.

BROWN, F.C., 'Effect of Pressure on the Electrical Resistance of Selenium Cells', Phys.Rev.,20, (1905), pp 185-186.

__________., 'Selenzellen von hoher Empfindlichkeit', Phys. Zeits., 11, (1910), pp 481-483.

__________., 'The Electrical Properties of Light-positive and Light-negative Selenium', Phys. Rev., 32, (1911), pp 237-239.

__________., 'The Nature of Light Action in Selenium', Phys. Rev., 33, (1911), pp 1-26.

__________., 'The Recovery of the Giltay Selenium Cell and the Nature of Light Action in Selenium', Phys. Rev., 33, (1911), pp 403-420.

__________., 'The Action of Mercury Vapour on Selenium', Phys. Rev., (2nd Series), 2, (1913), pp 153-160.

__________., 'Effect of Abrasion on the Conductivity of Selenium', Sci. Abs., (Phys.), (Phys. Zeits., 13, (1912), pp 859-864).

__________., 'The Effective Depth of Penetration of Selenium by Light', Phys. Rev., 34, (1912), pp 201-214.

__________., 'The Properties of Selenium', Phys. Rev., (2nd Series), 4, (1914), pp 48-61.

__________., 'The Crystal Form of Metallic Selenium and some of their Physical Properties', Phys. Rev., (2nd Series), 4, (1914), pp 85-98.

__________., 'The Application of the Electron Theory to the Explanation of the Eletrical Conduction in Crystals of Metallic Selenium', Phys. Rev., (2nd Series), 5, (1915), pp 75-76.

__________., 'Production of Isolated Crystals of Selenium', Phys. Rev., (2nd Series), 5, (1915), pp 236-237.

__________., 'The Electrical, the Photoelectrical and the Electro-mechanical Properties of Certain Crystals of Metallic Selenium, with Certain Applications to Crystal Structure,' Phys. Rev., (2nd Series), 5, (1915), pp 167-175.

__________., 'Isolated Crystals of Selenium of the 2nd and 5th Systems, and the Physical Conditions determining their Production', Phys. Rev., (2nd Series), 5, (1915), pp 236-237.

BROWN, F.C., 'The Nature of Electric Conduction as Required to Explain the Recovery of Resistance of Metallic Selenium following Illumination', Phys. Rev., (2nd Series), 5, (1915), pp 395-403.

__________., 'Some Experiments on the Nature of Transmitted Light Action in Crystals of Metallic Selenium,' Phys. Rev., (2nd Series), 5, (1915), pp 404-411.

BROWN, F.C., and SIEG, L.P., 'Sensibility Curve for Selenium - A new Sensibility-wavelength-maximum and a New Principle', Phys. Rev., (2nd Series), 2, (1913), pp 487-494.

__________., 'The Seat of Light Action in Certain Crystals of Metallic Selenium and some New Properties in Matter', Phil. Mag., (6th Series), 28, (1914), pp 497-508.

__________., 'Wavelength Sensibility Curves for Light Sensitive Selenium and their Significance', Phys. Rev., (2nd Series), 4, (1914), pp 48-61.

BROWN, F.C., and STEBBINS, J., 'The Variation of the Light Sensitivity of the Selenium Cell with Pressure', Phys. Rev., 25, (1907), pp 501-502.

__________., 'The Effect of Radium on the Resistance of the Selenium Cell', Phys. Rev., 25, (1907), pp 505-506.

__________., 'Some Studies on the Change of Eletrical Resistance of Selenium Cells', Phys. Rev., 26, (1908), pp 273-298.

BROWN, J., 'Theory of Voltaic Action', Phil. Mag., (5th Series), 11, (1881), pp 212-213.

BUCKLEY, O.E., 'The Hall Effect and Allied Phenomena in Silicon', Phys. Rev., (2nd Series), 4, (1914), pp 482-490.

BURNIE, W.B., and LEE, C.A., 'The Conductivity Analogy Between the Electric Arc and Certain Metal Oxides', Electrician, 43, (1899), pp 75-79.

C——, W.M., 'Selenium', Nature, 23, (1881), p 218.

CARPINI, C., 'Über den Photoelektrischen Effekt an Selen', Phys. Zeits., 7, (1906), pp 306-308.

CASE, T.W., 'Notes on the Change of Resistance of Certain Substances in Light', Phys. Rev., (2nd Series), 9., (1917), pp 305-310.

__________., ' "Thalofide Cell". A New Photo-electric Substance', Phys. Rev., (2nd Series), 15, (1920), pp 289-292.

__________., 'Infra-red Telegraphy and Telephony', J.Op.Soc.Amer., 6, (1922), pp 398-406.

CASWELL, A.E., 'An Extension of the Electron Theory of Metals. I. Thermoelectricity and Metallic Conduction', *Phys. Rev.*, (2nd Series), *13*, (1919), pp 386-403.

————————., 'An Extension of the Electron Theory of Metals. II. Thermoelectric and Conductivity Constants', *Phys. Rev.*, (2nd Series), *15*, (1920), pp 1-11.

CHAPMAN, A.K., 'Hall and Corbino Effects', *Phil. Mag.*, (6th Series), *32*, (1916), pp 303-326.

CHIARINI, V., 'The Electrical Properties of Selenium', *Sci. Abs.*, (Phys.), *12*, (1909), No. 884, p 305, (*Accad.Lincei.Ati.*, *18*, (1909), pp 246-253).

COBLENTZ, W.W., 'Positive and Negative Photoelectrical Properties of Molybdenite and Several Other Substances', *Sci.Pap.Bur.Stan.*, *16*, (1920), pp 595-639.

COLLET, P., 'Sur la Conductibilité électrique du Tellure', *Comp. Rend.*, *156*, (1913), pp 943-945.

——————., 'Variations de Résistance des Cristaux et Forces Electromotrices Résiduelles', *Comp. Rend.*, *158*, (1914), pp 1994-1997.

——————., 'Sur deux Modes de Rectification des Courants par les Galènes', *Comp. Rend.*, *170*, (1920), pp 1489-1491.

COLSON, A., 'Sur la Conditions nécessaires aux Reactions Directes et le Sens du Courant Electrique produit dans l'Attaqué des Métaux par la Soufre', *Comp.Rend.*, *148*, (1909), pp 1183-1186.

COOK, S.R., 'On the Theory of the Electrolytic Rectifier', *Phys. Rev.*, *20*, (1905), pp 312-321.

COOPER, W.R., 'Selenium Cells', *Electrician*, *76*, (1916), pp 676-738.

CORBINO, O.M., 'Das Experimentalle Studium das Halphänomens und die Elektronentheorie der Metalle', *Phys. Zeits.*, *12*, (1911), pp 914-920.

————————., 'Magnetic Variations of Resistance and Diminution of the Hall Effect', *Sci. Abs.*, (Phys.), *22*, (1919), No. 1557, p 573. (*N.Cim.*, *16*, (1918), pp 185-196).

COSTE, M., 'Sur la Conductibilité Electrique du Sélénium', *Comp. Rend.*, *141*, (1905), pp 715-717.

