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Early history of the physics and chemistry of semiconductors—from doubts to fact in a hundred years†

Georg Busch

Laboratory for Solid State Physics, Swiss Federal Institute of Technology, 8093 Zürich, Switzerland

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Abstract. Gray, Désagullier and Volta discovered and investigated electric conduction in solids. Davy found a decrease of the conductivity σ in metals and Faraday observed a strong increase with temperature in a number of binary chemical compounds. Hittorf's measurements on Ag_2S and Cu_2S led to a linear relation of log σ against $1/T$. The controversial case of Ag_2S is described. Hall and Rowland discovered a transverse voltage of a current carrying metal film in a magnetic field. Riecke and Drude developed the first electron theory of metals and Koenigsberger tried to explain the temperature dependence of the electrical conductivity by a dissociation theory.

Baedeker was the first to observe semiconducting properties of CuI depending on the stoichiometric composition. Wagner proved that the conductivity of Ag_2S is essentially electronic and not ionic. Gudden suggested that semiconduction is the result of impurities and imperfections in solids and Wagner and Schottky developed their theories of lattice defects (Fehlordnungs-Erscheinungen). Wilson presented the first band theory of intrinsic and extrinsic semiconductors. The existence of intrinsic conduction has been questioned by experimentalists and is verified only by the preparation and investigation of high-purity semiconducting elements.

Zusammenfassung. Gray, Désagullier und Volta entdecken und untersuchen als Erste die elektrische Leitfähigkeit von festen Körpern. Davy beobachtet die Abnahme der Leitfähigkeit σ in Metallen und Faraday findet eine starke Zunahme mit steigender Temperatur in einer Reihe von binären chemischen Verbindungen. Hittorf's Messungen an Ag_2S und Cu_2S führen zu einer linearen Beziehung von log σ als Funktion von $1/T$. Das lange Zeit widersprüchliche Verhalten von Ag_2S wird beschrieben. Hall und Rowland entdecken eine transversale Spannung in einem stromdurchflossenen Metallfilm in einem Magnetfeld. Riecke und Drude entwickeln die erste Elektronentheorie der Metalle und Koenigsberger versucht, die Temperaturabhängigkeit ihrer elektrischen Leitfähigkeit aufgrund einer Dissoziations-Theorie zu erklären.

Baedeker entdeckt als Erster die halbleitenden Eigenschaften des CuI, die von der stöchiometrischen Zusammensetzung der Proben abhängen. Wagner zeigt, dass die elektrische Leitfähigkeit des Ag_2S vorwiegend elektronisch und nicht elektrolytisch ist. Gudden vertritt die Auffassung, dass die halbleitenden Eigenschaften auf Verunreinigungen und Gitterbaufehlern der Festkörper beruhen, und Wagner und Schottky entwickeln ihre ersten Theorien der Gitterdefekte (Fehlordnungs-Erscheinungen). Wilson entwickelt die erste Bänder-Theorie der Eigen- und Störhalbleiter. Die Existenz der Eigenleitung wird von Experimentalphysikern lange Zeit bezweifelt und erst aufgrund der Herstellung und Untersuchung hochreiner halbleitender Elemente bestätigt.

1. Introduction

'In a sketch of this kind, and in the time allotted for it, I shall not be expected to produce a minute history of all the various insulated experiments that have been made. My endeavour will be rather to fix your attention upon leading and grand discoveries which form the epochs of this science. Many have developed new objects in it, but a very few only have ascertained principles.'

† Based on an Invited Paper delivered at the Spring Meeting of the American Physical Society, New Orleans, 23 March 1988.

Obviously these are not my own words. This is the introduction to a lecture by Humphry Davy [1] before the Royal Society in London on 'Electro-Chemical Science' in 1810! But in the following I shall keep Davy's recipe in mind.

I began to work on semiconductors 50 years ago, in March 1938 – on silicon carbide. This was a dangerous enterprise. My friends warned me: working on semiconductors means scientific suicide! As I was giving a seminar on semiconductors during the war, a colleague of mine, professor of applied physics, got up and asked me: 'What are semiconductors good for? They are good for nothing. They are erratic and not reproducible.' Indeed this was still in a period of poor knowledge. Silicon was believed to be a metal; grey tin, the low-temperature diamond-type structure of tin was said to be a superconductor, and in silicon carbide volume rectification was assumed. But the worst of all was a letter Pauli wrote to Rudolf Peierls from New York in 1931; 'Ueber Halbleiter sollte man nicht arbeiten, das ist eine Schweinerei, wer weiss, ob es überhaupt Halbleiter gibt' [2]. In loose translation this means: 'On semiconductors one should not do any work, that's a mess, who knows whether there are semiconductors at all'!