COSTIGAN, D.M., 'The Quest for the Crystal that Amplifies', *Popular Electronics*, (June, 1968), pp 40-44.

COURSEY, P.R., 'Selenium and Some of Its Uses', *Wireless World*, *8*, (1920), pp 145-149.

CROWTHER, J.G., The Cavendish Laboratory 1874-1974, (London, 1974).

CRUM, L.B., 'Certain Characteristics of Light Negative Selenium', Phys. Rev., 33, (1911), pp 538-548.

DEBYE, P., 'Theory of Electrons im Metals', Sci. Abs., (Phys.), 13, (1910), No. 1638, p 554. (Ann.d.Phys. 33, (1910), pp 441-489).

DEL REGNO, W., 'Nature of the Photoelectric Phenomena shown by Selenium', Sci. Abs., (Phys.), 18, (1915), No. 335, p 140. (N.Cim.,8, (1914), pp 295-329).

DIETERICH, E.O., 'The Influence of Annealing on the Characteristics of Light Sensitive Selenium', Phys. Rev., (2nd Series), 4, (1914), pp 467-476.

————————., 'The Effect of Temperature on the Light Sensibility Curves of Different Types of Selenium Cell', Phys. Rev., (2nd Series), 8, (1916), pp 191-194.

DIETERICH, K.J., 'The Effect of Temperature on the Resistance, the Light Sensitiveness and the Rate of Recovery of Certain Crystals of Metallic Selenium', Phys. Rev., (2nd Series), 7, (1916), pp 551-560.

DOELTER, C., 'Conduction of Electricity in Crystals at High Temperatures', Sci. Abs., (Phys.), 14, (1911), No. 387, p 140. (Zeits.f.anorg.Chem., 67, (1910), pp 387-397.

DOUGLAS, R.W., 'Semiconductors and their Applications', G.E.C. Journal, 17, (1950), p 107.

DOWSETT, H.M., 'Improvements in Crystal Detectors of Electric Currents', Br.Pat., No. 163448, (1921).

DRAPER, H.N., 'Effect of Light on the Electrical Conductivity of Selenium', Nature, 7, (1873), p 340.

DRAPER, H.N. and MOSS, R.J., 'On Some Forms of Selenium and on the Influence of Light on the Eletrical Conductivity of this Element', Proc. Roy. Irish Acad., 1, (1873-74), pp 529-533.

DRUDE, P., Physik des Aethers auf Elektromagnetischer Grundlage, (Stuttgart, 1894).

—————., 'Electron Theory of Metals', Sci. Abs., (Phys.), 3, (1900), p 473. (Ann.d.Phys., 1, (1900), pp 566-613).

—————., 'Electron Theory of Metals', Sci. Abs., (Phys.), 4, (1901), No. 840, pp 384-385. (Ann.d.Phys., 3, (1900), pp 369-402).

—————., 'Ionic Theory of Metals', Sci. Abs., (Phys.), 3, No. 1833, pp 702-705. (Phys. Zeits., 1, (1900), pp 161-165).

DUSSAUD, P., 'Nouvelles Expériences sur la Résistance Electrique du Sélénium et ses Applications à la Transmission des Images et des Impressions Lumineuses', *Comp. Rend.*, *135*, (1902), pp 790-791.

EINSTEIN, A., 'On a Heuristic Point of View about the Creation and Conversion of Light', (1905), in *The Old Quantum Theory*, Haar, D. ter (ed.), (London, 1967), pp 91-107.

ELLIOT, D.S., 'A Comparative Study of the Light Sensibility of Selenium and Stibnite at 20°C and -190°C', *Phys. Rev.*, (2nd Series), *5*, (1915), pp 53-64.

ERSKINE-MURRAY, J., 'On Contact Electricity of Metals', *Proc. Roy. Soc.*, *63*, (1898), pp 113-146.

FARADAY, M., *Experimental Researches in Electricity*, (Dover ed.), (New York, 1965).

__________., 'On Electric Conduction' (Discourse, Royal Institution; Friday May 25, 1855), in *Roy. Inst. Lib. Sci.*, (Phys. Sci.), *1*, (London, 1870), pp 164-172.

FERRIE, G., 'Le Détecteur Electrolytique à Pointe Métallique *Ecl.Elec.*, *44*, (1905), p 400.

FITZGERALD, F.A.J., 'Laboratory Notes on Some Electrical Properties of Silver Sulphide', *Trans.Amer.Electrochem. Soc.*, *25*, (1914), pp 393-413.

FLOWERS, A.E., 'Crystal and Solid Contact Rectifiers', *Phys. Rev.*, *29*, (1909), pp 445-460.

____________., 'Characteristics of Crystal Rectification', *Phys. Rev.*, (2nd Series), *3*, (1914), pp 25-46.

FOURNIER d'ALBE, E.E., 'Contemporary Electrical Science', *The Electrician*, *39-57*, (1897-1906).

__________________., *The Electron Theory*, (London, 1906).

__________________., 'On the Variation of the Resistance of Selenium with the Voltage', *Proc.Roy.Soc.*, (A), *86*, (1912), pp 452-461.

__________________., 'On the Efficiency of Selenium as a Detector of Light', *Proc. Roy. Soc.*, (A), *89*, (1913), pp 75-90.

__________________., *The Moon Element - An Introduction to the Wonders of Selenium*, (London, 1924).

FOWLER, R.H., 'Notes on Some Electronic Properties of Conductors and Insulators', *Proc. Roy. Soc.*, (A), *140*, (1933), pp 56-71.

____________., 'An Elementary Theory of Electronic Semi-Conductors, and Some of their Possible Properties', *Proc. Roy. Soc.*, (A), *140*, (1933), pp 505-522.

FRITTS, C.E., 'On a New Form of Selenium Cell, and Some Electrical Discoveries made by its Use', *Amer.J.Sci.*, *26*, (1883), pp 465-472.

FRITTS, C.E., 'On the Fritts Selenium Cell and Batteries', *Elec. Rev.*, *16*, (1885), pp 208-211.

FURTH, R., 'Nature of Electricity', *Sci. Abs.*, (Phys.), *23*, (1920), No. 245, p 90. (*Deutsch.Phys.Gesell.*, *21*, (1920), pp 517-528).

GEHLHOFF, G., and NEUMEIER, R., 'Thermal and Electrical Peculiarities of Bismuth and Antimony', *Sci. Abs.*, (Phys.), *17*, (1914), No. 536, p 184. (*Deutsch.Phys. Gesell.*, *15*, (1913), pp 876-896).

GILTAY, J.W., 'Selenium Resistance Cells', *Sci. Abs.*, (Phys.), *7*, (1904), No. 1186, p 361. (*Phys. Zeits.*, *4*, (1903), pp 287-289).

GLATZEL, B., 'Inertia and Sensitivity of Cells Sensitive to Light', *Sci. Abs.*, (Phys.), *15*, (1912), No. 1574, p 487. (*Deutsch.Phys.Gesell.*, *14*, (1912), pp 607-623).

GODDARD, R.H., 'On the Conduction of Electricity at Contacts of Dissimilar Solids', *Phys. Rev.*, *34*, (1912), pp 423-451.

GORDON, J.E.H., 'Anomalous Behaviour of Selenium', *Nature*, *12*, (1875), p 187.

GRANTHAM, G.E., 'The Time Factor in Selenium Resistance', *Phys.Rev.*, (2nd Series), *4*, (1914), pp 259-266.

GREINACHER, H., 'Light and Electricity in Selenium', *Sci.Abs.*, (Phys.), *20*, (1917), No. 539, p 242. (*Deutsch.Phys. Gesell.*, *18*, (1916), pp 117-134.

——————., 'Polarisation of Selenium Cells', *Sci. Abs.*, (Phys.), *22*, (1919), No. 938, p 340. (*Deutsch.Phys. Gesell.*, *19*, (1917), pp 51-71.

GRETNACHER, H., and MILLER, C.W., 'Rectifying Action in Selenium', *Sci. Abs.*, (Phys.), *22*, (1919), No. 1325, p 487. (*Deutsch.Phys.Gesell.*, *18*, (1916), pp 288-296).

GRIFFITHS, A.B., 'Changement de Résistance Electrique du Sélénium sous l'influence de Certaines Substances', *Comp.Rend.*, *137*, (1903), p 647.

GRIPENBERG, W.S., 'Selenium Vapour in the Preparation of Light Sensitive Cells', *Sci. Abs.*, (Phys.), *11*, (1908), No. 1472, p 522. (*Phys. Zeit.*, *9*, (1908), p 519).

——————., 'Selenium Cells with Fuller Use of the Light', *Sci. Abs.*, (Phys.), *13*, (1910), No. 622, p 202. (*Phys.Zeit.*, *11*, (1910), pp 132-133).

——————., 'Crystallisation of Selenium Plates', *Sci. Abs.*, (Phys.), *15*, (1912), No. 920, p 286. (*Phys. Zeit.*, *13*, (1912), p 161),

——————., 'Über die Tiefe der Lichtwirkung beim Selen', *Phys. Zeit.*, *15*, (1914), p 462.

——————., 'Compensated Selenium Cell', *Tech.Rev.*, *6*, (1920), p 786.

GRONDAHL, L.O., 'A New Type of Contact Rectifier', *Phys. Rev.*, (2nd Series), *27*, (1926), p 813.

GROVE, W.R., 'Inferences from the Negation of Perpetual Motion', (Discourse, Royal Institution, Friday, January 25, 1856), in *Roy. Inst. Lib. Sci.*, (Phys.Sci.), *1*, (London, 1970), pp 180-187.

GRUNEISEN, E., 'Leitfähigkeit der Halbleiter oder Variablen Leiter', *Handbuch der Physik*., (1928), pp 61-63.

GUDDEN, B., 'Elektrizitätsleitung in Kristallisierten Stoffen unter Ausschuss der Metalle', *Erg.d.Exat.Nat.*, *3*, (1924), pp 116-159.

__________., 'Über die Elektrizitätsleitung in Halbleitern', *Sitz.d.Phys.Med.Soz.,(Erlangen)*, *62*, (1930), pp 289-302.

__________., 'Elektrische Leitfähigkeit Elektronischer Halbleiter', *Erg.d.Exat.Nat.*, *13*, (1934), p 233-256.

GUDDEN, B., and POHL, R., 'Über Lichtelektrische Leitfähigkeit von Diamenten', *Zeits.f.Phys.*, *3*, (1920), pp 123-129.

______________________., 'Uber Lichtelektrische Leitfähigkeit von Zinkblende', *Zeits.f.Phys.*, *5*, (1921), pp 176-181.

______________________., 'Lichtelektrische Leitfähigkeit in Weiterem Zusammenhang', *Phys. Zeit.*, *23*, (1922), pp 417-420.

______________________., 'Über Lichtelektrische Leitung im Selen', *Zeits.f.Phys.*, *35*, (1925), pp 243-259.

GUILLEMINOT, H., 'Les Rayons N. Ne Paraissent pas Influencer la Résistivité du Sélénium', *Archives d'Electricite Medicale*, *13*, (1905), pp 243-244.

______________., 'Sur la Variation de Résistance du Sélénium Irradié par les Rayons X et les Rayons du Radium', *Comp.Rend.*, *156*, (1913), pp 1155-1157.

GUINCHANT, J., 'Resistivity of Metallic Sulphides', *Sci.Abs.*, *5*, (1902), No. 2085, pp 849-850. (*Comp.Rend.*, *134*, (1902), pp 1224-1226).

GUTHRIE, F., 'On a Relation between Heat and Electricity', *Phil. Mag.*, (4th Series), *46*, (1873), pp 257-266.

HAAR, D. ter, *The Old Quantum Theory*, (London, 1967).

HALL, E.H., 'On a New Action of the Magnet on Electric Currents', *Amer.J.Math.*, *2*, (1878), pp 287-292, and *Phil.Mag.*, (5th Series), *9*, (1880), pp 225-230. Reprinted in Magie,W., (ed.), *Source Book in Physics*, (Harvard, 1965).

__________., 'On Electric Conduction and Thermoelectric Action in Metals'., *Proc.Amer.Acad.*, *50*, (1914), pp 67-103.

__________., 'A Possible Function of the Ions in the Electric Conductivity of Metals', *Proc.Nat.Acad.Sci.*, *3*, (1917), pp 163-171.

HALL, E.H., 'The Number of Free Electrons within a Metal', *Proc.Nat.Acad.Sci.*, *11*, (1925), pp 36-38.

HARTSOUGH, R.C., 'Characteristics of Contact Rectification with a Silicon-Carbon Contact', *Phys.Rev.*, (2nd Series), *4*, (1917), pp 306-314.

HAUSMANN, E., 'The Properties of Selenium and their Applications in Electrotechnics', *Sci.Amer.Supp.*, No. 1881, (1912), pp 44-45.

HEAPS, C.W., 'The Hall Effect in Galena and Molybdenite', *Phil.Mag.*, (7th Series), *6*, (1928), pp 1283-1286.

HEIL, A., 'Beobachtungen über Thermoelektrische Ströme und Mitteilungen über Neues Thermoelement', *Zeits.f.Elektrochem.*, *9*, (1903), pp 91-97.

HEIL, O., 'Improvements in or Relating to Electrical Amplifiers and Other Control Arrangements', *U.K. Patent*, No. 439,457, (1935).

HEILBRON, J., *A History of the Problems of Atomic Structure from the Discovery of the Electron to the Beginning of Quantum Mechanics*, (Ph.D. Thesis, University of California, 1964).

HELMHOLTZ, H., 'On the Modern Development of Faraday's Conception of Electricity', *J.Chem.Soc.*, *39*, (1881), pp 277-304.

HENISCH, H.K., *Metal Rectifiers*, (Oxford, 1949).

___________., *Rectifying Semiconductor Contacts*, (Oxford, 1955).

HEROLD, E.W., 'Semi-Conductors and the Transistor', *Journal of the Franklin Institute*, *259*, (1955), pp 87-106.

HESEHUS, N., 'Influence of Illumination on Conductivity of Selenium', *Sci. Abs.*, (Phys.), *7*, (1904), No. 613, p 177. (*J.Russk.Fisik.Chim.Obs.*, *35*, (1903), pp 661-664).