2. Early research on electrical conduction

I think I have to begin with Stephen Gray [3], who lived from 1666 or 1667 to 1736 in London and Canterbury. On 8 February 1731 he wrote a letter to Cromwell Mortimer, the secretary of the Royal Society, containing the description of several experiments concerning electricity. His source of electricity was a long tube of flintglass, closed at each end with a cork. When he excited the tube by rubbing, he observed that not only the glass tube, but also the corks at the ends attracted light metal foils or downfeathers very strongly. This observation led him to ask whether the electric charge might be transmitted to other bodies also by other materials and at what distance. He began with short fir sticks and pieces of metals and ended up with a 'communication line' of over 250 m. The 'electrick effluvium' was transported not only by a horizontal, but also by a vertical line of wood or packthread, and also in hoops of various diameters. He also observed that bubbles of soapy water, i.e. a liquid, are able to carry away electricity. In addition he investigated whether the magnetic field of a piece of loadstone would influence the transmission of the electric charge. No doubt, Stephen Gray is the discoverer of electric conduction in solids and liquids, without using this term in his letter, however. In my opinion the intuition and originality of Gray's experiments is comparable to Galilei's question, whether light is a state of the space, or whether it propagates in space with a measurable velocity. Due to entirely inadequate means, his experiments tried in 1607 were unsuccessful, but the idea was born.

The first to introduce the concept of an *electrical conductor* was Jean Théophile Désagulliers. Désagulliers was born in 1683 at La Rochelle, the home town of the famous Seignette Dynasty of apothecaries, and he lived as a religious refugee in London until 1744. In a 'Dissertation sur l'électricité des corps', which is not equivalent to a PhD thesis in today's sense of the word, he distinguishes between 'electric' and 'non-electric' bodies and introduces the term *electric conductor* (conducteur d'électricité) explicitly for the first time. This work was awarded a prize by the 'Académie Royale des Belles Lettres et Arts' at Bordeaux in 1742 [4].

After searching the literature of the 18th century I came to the conclusion that Alessandro Volta was the first to introduce the *word* semiconductor, or at least *materials of semiconducting nature*. This can be found in a paper read in English before the Royal Society in London on 14 March 1782 [5].

After the invention of his famous pile Volta had powerful sources of electricity at his disposal. Apart from many other experiments, he observed the speed with which an electrometer is discharged by touching its knob with different materials. Metals do it instantaneously, semiconductors slowly and insulators not at all. To read Volta's long and numerous papers is a difficult and time consuming task. He not only published in Italian, but also in French, German and Latin, and from translations it is often difficult to find out what the original version really meant.

The next person to be mentioned is Humphry Davy again, the father of electrochemistry. He had built Volta piles up to several hundred volts, which enabled him to do experiments under rather stable electrical conditions. He was interested in the influence of the temperature on the conductivity of metals, such as Cu, Ag, Sn, Pb, Fe and Pt. In 1840 he wrote: 'The most remarkable general result that I obtained by these researches, and which I shall mention first, as it influences all the others, was, that the *conducting power of metallic bodies varied with temperature, and was lower, in some inverse ratio, as the temperature was higher* [6]. It took nearly a century to explain these observations theoretically.

Michael Faraday [7] knew about Davy's experiments, and he extended them to a great number of *compounds* that he had prepared himself. Not only was he interested in the sulphides of various metals, but also in oxides, carbonates, sulphates, nitrates, halides, amongst others and also in periodide of mercury HgI_2. Faraday soon realised that the change of the conductivity with temperature of the various compounds was opposed to what his master had found on metals. He perceived as a material of particular interest and surprising behaviour 'sulphuret of silver', i.e. Ag_2S. At room temperature its conductivity was very low, but at about 175 °C an abrupt rise to nearly 'metallic' magnitude occurred. Unfortunately, Faraday published no quantitative results and no curves to show the resistivity as a function of temperature.

3. The puzzle of Ag_2S

Neither did Johann Wilhelm Hittorf, Professor of Chemistry and Physics at the University of Münster in Westfalen, Germany. His main work was dedicated to the electric conduction of electrolytes, gases and the physics of cathode rays. In 1851 Hittorf published a paper on the electric conductivity of Ag_2S and Cu_2S as a function of temperature [8]. Table 1 shows his results. The resistivity of his specimens, which were prepared by direct reaction of the elements, was compared with the length of a platinum wire of equal resistance. Again, no plot is shown, and so I was curious to do it myself, as I prepared this paper. Figure 1 shows the result. I must confess I was flabbergasted as I saw the points laying on a straight line in a log σ against $1/T$ diagram for Cu_2S. As I did the same for Ag_2S, I was somewhat disappointed: No straight line, and what about the jump at 170 °C?

Ag_2S is a very intricate substance indeed. It kept chemists and physicists busy for more than 120 years, and the literature about it is so enormous that I only can pick out the most important results. Ag_2S occurs in nature as black, shiny crystals and undergoes a first-order transition at 170 °C from an orthorhombic β- to a cubic α-structure type. Above the transition temperature the sulphur atoms form a body-centred cubic lattice and for the silver atoms 42 possible sites are available, which are occupied by four atoms at random.

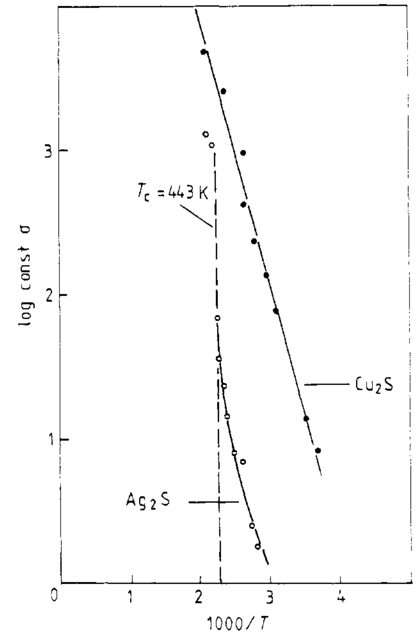


Figure 1. Electrical resistivity of Cu_2S and Ag_2S as a function of temperature plotted according table 1.