HILSEH, R., and POHL, R.W., 'Steuerung von Elektronenstiömen mit einen Dreielektroden Kristall und ein Modell einer Sperrschicht', *Zeits.f.Phys.*, *111*, (1938), pp 399-408.

HIROSIGE, T., 'Origins of Lorentz's Theory of Electrons and the Concept of the Electromagnetic Field', *Hist.Stud.Phys.Sci.*, *1*, (1969), pp 151-209.

HOPIUS, E.A., 'Conductivity of Selenium and the Intensity of the Incident Light', *Sci. Abs.*, (Phys.), *7*, (1904), p 102, (*J.Russk.Fisik.Chim.Obs.*, *35*, (1903), pp 581-585.

HORNBECK, J.W., 'Thermal and Electrical Conductivities of the Alkali Metals', *Phys. Rev.*, (2nd Series), *2*, (1913), pp 217-240.

HOUSTOUN, R.A., 'Electrons and the Absorption of Light', *Nature*, *80*, (1909), pp 338-339.

HUGHES, A.L., and DUBRIDGE, L.A., Photoelectric Phenomena, (New York, 1932).

HUME-ROTHERY, W., The Metallic State: Electrical Properties and Theories, (Oxford, 1931).

HURD, D.L., and KIPLING, J.J., The Origins and Growth of Physical Science, (Pelican ed. 2v.), (London, 1964).

JAMMER, M., The Conceptual Development of Quantum Mechanics, (New York, 1966).

JENISCH, P., 'Neue Selenzellen', Zeits.f.Elektrochem., 19, (1912), pp 61-63.

JENSEN, J.C., 'Some Laboratory Uses for the Contact Rectifier', Phys. Rev., (2nd Series), 15, (1920), pp 224-225.

JOLLEY, A.C., 'Some Observations on A.C. Rectifiers', The Electrician, 57, (1906), pp 998-1000.

JONES, D.D., 'Semi-Conductors, (2) Devices and Applications', Research Review, (G.E.C. House Journal), (Spring, 1955), pp 2-5.

KAEMPF, F., 'Saturation Currents in Selenium', Sci.Abs., (Phys.), 15, (1912), No. 1430, p 440. (Phys. Zeits., 13, (1912), pp 689-694).

KAHL, R., (ed.), Selected Writings of Hermann von Helmholtz, (Middletown, Conn., 1971).

KAMERLINGH ONNES, K., and BECKMAN, B., 'Hall Effect and Change in Resistance in a Magnetic Field at Low Temperatures', Sci. Abs., (Phys.), 16, (1913), No.1351, p 440. (Proc. Konink.Akad.Wetensch.Amsterdam, 15, (1913), pp 981-987.

————————————————., 'Hall Effect in Tellurium and Bismuth at Low Temperatures', Sci. Abs., (Phys.), 16, (1913), No. 1353, p 441. (Proc. Konink.Acad.Wetensch. Amersterdam, 15, (1913), pp 997-1003).

KAWAKAMI, M. and TAKAHASHI, K., 'The Evolution of Semi-Conductor Electronics', Elec.Indus., 24, (1965), pp 72-73.

KELVIN, Lord, 'Contact Electricity of Metals', Phil.Mag., (5th Series), 46, (1898), pp 82-120.

KINSKY, J., 'Die Elektrizitätsleitungen in Metallen und Amalgamen', Zeits.f.Elektrochem., 9, (1908), pp 406-410.

KNOTHE, A., 'Method of Rendering Selenium Conducting', Elektrotech.Runds., 21, (1903), pp 23-24.

KNOX., G.I., 'On the Direction and Mode of Propagation of the Electric Force Traversing Interposed Media, I.', Proc.Roy.Irish Acad., 19, (1839), pp 147-153.

KNOX, G.I., 'On the Direction and Mode of Propagation of the Electric Force Traversing Interposed Media, II', Proc. Roy. Irish Acad., 19, (1840), pp 253-263.

KOENIGSBERGER, J., 'Stand Forschung über die Elektrizitätsleitungem in festen Körpern und ihre Beziehung zur Elektronentheorie', Jahr.d.Radioak.u.Elek., 4, (1908), pp 158-194.

——————————., 'Conduction of Electricity', Sci.Abs., (Phys.), 12, (1909), No. 891, pp 307-308. (Zeits.f. Elektrochem., 15, (1909), pp 97-105).

——————————., 'Das Elektrische Verhaltender Variablen Leiter und deren Beziehungen zur Elektronentheorie', Jahr.d.Radioak.u.Elek., 11, (1914), pp 84-142.

KOENIGSBERGER, J., and GÖTTSTEIN, G., 'Uber den Halleffekt', Phys. Zeits., 14, (1913), pp 232-237.

KOENIGSBERGER, J., and KILCHING, K., 'Uber das Verhalten Gebundener und "Freier" Elektronen gegen Elektromagnetische Strahlung', Ann.d.Phys., 28, (1909), pp 889-894.

KOENIGSBERGER, J., and SCHILLING, K., 'Uber Elektrizitätsleitung in festen Elementen und Verbindungen, I. Minima des Widerstandes Prüfung auf Elektronenleitung, An wendung der Dissoziationsformeln', Ann.d.Phys., 32, (1910), pp 179-230.

KOHLER, F., 'Selenium Photometry', Sci. Abs., (Phys.), 22, (1919), No. 885, p 323. (Zeits.f.Elektrotech., 40, (1919), pp 104-106).

KORN, A., 'Sur un Appareil a Compenser l'inertie de Sélénium', Comp.Rend., 143, (1906), pp 892-895.

————., 'On an Apparatus for Compensating the Inertia of Selenium', The Electrician, 58, (1907), p 577.

KRUYT, H.R., 'Die Dynamische Allotropie des Selens', Zeits.f.anorg.Chem., 64, (1909), pp 305-326.

KUNZ, J., 'On the Corpuscular Theory of Thermoelectric Forces', Phil. Mag., (6th Series), 16, (1908), pp 767-789.

LANG, V. von, 'Über die Elektromotorisch Gegen Kraft des Aluminiumlichtbogens', Ann.d.Phys.Chem., 63, (1897), pp 191-194.

LARK-HOROVITZ, K., 'The New Electronics' in The Present State of Physics, (A.A.A.S., 1954).

LEIMBACH, G., 'Unipolares Leitvermögen von Kontakdetetoren und ihre Gleichrichterwirkung', Phys. Zeits., 12, (1911), pp 228-231.

Le ROY, F., 'Sur la Résistance Electrique du Silicium Cristallisé', Comp. Rend., 126, (1898), pp 244-246.

LILIENFELD, J.E., 'Method and Apparatus for Controlling Electric Currents', *U.S. Pat.*, No. 1745,175. (1926).

LINDEMANN, F.A., 'Note on the Theory of the Metallic State', *Phil. Mag.*, (6th Series), 29, (1915), pp 127-140.

LINDNER, O., and REPLOGLE, J.B., 'Selenium Cell', *Electrical World*, 59, (1912), p 251.