Table 1. Electrical resistivity of Cu_2S and Ag_2S as a function of temperature (from Hiltorf [8]).

Halbschwefelkupfer

Bei der Temp. 0° C.	1130 Meter Platindraht, dessen Durchmesser 0,4987mm.
» 10	681 Meter
» 51	120 »
» 67	68 »
» 85	40 »
» 103	22,4 »
» 107	9,4 »
» 113	8,3 »
» 136	5,2 »
» 152	3,8 »
» 184	2,2 »
» 192	2 »

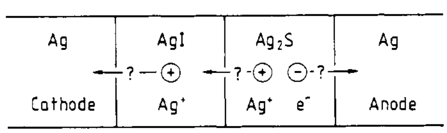
Schwefelsilber

Temperatur.	Widerstand.
84,1° C.	537 Meter Platindraht (Durchm. 0,4987mm)
93	395 » »
113,2	142 » »
129,2	120 » »
148	67 » »
158,2	40,5 » »
165,2	25,6 » »
170	13,8 » »
180,5	0,88 » »
195	0,77 » »

Für niedrigere Temperaturen als 84°, habe ich keine Bestimmungen gemacht, da meine Widerstandsrollen nicht ausreichen.

Hittorf believed that he had observed *electrolytic* conductivity. He could not know any better. But the question, whether the conductivity is really ionic or electronic remained controversial for nearly a century. In 1921 Tubandt, Schibbe and Eggert [9, 10] verified Faraday's law by an ingenious sandwich method, shown in figure 2, based on the pure ionic conductivity of silver iodide. Silver iodide acts as a barrier for electrons and prevents the formation of silver threads in the silver sulphide. By measuring current and time and by exact weighing of both anode and cathode, Tubandt hoped to verify Faraday's law exactly. However, in 1933 Carl

Figure 2. Tubandt's sandwich method to verify Faraday's law in Ag_2S [9, 10].



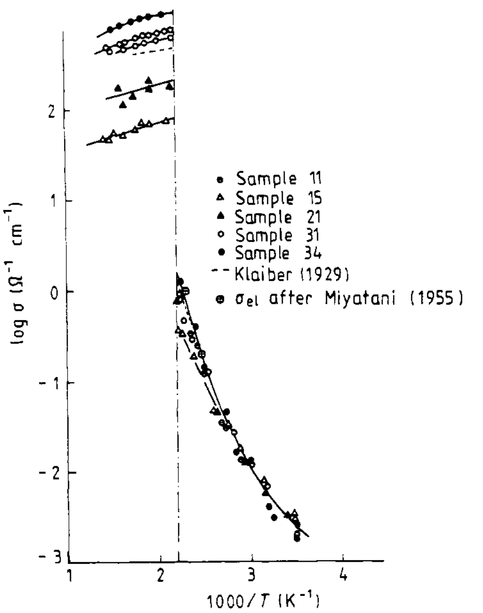


Figure 3. Electrical conductivity of Ag_2S as a function of temperature (after [13]).

Wagner, [11], Professor of Physical Chemistry in Jena, repeated the experiments and came to the conclusion that the validity of Faraday's law was only the result of a secondary reaction and that the ionic contribution in both the β and α phases was less than a per cent of the total current. This opinion was supported already in 1929 by Klaiber [12] in Erlangen, who observed a Hall effect in both the α and β phases. His results were confirmed in 1959 by Junod [13], and by Junod and co-workers [14] who showed that the results are very sensitive to the preparation of the specimens, essentially purity and deviations from stoichiometry. This is a serious problem, because a considerable homogeneity range exists in the phase diagram. Zone refining under controlled sulphur pressure is necessary. It could be shown that with the change of the structure at 170 °C a *semiconductor–metal* transition occurs. Junod's results of measurements of the electrical conductivity and the Hall coefficient as a function of temperature are shown in figure 3 and figure 4.

The story of silver sulphide is not yet finished, however. In the last twenty years several hundred papers appeared on this particular substance treating the whole spectrum of its solid state physical and chemical properties. A review article was published by Rickert in 1967 [15].

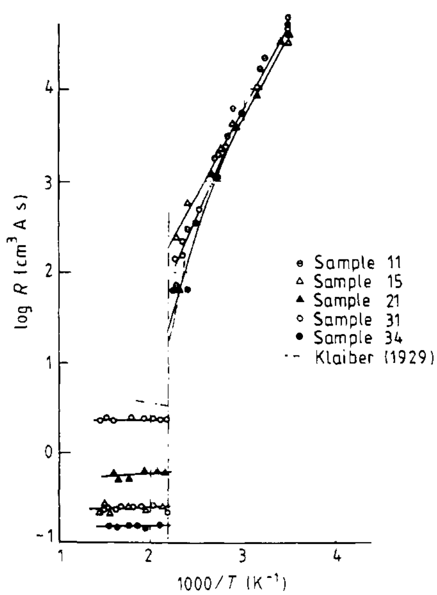
To conclude, it appears to me that Hittorf in 1851 was the first to have measured quantitatively the electrical conductivity of a semiconductor as a function of temperature, albeit not knowing what kind of charge carriers were responsible for the conduction. The mechanism of the electrical conductivity of many other solids also remained obscure for a long time, and the observation of the photoconductivity in selenium by Smith in 1873, [16], the important discovery by Hall [17] in 1879 and other galvano- and thermomagnetic effects failed to elucidate the problem.

4. The Hall effect

Edwin Herbert Hall was a student of Professor H A Rowland at the Johns Hopkins University at Baltimore. Rowland is best known for his construction of high precision ruling machines and his realisation of concave gratings, so important for spectroscopic work. While reading Maxwell's book on 'Electricity and Magnetism' in connection with Professor Rowland's lectures, Hall's attention was attracted by Maxwell's statement, that '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 . . .'.

Both Hall and Rowland doubted the truth of Maxwell's statement and Hall learned that Rowland himself had made some hasty experiment to detect, if possible, some action of a magnet on the current itself, though without success. Hall asked Rowland for permission to do a somewhat different experiment, based on the following idea. If the current in a conductor itself is attracted by a magnet, it should be drawn to one side of a wire, and, therefore, its resistance should increase. Within the limits of error no change of the resistivity was detected and Hall

Figure 4. Hall coefficient of Ag_2S as a function of temperature (after [13]).



came to the conclusion that it was more promising to look for a transverse potential difference at right angles to the current and the magnetic field. This was the arrangement formerly conceived by Rowland apparently, but tried on too thick a sheet of metal. Following Rowland's advice Hall repeated the experiment with a thin gold leaf mounted on a plate of glass, and on 28 October 1879 the expected effect was detected. The transverse potential difference was found to be proportional to the current and to the magnetic field. In addition, Hall concluded that the electric field driving the current was deflected by an angle proportional to the magnetic field, i.e. the Hall angle was conceived already a hundred years ago. Shortly after Hall published his paper, Rowland repeated the experiment with iron and found opposite signs of the potential differences observed for gold and germansilver [18]. In retrospect, it would seem justified to name the observed phenomenon the 'Hall–Rowland' effect, which is so important to characterise the nature of electronic conductors. (For a more elaborate account of the history of the Hall effect see [19]).

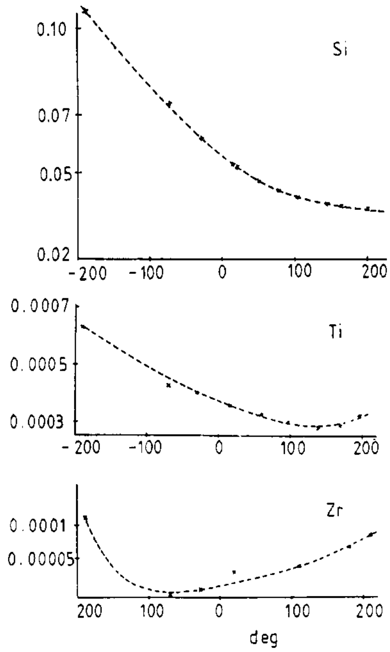


Figure 5. Electrical resistivity of Si, Ti and Zr as a function of temperature (after [25]).

5. The electronic conduction of solids

A decisive step forward in our recognition of the mechanism of the electric conduction in solids was achieved by Carl Viktor Emanuel Riecke's [20] experiment at the Institute of Physics at Göttingen in 1901, soon after J J Thomson discovered the electron in 1897. Riecke switched a cylinder of copper between two cylinders of aluminium into the main line of the battery, feeding the whole laboratory for a year, and he determined very carefully the weight of the copper cylinder before and after the experiment. A total charge of 3.42×10^6 C had flown through the copper cylinder, and if the current were connected with a transport of copper atoms, a deposit of 1.14 kg of copper at one of the connecting electrodes ought to have shown up. But within the limits of errors of his measurements there was no change of the weight. So he concluded that *electrons* must carry the current. That this hypothesis was correct was shown by Tolman and Steward [2] only in 1916. They were able to prove that the ratio e/m of the electrons in a metal was approximately identical to the ratio found for the free electron. Whether by inertia experiments of this kind one determines the *rest* mass of the electron or the *effective* mass was a puzzle for many years!

Immediately after Thomson's discovery Riecke [22] in 1899 and Drude [23] at the University of Leipzig in 1900 proposed their first theories of the electric conduction of metals by the assumption of an 'electron gas' carrying the current. It is remarkable that Riecke already gave room for the existence of not only negatively, but also positively, charged carriers of possibly different concentrations and unequal mobilities, which led him finally to a formula of the Hall coefficient, which is practically identical to the one derived by Peierls in 1929 [24]. However, neither Riecke nor Drude was able to make any realistic predictions concerning the concentrations of the charge carriers as a function of temperature. Whereas Riecke assumed a linear increase of the number of mobile negatively or positively charged particles with temperature, Drude hesitated to make any predictions. Both agreed about the decrease of the mobilities with temperature to explain the generally observed decrease of the conductivity of metals at high temperatures, but they were not in a position to give an explanation for the *resistivity minimum* of a number of metals at low temperatures, observed for instance for titanium and zirconium found by Koenigsberger and Schilling [2] in 1908. Their results are shown in figure 5.