LIVENS, G.H., 'On the Electron Theory of Metallic Conduction', *Phil. Mag.*, (6th Series), 29, (1915), pp 105-124, 173-183, 425-432 and *Phil. Mag.*, (6th Series), 30, (1915), pp 287-295, 549-559.

———., 'On the Electron Theory of the Hall Effect and Allied Phenomena', *Phil. Mag.*, (6th Series), 30, (1915), pp 526-548.

LODGE, O., 'The Relation between Electricity and Light', *Nature*, 23, (1881), pp 304-306.

———., 'On the Seat of the Electromotive Forces in a Voltaic Cell', *Journ.I.E.E.*, 14, (1885), pp 186-296.

———., 'On Electrolysis', *B.A. Report*, (1885), pp 723-772.

———., *Modern Views of Electricity*, 1st ed., (London, 1889), 2nd ed., (London, 1892), serialised in *Nature*, 36-39, (1887-1889).

———., 'On the Controversy surrounding Volta's Contact Force', *Phil. Mag.*, (5th Series), 49, (1900), pp 351-383, 454-475.

———., *Electrons*, (London, 1906).

LORENTZ, H.A., *The Theory of Electrons and its Application to the Phenomenon of Light and Radiant Heat*, (Leipzig, 1909), (Dover reprint, New York, 1952).

LUTERBACHER, J., 'Der Einfluss der Elektromotorischen Kraft auf der Elektrischen Widerstand des Selens', *Ann.d.Phys.*, 33, (1910), pp 1392-1412.

McDOWELL, L.S., 'Some Electrical Properties of Selenium,I', *Phys. Rev.*, 29, (1909), pp 1-36.

———., 'Some Electrical Properties of Selenium,II. The Recovery from Excitation by X-Rays', *Phys. Rev.*, 30, (1910), pp 474-481.

———., 'Some Electrical Properties of Selenium III. The Influence of Temperature upon the Recovery', *Phys. Rev.*, 31, (1910), pp 524-535.

———., 'Permanent Contact Crystal Detectors', *Phys. Rev.*, (2nd Series), 13, (1919), pp 288-289.

McKAY, T.C., 'The Hall Effect: a Bibliography', *Proc. Amer.Acad.*, 41, (1906), pp 385-395.

McMAHON, A.M., 'The Action of Roentgen and $\gamma$- radiations upon the Electrical Conductivity of Selenium', *Phys. Rev.*, (2nd Series), 16, (1920), pp 558-564.

M'WHAN, J., 'On the Electron Theory of Thermo-Electricity', *Proc. Roy. Soc. Edin.*, 23, (1912-1913), pp 169-176.

MAGIE, W.F. (ed.), *A Source Book in Physics*, (Cambridge, Mass., 1965).

MARC, R., 'Über das Verhalten des Selens gegen Licht und Temperatur', *Zeits.f.anorg.Chem.*, 37, (1903), pp 459-474.

————., 'Über das Verhalten des Selens gegen Licht und Temperatur', *Zeits.f.anorg.Chem.*, 48, (1906), pp 393-426.

————., 'Über das Verhalten des Selens gegen Licht und Temperatur', *Zeits.f.anorg.Chem.*, 50, (1906), pp 446-464.

MARCH, A., 'Zur Elektronentheorie der Metalle', *Ann.d.Phys.*, 49, (1916), pp 710-724.

MARTIN, M.J., 'Selenium', *Wireless World*, pp 681-685.

MARX, E., 'Hall Effect in Gases', *Sci. Abs.*, (Phys.), 3, (1900), No. 2211, pp 870-871. (*Ann.d.Phys.*, 2, (1900), pp 798-834).

MATTHIESSEN, A., 'On the Electric Conducting Power of the Metals', *Proc. Roy. Soc.*, 9, (1857-1859), pp 95-100.

————., 'On the Thermo-Electric Series', *Phil.Trans.*, 148, (1858), pp 369-381.

————., 'On the Electric Conducting Power of the Metals', *Phil. Trans.*, 148, (1858), pp 383-387.

MAXWELL, J.C., 'A Dynamical Theory of the Electromagnetic Field', *Phil. Trans.*, 155, (1865), pp 459-512.

————., *Treatise on Electricity and Magnetism*, (London, 1873).

MERRITT, E., 'The Recovery of Selenium Cells after Exposure to Light', *Phys. Rev.*, 25, (1907), pp 502-505.

————., 'The Silicon Detector used with Short Electric Waves and the Theory of Rectification', *Phys. Rev.*, 32, (1911), p 630.

————., 'On Contact Rectification by Metallic Germanium', *Proc. Nat. Acad.Sci.*, 11, (1925), pp 743-748.

MINCHIN, G.H., 'The Seleno-Aluminium Cell', *Proc. Roy. Soc.*, (A), 81, (1908), pp 9-21.

MONTEN, F., 'Influence of Pressure on the Electrical Resistance of Selenium', *Sci. Abs.*, (Phys.), 12, (1909), no. 281, pp 99-100. (*Ark.f.Mat.Astron.o.Fysik, (Stockholm)*, 4, (1908), pp 1-6.)

MORETTO, P., 'Hall Effect', *Sci. Abs.*, (Phys.), *3*, (1900), pp 800-801, (*N.Cim.*, *11*, (1900), pp 278-290).

MORRIS-AIREY, H., and SPENCER, E.D., 'On the Temperature Coefficient of Electrical Resistance of Carbon at Low Temperatures', *Mem.Man.Lit.and Phil.Soc.*, *49*, (1905), pp 1-8.

MORSE, P.M., 'The Quantum Mechanics of Electrons in Crystals', *Phys. Rev.*, (2nd Series), *35*, (1930), pp 1310-1324.

MORTON, J., 'From Research to Technology', *International Science and Technology*, No. 29, (May, 1964), pp 82-92.

MOSER, J., 'The Microphonic Action of Selenium Cells', *Proc. Phys. Soc.*, *4*, (1880-1881), pp 348-360.

MOSS, R.J., 'The Photoelectric Property of Selenium', *Nature*, *77*, (1908), p 198.

MOSS, T.S., *Photoconductivity in the Elements*, (London, 1952).

MOTT, N.F., 'Theory and Experiment since Schrödinger's Equation', *Inst. Phys. Bulletin*, *25*, (1974), pp 448-451.

MOTT, N.F., and GURNEY, R.W., *Electronic Processes in Ionic Crystals*, (Oxford, 1940).

MUNCKapROSENSCHÖLD, P.S., 'Versuche über die Fähigkeit starrer Körper zur Leitung der Elektricität', *Pogg.Ann.*, *34*, (1835), pp 437-463.

NICHOLSON, P.J., 'Physical Properties of Selenium', *Phys. Rev.*, (2nd Series), *3*, (1914), pp 1-24.

NUTTING, P.G., 'Some New Rectifying Effects in Conducting Gases', *Phys. Rev.*, *19*, (1904), pp 1-7.

NYE, M.J., *Molecular Reality. A Perspective on the Scientific Work of Jean Perrin*, (London, 1972).