6. Koenigsberger's dissociation theory

In contrast to Riecke and Drude, Koenigsberger postulated that the mobile charge carriers were the result of a *dissociation* of the atoms of a 'metallic' conductor into electrons and the remaining positive ions according to the equation $N = N_0 \exp(-Q/T)$, where Q is proportional to the dissociation energy.

Johann Koenigsberger, Professor of Physics at the University of Freiburg im Breisgau was a versatile scientist. He was mainly interested in the electrical, optical and thermal properties of minerals, and he was an expert on the mineral world especially of the Swiss Alps. Together with a number of collaborators he studied mainly oxides and sulphides, such as Fe_2O_3, Fe_3O_4, $FeTiO_3$, Fe_2TiO_5, PbS, FeS, MoS_2, pyrrhotite and silicon. But apart from these solid-state problems, he was interested in spectroscopy, canal rays, thermal radiation, geophysical phenomena and related subjects. His list of publications is impressive not only with respect to its length, but also to his originality. His dissociation theory to describe the temperature variation of solids deserves attention.

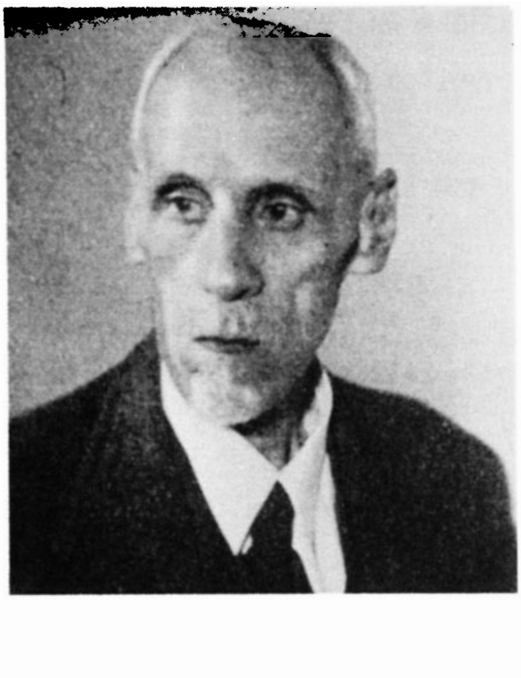
For the temperature variation of the mobility of the electrons he proposed a decrease proportional to the inverse of an expression $(1+\alpha t \pm \beta t^2)$, which led him to a formula for the resistivity

$$\rho = \rho_0(1+\alpha t \pm \beta t^2)\exp[Q/(t+273)]$$

which indeed leads to a minimum of the resistivity. Koenigsberger and Reichenheim [26] in 1908 claimed that the electrical resistivity of solids was represented quite generally by their formula. Although this conclusion certainly goes too far, it supported the belief that the resistivity of metals becomes infinitely large at zero absolute temperature, an opinion which was shared even by Kamerlingh-Onnes, before he discovered superconductivity in 1911 [27]!

Although Koenigsberger was unable to make any prediction of the value of the dissociation energy Q, he classified the electronically conducting solids into metals, insulators and '*variable conductors*', according to the value of Q [28]. For insulators Q tends to infinity, for metals at high temperature to zero, which means that all the atoms of a solid are split into a positive ion and a free electron. For 'variable conductors' Q was supposed to have a *finite* value, which means that the resistivity decreases exponentially with rising temperature. With this assumption Koenigsberger indeed came very close to the truth; already in 1913! He also observed that the values of Q and the mobility of the various variable conductors depended markedly on their purity and the structural imperfections of the specimens he investigated. Koenigsberger quite definitely belongs to the pioneers of semiconductor physics.

Johann Georg Koenigsberger 1874–1946 (by courtesy of Mrs M J Loveday-Koenigsberger).



But who introduced the term 'semiconductor' in todays sense of the word?

In 1910 Weiss, a student of Koenigsberger, published his doctoral thesis entitled 'Experimentelle Beiträge zur Elektronentheorie aus dem Gebiet der Thermoelektrizität' [29]. He measured the thermoelectric power, the Thomson heat and the Peltier coefficient of various combinations of different metals with the oxides and sulphides of iron and titanium and he compared his results with the electron theories of Riecke, Drude, J J Thomson, Lorentz and Koenigsberger. It is in *this* paper that the concept of a 'Halbleiter', i.e. a *semiconductor*, appears for the first time, and then again in a common publication by Koenigsberger and Weiss in 1911 [30]. In a footnote of this paper, attention is drawn to the fact that the authors do not agree in every respect, but they do not specify their disagreement.

In this context it is remarkable to notice that Koenigsberger in a review article even in 1923 [31] included a chapter on '*Variable Leiter*' (variable conductors) and avoided the concept 'Halbleiter' (semiconductor) throughout. So it appears that the term 'Halbleiter' actually was coined by Weiss! But it is obvious that variable conductors and semiconductors have the same significance.