OBERBECK, A., 'Theory of Galvanic Polarisation', *Sci.Abs.*, *1*, (1898), No. 154, pp 77-78. (*Ann.d.Phys.Chem.*, *63*, (1897), pp 20-25).

OWEN, D., 'Influence of Time Element on Resistance of a Rectifying Contact', *Proc.Phys. Soc.*, *29*, (1916), pp 33-47.

OXLEY, A.E., 'The Hall Effect in Liquid Electrolytes', *Proc. Roy. Soc.*, (A), *88*, (1913), pp 588-604.

PEARSON, G.L., and BRATTAIN, W.H., 'History of Semiconductor Research', *Proc. I.R.E.*, *43*, (1955), pp 1794-1806.

PEIERLS, R., 'Zur Theorie der Elektrischen und Thermischen Leitfähigkeit von Metallen', *Ann.d.Phys.*, *4*, (1930), pp 121-141.

PERREAU, J., 'Influence des Rayons-X sur la Résistance électrique du Sélénium', Comp. Rend., 129, (1899), pp 956-957.

PFUND, A.H., 'A Study of the Selenium Cell', Phil. Mag., (6th Series), 7, (1904), pp 26-39.

——————., 'The Electrical and Optical Properties of Selenium', Phys. Rev., 28, (1909), pp 324-336.

——————., 'Selenium Photometry', Phys. Rev., 34, (1912), pp 370-380.

——————., 'Light Sensibility of Copper Oxide', Science, 42, (1915), pp 805-806.

——————., 'The Light Sensitiveness of Copper Oxide', Phys. Rev., (2nd Series), 7, (1916), pp 289-301.

PIERCE, G.W., 'Crystal Rectifiers for Electric Currents and Electric Oscillations, Part I, Carborundum', Phys. Rev., 25, (1907), pp 31-60.

——————., 'Crystal Rectifiers for Electric Currents and Electric Oscillations, Part II, Carborundum, Molybdenite, Anatase, Brookite, Phys. Rev., 27, (1908), pp 153-187.

——————., 'Crystal Rectifiers for Electric Currents and Electric Oscillations, Part III, Iron Pyrites', Phys. Rev., 29, (1909), pp 478-484.

PIGNATARO, P., 'Behaviour of Selenium Towards Luminous Radiations', Sci. Abs., (Phys.), 17, (1914), No.735, p 251, (N.Cim., 6, (1913), pp 326-334).

PLATNER, G., 'Die Maxwellsche Theorie der Elektrizität und ihre Bedeutung für die Elektrolyse', Elektrochem.Zeits., 9, (1902), pp 55-63, 123-129.

PLEDGE, H.T., Science Since 1500, (2nd ed.), (London,1966).

POCHETTINO, A., 'Resistance of Selenium at Low Temperatures', Sci. Abs. (Phys.), 5, (1905), No. 1888, p 785. (Accad.Lincei.Atti., 11, (1902), pp 286-289.

——————., 'Effect of Selenium Cell on Alternating Currents', Sci. Abs., (Phys.), 13, (1910), No. 273, p 89. (Accad.Lincei.Atti., 18, (1909), pp 445-451).

——————., 'Sensitiveness of Selenium Preparation', Sci. Abs.(Phys.), 14, (1911), No. 926, p 322. N.Cim., 1, (1911), pp 147-210).

——————., 'Action of Selenium', Sci.Abs., 16, (1913), No. 233, p 77. (N.Cim., 4, (1912), pp 189-203).

RANKINE, A.O., 'La Téléphonie pas la Lumière', La Nature, 47, (1919), pp 307-309.

——————., 'On the Transmission of Speech by Light', Proc. Phys. Soc., 31, (1919), pp 242-268.

RANKINE, F.C., 'On the Relation between Illumination and Electrical Conductivity', Phil. Mag., (6th Series), 39, (1920), pp 482-488.

RAYLEIGH, Lord, 'The Photophone', Nature, 23, (1881), p 274.

REINGANUM, M., 'Beitrag zu einer Elektrolytischen Selenzelle', Phys. Zeits., 8, (1907), pp 293-296.

REYVAL, J., 'Les Propriétes Electriques du Sélénium', Ecl.Elec., 17, (1898), pp 311-316.

RICHARDS, J.W., 'Conduction in Fused and Solid Electrolytes', Trans.Amer.Electrochem.Soc., 7, (1905), pp 71-77.

RICHARDSON, O.W., 'The Electron Theory of Contact Electro-motive Force and Thermoelectricity', Phil. Mag., (6th Series), 23, (1912), pp 263-278.

_______________., 'The Electron Theory of Thermoelectricity and Thermionic Effects', Phil.Mag., (6th Series), 24, (1912), pp 737-744.

_______________., 'Metallic Conduction', Phil. Mag., (6th Series), (1915), pp 295-299.

_______________., The Electron Theory of Metals, (Cambridge, 1916).

RIECKE, E., 'Theory of Galvanism and Heat', Sci. Abs., 1, (1898), No. 1238, pp 653-654.

RIES, C., 'Entgegengesetztes Verhalten des Selens', Phys. Zeits., 9, (1908), pp 228-233.

_______., 'Die Ursache der Lichtempfindlichkeit des Selens', Phys. Zeits., 12, (1911), pp 480-490, 522-533.

_______., 'Der Spannungseffekt am Selen und Antimonit', Ann.d.Phys., 36, (1911), pp 1055-1065.

RIGHI, A., 'Sur le Phenomene de Hall', J.de Phys., 12, (1883), pp 512-513.

RONTGEN, W.C., 'Electric Conductivity of Certain Crystals', Sci.Abs., (Phys.), 16, (1913), No. 1492, p 488. (Ann.d.Phys., 41, (1913), pp 449-498).

ROSSE, Earl of, (4th Earl), 'On the Electric Resistance of Selenium', Phil. Mag., (4th Series), 47, (1874), pp 161-164.

ROWLAND, H.A., 'Preliminary Notes on Mr. Hall's Recent Discovery', Proc. Phys. Soc., 4, (1880-1881), pp 10-13.

RUHMER, E., 'Über die Empfindlichkeit und Trägheit von Selenzellen', *Phys. Zeits.*, *3*, (1902), pp 468-474.

__________., 'Neuer Versuche mit Lichtelephonie', *Elektrotech.Zeits.*, *23*, (1902), pp 859-862.

__________., 'Uber des Selen und seine Bedeutung für die Elektrotechnik unter besonderer Berücksichtigung der Lichtelephonie', *Elektrotech.Zeits.*, *25*, (1904), pp 1021-1030.

__________., 'Vielfach - Telephonie mittels der Telegraphons', *Phys. Zeits.*, *7*, (1906), pp 601-602.

RUSSELL, C.A., *The History of Valency*, (Leicester, 1971).

SABINE, R., 'Some Electrical Experiments with Crystalline Selenium', *Phil. Mag.*, (5th Series), *5*, (1878), pp 401-415.

SALE, W., 'The Action of Light on the Electrical Resistance of Selenium', *Proc. Roy. Soc.*, *21*, (1873), pp 283-285.

SAUNDERS, A.P., 'The Allotropic Forms of Selenium', *J.Phys.Chem.*, *4*, (1899-1900), pp 424-513.

SCHROTT, P.V., 'Das Elektrische Verhalten der Allotropen Selenmodifikationen unter dem Einflusse von Wärme und Licht', *Akad.Wiss.Wien.*, *115*, (1906), pp 1081-1170.

SCHULZE, F.A., 'Über des Verhalten des Eisens in Bezug auf das Gesetz von Wiedemann und Franz', *Ann.d.Phys.Chem.*, *63*, (1897), pp 23-38.

SCHUSTER, A., 'On Unilateral Conductivity', *Phil. Mag.*, (4th Series), *48*, (1874), pp 251-278.

__________., 'On Helmholtz's Views on Electrolysis, and on the Electrolysis of Gases', *Chem. News*, *52*, (1885), p 193.

SCOTT, T.R., *Transistors and Other Crystals Valves*, (London, 1955).

SEBOR, J., and SIMEK, L., 'Über Elektrolytische Gleichrichtung von Wechelstrom', *Zeits.f.Elektrochem.*, *13*, (1907), pp 113-115.

SEITZ, F., *Modern Theory of Solids*, (New York, 1940).

SHOCKLEY, W., *Electrons and Holes in Semiconductors*, (New York, 1950).

SIEG, L.P., and BROWN, F.C., 'Wavelength Sensibility Curves of Certain Crystals of Metallic Selenium and a Partial Explanation of the Light Action in Selenium Cells', *Phys. Rev.*, (2nd Series), *4*, (1914), pp 507-516.

______________________., 'An Extension towards the Ultra-voilet of the Wavelength Sensibility Curves for Certain Crystals of Metallic Selenium', *Phys. Rev.*, (2nd Series), *5*, (1915), pp 65-67.

SIEMENS, C.W., 'The Action of Light on Selenium', *Proc. Roy. Inst.*, *8*, (1875-1878), pp 68-79. Also in *Roy. Inst.Lib.Sci.*, (Phys.Sci.), *1*, (London, 1970), pp 466-477.

SIEMENS, W., 'On the Influence of Light upon the Conductivity of Crystalline Selenium', *Phil. Mag.*, (4th Series), *50*, (1875), p 416.

SMITH, A.W., 'The Variation of the Hall Effect in Metals with Change of Temperature', *Phys. Rev.*, *30*, (1910), pp 1-34.

——————., 'The Hall Effect in Bismuth with High Frequency Currents', *Phys. Rev.*, *35*, (1912), pp 81-85.

——————., 'The Hall Effect and Some Allied Effects', *Phys. Rev.*, (2nd Series), *1*, (1913), pp 339-354.

——————., 'On the Hall Effect and Allied Phenomena', Phil. Mag., (6th Series), 31, (1916), pp 367-368.

SMITH, R.A., *Semiconductors*, (Cambridge, 1959).

SMITH, W., 'The Action of Light on Selenium', *Soc.Tel.Eng.J.*, *2*, (1873), pp 31-33.

——————., 'Effect of Light on Selenium during the Passage of an Electric Current', *Nature*, *7*, (1873), p 303.

——————., 'Selenium', *Nature*, *7*, (1873), p 361.

——————., 'Selenium, its Electrical Properties and the Effect of Light Thereon', *Soc.Tel.Eng.J.*, *6*, (1877), pp 423-448.

SOMERVILLE, A.A., 'Temperature Coefficients of Electrical Resistance, I', *Phys. Rev.*, *30*, (1910), pp 532-534.

——————., 'Temperature Coefficients of Electrical Resistance, II, *Phys. Rev.*, *31*, (1910), pp 261-277.

——————., 'Temperature Coefficients of Electrical Resistance, III', *Phys.Rev.*, *33*, (1911), pp 77-80.

——————., 'Variation of Electrical Resistance of Oxides with Temperature', *Met. & Chem. Eng.*, *10*, (1912), pp 422-423.

SOMMERFELD, A., 'Zur Elektronentheorie der Metalle auf Grund der Fermishen Statistik', *Zeits.f.Phys.*, *47*, (1928), pp 1-32.

SPOTTISWOODE, W., 'Matter and Electromagnetic Action', (Discourse, Royal Institution; Friday, March 31, 1882), in *Roy. Inst. Lib. Sci.*, *3*, (London, 1970), pp 216-226.

STEBBINS, J., 'The Color Sensibility of Selenium Cells', *Astrophys.J.*, *26*, (1907), pp 183-187.

STEINBERG, K., 'Über der Halleffekt bei jodhaltigen Kupferjodur', *Ann.d.Phys.*, *35*, (1911), pp 1009-1033.

STREINTZ, F., 'Uber die Elektrische Leitfähigkeit von gepressten Pulver', *Akad.Wiss.Wien.*, *111*, (1902), pp 345-378.

————————., 'Positiver und Negativer Temperatur Koeffizient des Widerstandes Nichtelektrolytischer Leiter', *Ann.d.Phys.*, *44*, (1914), pp 545-555.

STREINTZ, F., and WELLIK, A., 'Über den Widerstand zwischen Metall und Kristall an ebenen Grenzflachen', *Phys. Zeits.*, *12*, (1911), pp 845-854.

STREINTZ, F., and WESELEY, A., 'Uber unipolare Leitungen Kristallen', *Phys. Zeits.*, *21*, (1919), pp 42-50.

SWANN, W.F.G., 'The Expression for the Electrical Conductivity of Metals as Deduced from the Electron Theory', *Phil. Mag.*, (6th Series), *27*, (1914), pp 441-454.

TAIT, P.G., *Recent Advances in Physical Science*, (London, 1876).

TAUDIN CHABOT, J.J., 'New Rays or a New Emanation', *Sci.Abs.*, (Phys.), *7*, (1904), No. 1428, p 436, (*Phys. Zeits.*, *5*, (1904), pp 103-104).

————————., 'Photanthistan: A New Instrument for the Comparison of Luminous Intensities and Absorption Coefficients', *Phil. Mag.*, (6th Series), *14*, (1907), p 428.

THOMSON, J.J., 'Professor Rowland's New Theory of Magnetic Action', *Nature*, *24*, (1881), pp 204-206.

————————., 'Report on Electrical Theories', *B.A. Report*, (1885), pp 97-155.

————————., *Notes on Recent Researches in Electricity and Magnetism*, (Oxford, 1873).

————————., *Electricity and Magnetism*, (Newhaven,Conn., 1904).

————————., *The Corpuscular Theory of Matter*, (New York, 1907).

————————., 'Conduction of Electricity through Metals', *Phil. Mag.*, (6th Series), *30*, (1915), pp 192-202.

THOMSON, J.J., and THOMSON, G.P., *Conduction of Electricity through Gases*, (2nd ed., 2v.), (Cambridge, 1933).

THOMPSON, S.P., 'The Photophone', *Nature*, *22*, (1880), p 481.

————————., 'Notes on the Construction of the Photophone', *Proc. Phys. Soc.*, *4*, (1881), pp 184-190.

————————., 'Solid Electrolytes', *Nature*, *32*, (1885), p 366.

TILTON, J.E., *Diffusion of Semiconductor Technology*, (Washington, 1971).