7. Baedeker's research on CuI

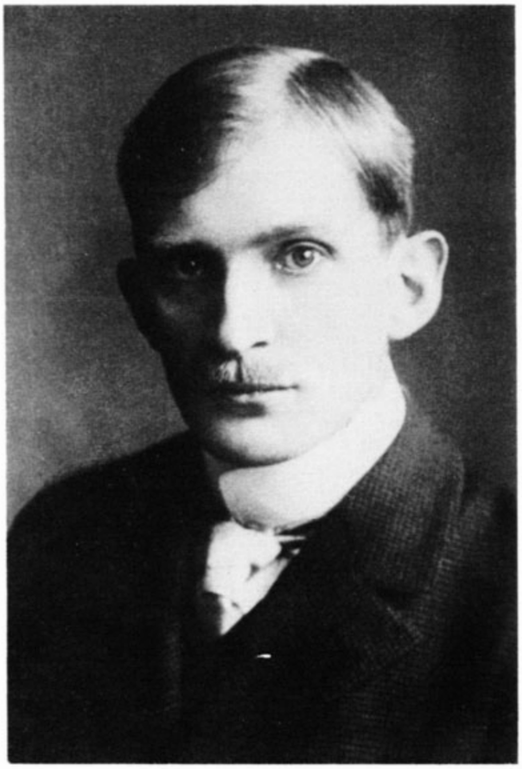
An important step forward is due to Karl Baedeker [31–35] who was Professor of Physics at the University of Jena, Germany. Karl Baedeker was born in 1877 as a son of Fritz Baedeker, the editor of the world famous travel guides. He was killed in action in the first week of World War I at the age of 37. His list of publications is short, but his few papers are fundamental. In 1911 he published a book entitled 'Die elektrischen Erscheinungen in metallischen Leitern' [35] which served as a handbook in the field for more than two decades.

Baedeker was acquainted with Koenigsberger's observations on minerals and their erratic behaviour, which is partly due to inhomogeneity, impurities, structural imperfections and unreliable contacts. The poor reproducibility of the results is the main reason for the bad reputation semiconductor research suffered for many years to come.

Baedeker tried a new method. He produced thin metallic layers on sheets of glass or mica by sputtering. Their thickness was estimated by weighing with a high sensitivity torsion balance. He then exposed these films to oxygen or the vapours of sulphur, selenium, arsenic and iodine to produce the respective compounds of copper, silver, cadmium, lead and thallium. Today this seems to be a trivial method, but in 1907 it was an ingenious idea. Most of the layers were transparent and coloured, and their homogeneity was checked under the microscope. Burned-in platinum, prior to the sputtering, served as electrodes.

The most important results were obtained with copper iodide. CuI is a colourless substance with a surprisingly low electrical resistivity of approximately $10^{-2}\,\Omega\,\mathrm{cm}$. Baedeker hesitated to ascribe this low value to electrolytic conductivity, and in a subsequent paper he was able to show that the conduction was of 'metallic' character, i.e. electronic. Left in open air at room temperature, the CuI layers became practically insulators, but exposed to iodine vapour or to an alcoholic solution of iodine the conductivity immediately increased by several orders of magnitude in a reversible way. This means that the conductivity is extremely sensitive to the iodine content of the specimens; an entirely new phenomenon. By the same method he also produced Ag_2S. His results were compatible with the assumption of a transition from ionic to 'metallic' conductivity at the transition temperature which Faraday had observed nearly 75 years earlier.

Kark Baedeker 1877–1914 (by courtesy of Universitäts-Archiv, Friedrich-Schiller-Universität, Jena).



The next step was the measurement of the Hall effect, which was considered as a proof of metallic conduction. But the sign of the Hall voltage was opposite to the one in bismuth, i.e. apparently due to positively charged carriers. The Hall coefficient again varied considerably with the iodine concentration in agreement with the change of the conductivity. Under the assumption of one kind of charge carrier, from the Hall coefficient Baedeker indicates, one obtains an unrealistically low concentration of the order of $10^8\,\mathrm{cm}^{-3}$. According to our present knowledge this indicates two kinds of carriers, electrons and holes. But Baedeker came to the conclusion that CuI is a 'metallic' conductor with a *concentration of electrons increasing with temperature*, which is essentially correct. (For a more detailed appreciation of Baedeker's work see [37].

8. Gudden's impurity hypothesis

During world War I, research activities on semiconductors practically came to a standstill, and were revived only in the early 1920s. In 1924 Gudden [38] at the University of Göttingen, a close cooperator of R W Pohl, published a detailed review on the electrical conductivity of crystalline substances, excluding ordinary metals. He gave a rather complete description of the results obtained on ionic or electrolytic conductors, but as far as semiconductors are concerned, no real progress in understanding their properties was made in the following years.

In 1930 Gudden published a new review article on the electrical conduction of semiconductors [39]. In his opinion no *chemically pure* substance would ever be a semiconductor. The observed properties were believed to be due entirely to *impurities*, and he came to the conclusion, that 'semiconductors in the scientific sense of the word – *if they exist at all* – are by far scarcer than originally assumed'.