TISDALE, W.E., 'The Effects of Gases and Metallic Vapours on the Electrical Properties exhibited by Selenium Crystals of the Hexagonal System', *Phys. Rev.*, (2nd Series), 12, (1918), pp 325-335.

TOPPER, D.R., *J.J. Thomson and Maxwell's Electromagnetic Theory*, (Ph.D., Thesis, Case Western Reserve Univ. 1970).

TRICKER, R.A.R., *The Contributions of Faraday and Maxwell to Electrical Science*, (London, 1966).

TUBANDT, C., 'Über Einseitige Ionen und gemischte Stromleitung in Kristallen', *Zeits.f.Elektrochem.*, 26, (1920), pp 358-364.

TYNDALL, J., 'On the Identity of Light and Heat', (Discourse, Royal Institution; Friday, 2nd Feb., 1872), in *Roy. Inst. Lib. Sci.*, (Phys.Sci.), 2, (London, 1970), pp 330-334.

VACROUX, A.G., 'Microcomputers', *Sci. Amer.*, 232, (1975), pp 32-40.

VONWILLER, O.U., 'Observations of the Effect of Light on Selenium', *Roy. Soc., (N.S.W.) J. and Proc.*, 43, (1910), pp 361-380.

WEINER, C., 'How the Transistor Emerged', *I.E.E.E.Spectrum*, (Jan.,1973), pp 24-33.

WEISS, J., and KOENIGSBERGER, J., 'Über die ThermoKrafte einiger Metaloxyde und-sulfide', *Phys. Zeits.*, 10, (1909), pp 956-957.

WEISSENBERGER, A., 'Thermoelectric Forces of Bad Conductors', *Sci. Abs.*, (Phys.), 17, (1914), No. 738, p 252. (*Phys. Zeits.*, 15, (1914), pp 105-107).

_______________., 'Über die ThermoKraft und Elektrizitätsleitung variables Leiter. Beitrage zur Elektronentheorie', *Ann.d.Phys.*, 49, (1916), pp 481-530.

WESELEY, A., 'Über den Widerstand zwischen Metall und Kristall an Ebenen Grenzflächen', *Phys. Zeits.*, 14, (1913), pp 77-81.

WHETHAM, W.C.D., *A Treatise on the Theory of Solutions including the Phenomena of Electrolysis*, (Cambridge, 1902).

_______________., 'The Theory of Electrolytic Dissociation', *Phil. Mag.*, (6th Series), 5, (1903), pp 279-290.

WHITE, G.W., 'The Properties of Selenium Blocks', *Phil. Mag.*, (6th Series), 29, (1914), pp 370-382.

WHITE, W.C., 'Evolution of Electronics', *Electronics*, 25, (1952), pp 98-99.

WICK, F.G., 'Some Electrical Properties of Silicon, I. Thermoelectric Behaviour of Metallic Silicon', *Phys. Rev.*, 25, (1907), pp 382-390.

__________., 'Some Electrical Properties of Silicon, II, The Electrical Resistance of Silicon at Low Temperatures', *Phys. Rev.*, 27, (1908), pp 11-17.

__________., 'Some Electrical Properties of Silicon, III. The Hall Effect in Silicon at Ordinary and Low Temperatures', *Phys. Rev.*, 27, (1908), pp 76-86.

__________., 'Some Electrical Properties of Silicon IV. The Electromotive Force of Cells in which Silicon forms one Electrode', *Phys. Rev.*, 27, (1908), pp 238-249.

WILSON, A.H., 'The Theory of Electronic Semi-Conductors, I., *Proc. Roy. Soc.*, (A), 133, (1931), pp 458-491.

__________., 'The Theory of Electronic Semi-Conductors, II, *Proc. Roy. Soc.*, (A), 134, (1931), pp 377-387.

__________., 'Theory and Experiment in Solid State Physics', *Inst. Phys. Bulletin*, 14, (1963), pp 173-180.

WOLD, P.I., 'The Hall Effect and Allied Phenomena in Tellurium', *Phys. Rev.*, (2nd Series), 7, (1916), pp 169-193.

WOOD, R.W., 'Absorption, Dispersion and Surface Colour of Selenium', *Phil. Mag.*,(6th Series), 3, (1902), pp 607-622.

ZAHN, H., 'Theory of Thermomagnetic Effects', *Sci. Abs.*, (Phys.), 17, (1914), No. 556, p 191.
(*Phys. Zeits.*, 14, (1913), pp 926-928.

## CORRESPONDENCE.

Except as indicated otherwise all letters were addressed to the present writer.

BARR and STROUD, LTD., Glasgow. Fournier d'Albe's Optophone. 4/9/72.

BENEDIKZ, B.S., University of Birmingham Library. Notes on Fournier d'Albe. 7/9/73.

BLOCH, F., Stanford University. Comments on his first reactions to Wilson's ideas. 3/3/76.

CLAYTON, R.J., Technical Director, G.E.C. G.E.C's. early involvement in semiconductor research. 29/10/76.

HUGHES, M., Librarian, Royal Radar Establishment. Comment on early work at R.R.E. 19/12/75.

MACDONALD, S., University of Aston, Technology Policy Unit. Outline of interests in semiconductor devices. 23/1/74.

MASON, S.F., King's College, London. Notes on W.G. Adams, 13/1/77.

MOTT, SIR NEVILL, Cambridge University. Comments on Transcript of interview with Pohl. 28/8/74.

NICHOLSON, I., Archivist, Mullards Ltd. 11/11/76.

PEARSON, G.L., Stanford Electronics Lab. 8/8/72.

PEIERLS, SIR RUDOLF, Oxford. Early Contribution to theory of the solid state. 21/4/75.

______________, Comments on transcripts of interviews with Mott and Wilson. 20/8/75.

POHL, R.W., Göttingen. Personal memories of Gudden. 11/7/74.

PRICHARD, G.D., Hirst Research Centre, G.E.C. Notes on Sources at G.E.C. 4/11/76.

ROBINSON, N.H., Librarian, Royal Society, Unpublished letters of Bidwell. 9/11/76.

SCHOTTKY, W. to WILSON, SIR ALAN, Comments on Wilson's ideas. 1/5/31.

SMITH, R.A., Heriot-Watt University, Edinburgh. Comments on the reception of Wilson's ideas at Cambridge in the 1930's. 18/9/76.

__________., Comments on significance of Pohl's researches. 8/1/76.

WARBURG, T.R., STC, Harlow. Reporting no records of early work. 9/7/76.

WILSON, SIR ALAN, Comment on early history of semiconductor research, c1930. 5/10/72.

______________, Discussion of Fowler's and Pauli's early efforts in the solid state and their cessation of work having taken the initial steps. 21/11/74.

WILSON, SIR ALAN, to MACDONALD, S. Short discussion of work on semiconductor devices in the 1930's. 8/5/75.

## INTERVIEWS.

| | | |
|---|---|---|
| 25th July | 1974. | R.W. Pohl in Krefeld. (Federal Republic of Germany). |
| 1st November | 1974. | Sir Nevill Mott in Cambridge. |
| 8th November | 1974. | Sir Alan Wilson in London. |