9. 'Fehlordnungs-Erscheinungen' in solids

In the early 1930s Frenkel [40], Wagner and Schottky [41] and Jost [42] developed their models of point defects in lattices, which led not only to an understanding of diffusion and ionic conductivity, but also to the explanation of the *electronic* conduction of *ionic* crystals. This was the birth of the so-called 'Fehlordnungs-Erscheinungen' in solids, which has become fundamental for the whole field of solid state physics ever since. Figure 6 and 7 show examples of ionic lattices with cation and anion defects respectively. Defects in the anion lattice lead

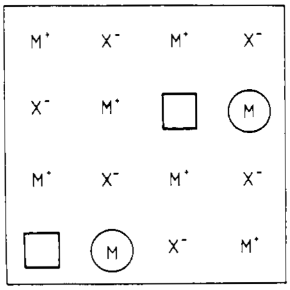


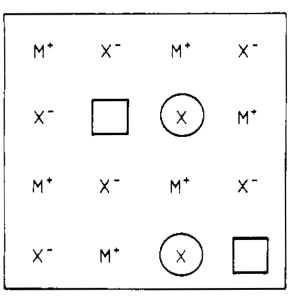
Figure 6. Ionic lattice with anion vacancies: electron (excess) conductor.

to electron conduction, defects in the cation lattice to hole conduction. In opposition to Gudden's original idea, impurities are not necessary to produce semiconductivity therefore!

In the following years an enormous number of mostly binary compounds – oxides, sulphides, selenides, carbides, nitrides and others – were investigated with respect to their electrical properties. It is impossible to give a full account of all these results. Very often the conductivities found on the same substance by different authors were in striking contradiction. Cu_2O is one of the most instructive examples, shown in figure 8. The conductivities of different samples measured at the same temperature differed by 6 or 7 orders of magnitude! It soon was recognised that deviation from stoichiometry was the reason for these discrepancies. As shown in figure 9 the conductivity of Cu_2O increases with oxygen pressure, according to measurements by Dünwald and Wagner [43].

Zinc oxide is an opposite example. Measurements by Fritsch [14] in 1935 on artificially grown crystals as a function of temperature (figure 10) and by von Baumbach and Wagner [43] show that the conductivity rises rapidly with decreasing content of oxygen (figure 11), i.e. a deficit of the anion, in contrast to Baedeker's measurement on CuI. Carl Wagner [46] in 1933 was the first to distinguish between '*Elektronen-Ueberschuss-*' and '*Elektronen-Defekt-Leitung*', i.e. excess and defect conduction, the reason being missing positive or negative ions in the lattice. Examples of semiconductors of both natures are given in table 2 including so-called 'amphotheric conductors', in which either positive or negative ion sites may be unoccupied. Excess and defect conductors show opposite signs of the Hall coefficient, which is well known.

Figure 7. Ionic lattice with cation vacancies: hole (defect) conductor.



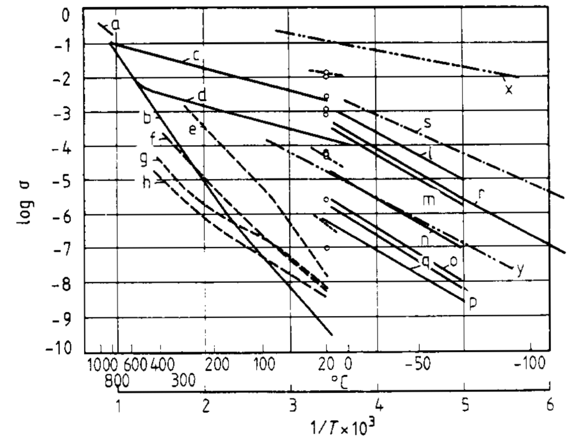


Figure 8. Electrical conductivity of Cu_2O according to different authors (after [38]).

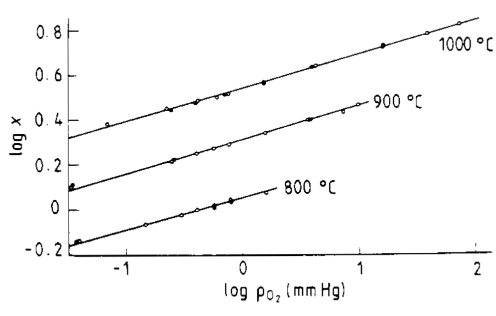
This is in short the chemical aspect of the semiconductor problem. It cannot be emphasised enough that semiconductor physics does not make sense on specimens of unknown purity and structural perfection. This remains true even today!

10. Wilson's theory of semiconductors

But what about physics? Apart from Koenigsberger's dissociation theory, there was neither a quantitative explanation of the exponential increase of the conductivity of semiconductors with temperature nor of the different signs of the Hall coefficient in different substances.

The breakthrough came with wave mechanics. Maximilian Strutt [47], a young engineer at the

Figure 9. Electrical conductivity of Cu_2O as a function of oxygen pressure (after [43]).



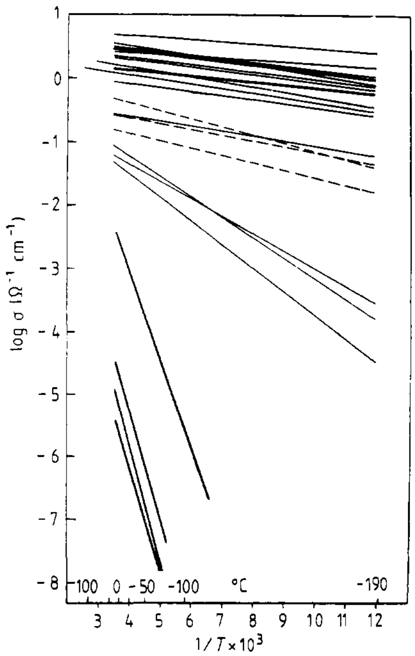


Figure 10. Electrical conductivity of ZnO as a function of temperature for various specimens, single crystals and evaporated layers (after [44]).

Philips Laboratory in Holland and later a Professor of Electrical Engineering at ETH in Zürich, was the first to treat Schrödinger's equation for a periodic potential, which leads to Mathieu's differential equation, solved by Floquet in 1873. Figure 12 gives the well known diagram, showing the typical finite regions for real and imaginary solutions. At the end of his short paper in 1928 Strutt modestly concluded that his results 'might have some bearing on the understanding of metallic conduction, or particularly superconductivity'!

The problem was taken up by Felix Bloch [48, 49] immediately. He was a post-doctoral fellow at the Institute for Theoretical Physics at the University of Leipzig, directed by Heisenberg. In his famous paper in 1928 he showed the general mathematical character of the eigenfunctions of an electron in a periodic potential: the Bloch functions. Especially, he developed a theory of the temperature-

Figure 11. Electrical conductivity of ZnO as a function of oxygen pressure (after [45]).

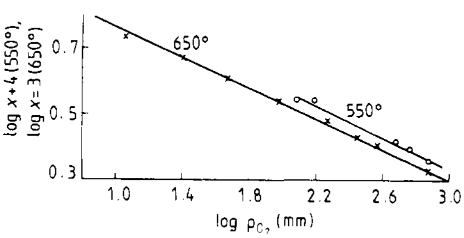


Table 2. Semiconducting compounds known in 1950.

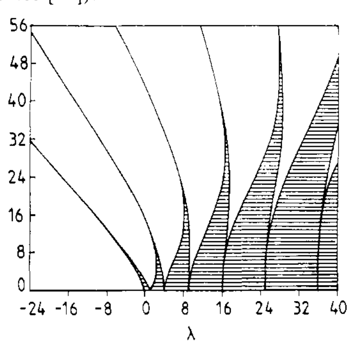
Excess conductors
Al_2O_3, TiO_2, V_2O_5, Fe_2O_3, CuO, Cu_2O_3, ZnO, MoO_3, ScN, Nb_2O_5, CdO, CdS, CdSe, SnO_2, SnSe, Cs_2S, Cs_2Se, BaO, $BaTiO_3$, Ta_2O_5, WO_3, Au_2O_3, Hg_2S red, Hg_2S black, Tl_2O_3, $PbCrO_4$, Bi_2Se_3, U_3O_8, UO_3
Defect conductors
Cr_2O_3, MnO, CoO, Co_3O_4, NiO, CuI, Cu_2O, Cu_2S, Cu_2Se, Cu_2Te, GeO, MoO_2, Ag_2O, SnO, SnS, Sb_2S_3, Tl_2O, Tl_2S, Bi_2O_3, Bi_2S_3, Bi_2Se_3, Bi_2Te_3
Amphoteric conductors
SiC, Cr_5O_9, Mn_2O_3, Mn_3O_4, Co_3O_4, Ge, RuO_2, Os_2S_2, IrO_2, PbO, PbS, PbSe, UO_2

dependence of the electrical conductivity of metals, which lead to the well known T^5 law at low temperature. But Bloch did not try to give any explanation for the existence of metals, insulators or semiconductors.

This is the merit of Alan Wilson who was a student of R H Fowler at Cambridge. In 1931 he spent about a year at the Leipzig Institute where he found a very inspiring scientific atmosphere. He drew the conclusions from Strutt's and Bloch's calculations and was the first to explain the difference between metals and insulators based on his idea of filled and empty energy bands. Alan Wilson, from London, is the real father of the *band theory* of *solids* which has dominated solid state physics ever since. Bloch apparently was very reluctant at first to accept Wilson's ideas, but he finally agreed.

In 1931 Wilson produced his classic papers [50, 51] on semiconductors and distinguished between 'intrinsic' and 'extrinsic' semiconductors, by taking account of the presence of *donors* and *acceptors*. The scheme is shown in figure 13. Wilson's model immediately explains the exponential increase of the concentration of the charge

Figure 12. Floquet's solution of Mathieu's differential equation. Shaded areas real, white areas imaginary solutions (after [47]).



Alan H Wilson (by courtesy of Sir Alan Wilson).

carriers, electrons and holes, with temperature. That the empty states in the nearly full band, the holes, are equivalent to positively charged carriers was shown by Heisenberg also in 1931 [52]. The existence of electrons and holes explains the different signs of the Hall coefficient observed in semiconductors.

As late as 1939, just before World War II, Gudden gave a seminar in Zürich. He still was extremely pessimistic with respect to semiconductor physics, especially as far as theory was concerned, and he did not believe in the existence of *intrinsic* semiconductors. He was right insofar as at that time no clear cut case was known. The answer to this question was given only by research on the *semiconducting elements* silicon and germanium done at Purdue University under the direction of Professor Lark-Horovitz [53], during and after the war. Since this time semiconductor physics and chemistry have been among the most important fields in fundamental and applied science of condensed matter.

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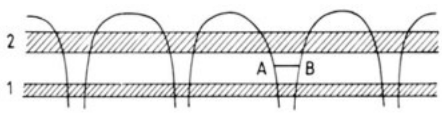
Figure 13. A H Wilson's first energy band diagram of an extrinsic semiconductor.



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