



## Solid State Physics 1925-33: Opportunities Missed and Opportunities Seized

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## Solid state physics 1925–33: opportunities missed and opportunities seized

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### THE PERIOD UP TO 1929

The discovery of the electron by J. J. Thomson in 1897 enabled P. Drude to produce in 1900 what seemed at first to be a very satisfactory theory of the electrical and thermal conductivities of metals. In 1904–5, H. A. Lorentz gave an improved mathematical formulation of Drude's theory but without essentially adding anything to its physical content. However, as endeavours were made to embrace more and more of the properties of metals within the theory, it became clear during the next decade or so that it was impossible to encompass all of them without introducing a number of *ad hoc* and conflicting assumptions. The theory therefore fell into a state of disrepute and disorder which is well portrayed in the Report of the Solvay Conference of 1924.

It was not until 1925 that a theory could have emerged which would have been an advance on that of Drude and Lorentz, the occasion being the publication by W. Pauli of his paper 'Über den Zusammenhang des Abschlusses der Elektronengruppen im Atom mit der Komplexstruktur der Spektren.' This formulated the Exclusion Principle in the following words (slightly simplified):

Es kann niemals zwei oder mehrere äquivalente Elektronen im Atom geben, für welche die Werte aller Quantenzahlen ... übereinstimmen. Ist ein Elektron im Atom vorhanden, für das diese Quantenzahlen ... bestimmte Werte haben, so ist dieser Zustand 'besetzt'.

Eine nähere Begründung für diese Regel können wir nicht geben, sie scheint sich jedoch von selbst als sehr naturgemäss darzubieten.

Pauli did not go on to extend his Exclusion Principle to the conduction electrons in a metal. Neither did E. Fermi, though he is often credited with having done so. The paper published in 1926 in which the Fermi distribution function is introduced is entitled 'Zur Quantelung des idealen einatomigen Gases', and its abstract is as follows:

Wenn der Nernstsche Wärmesatz auch für das ideale Gas seine Gültigkeit behalten soll, muss man annehmen, dass die Gesetze idealer Gase bei niedrigen

Temperaturen von den klassischen abweichen. Die Ursache dieser Entartung ist in einer Quantelung der Molekularbewegungen zu suchen.

He goes on to say:

Bei allen Theorien der Entartung werden immer mehr oder weniger willkürliche Annahmen über das statistische Verhalten der Moleküle, oder über ihre Quantelung gemacht. In der vorliegenden Arbeit wird nur die von Pauli zuerst ausgesprochene... Annahme benutzt, dass in einem System nie zwei gleichwertige Elemente vorkommen können, deren Quantenzahlen vollständig übereinstimmen. Mit dieser Hypothese werden die Zustandsgleichung und die innere Energie des idealen Gases abgeleitet; der Entropiewert für grosse Temperaturen stimmt mit der Stern-Tetrodeschen überein.

In addition to assuming the Pauli principle, Fermi used the old quantum theory to determine the allowed energy levels of the individual atoms by supposing that they behaved like harmonic oscillators with quantum numbers  $s_1, s_2, s_3$  ( $s_i = 0, 1, 2, \dots$ ) and energies  $h\nu s$ , with  $s = s_1 + s_2 + s_3$ . Then, if the total number of atoms is  $N$  and the total energy is  $Eh\nu$ ,

$$\sum N_s = N, \quad \sum s N_s = E, \quad (1)$$

where  $N_s$  is the number of atoms with quantum numbers  $s$ . The number of complexions for given  $s$  is

$$Q_s = \frac{1}{2}(s+1)(s+2)N, \quad (2)$$

and the number of arrangements of the  $N_s$  atoms over the  $Q_s$  levels complying with the Pauli principle is

$$W_s = Q_s!/[N_s!(Q_s - N_s)!]. \quad (3)$$

Hence, maximizing  $W_s$  subject to the conditions (1), we have

$$N_s = Q_s \alpha e^{-\beta s} / (1 + \alpha e^{-\beta s}). \quad (4)$$

This is the first appearance of the Fermi function, but, though the derivation is correct according to the assumptions made, Fermi (or Pauli) statistics is inapplicable to structureless monatomic gases (i.e. gases whose atoms have no uncompensated electronic or nuclear spin). The same error was made by P. A. M. Dirac later in 1926 in his paper 'On the theory of quantum mechanics', and perhaps with less justification. Fermi based his arguments on the old quantum theory, whereas Dirac wrote in the context of the new quantum theory. Starting from the consideration that the Hamiltonian of a system of indistinguishable particles is a symmetrical function of the coordinates of the individual particles, Dirac correctly deduced that the wavefunction must be either a symmetrical or an antisymmetrical function of those coordinates. To comply with the Pauli principle, symmetrical wavefunctions must be excluded. Dirac wrote, 'The solution with symmetrical eigenfunctions must be the correct one when applied to light quanta, since it is known that the Einstein-Bose statistical mechanics leads to Planck's law of black-body radiation. The solution with antisymmetrical eigenfunctions, though, is probably the correct one for gas molecules, since it is known to be the correct one for electrons in an atom, and one would expect molecules to resemble electrons more closely than light

quanta.' Dirac's mistake, like Fermi's, is, of course, the omission of the spin of the electron. But whereas the electron was considered to be a structureless mass point in 1925, in 1926 the hypothesis of G. E. Uhlenbeck & S. Goudsmit, that the electron possessed an intrinsic spin, was generally accepted, and it therefore followed that the eigenfunctions of an ideal spinless gas should be symmetrical functions of the space coordinates, and that Fermi-Dirac statistics is not applicable to such a gas.

The first practical as distinct from theoretical problem to which the Fermi-Dirac statistics was correctly applied was that of the behaviour of White Dwarf stars. In what is probably his most important paper, published late in 1926 and entitled 'On dense matter', R. H. Fowler put forward the hypothesis that matter in a White Dwarf consists of bare nuclei and free electrons, and that the ultimate fate of a White Dwarf is to become a Black Dwarf similar to a single gigantic molecule in its lowest quantum state, the specific heat of the condensed electron (and nuclear) gas being effectively zero.

This major step forward, though acclaimed by astrophysicists, received scant attention by physicists, and a paper by Pauli, published early in 1927 and entitled 'Über Gasentartung und Paramagnetismus', received little more. Pauli wrote:

Die ... von Fermi herrührende Quantenstatistik des einatomigen idealen Gases wird auf den Fall von Gasatomen mit Drehimpuls erweitert ... Betrachtet man die Leitungselektronen im Metall als entartetes idealen Gas – was gewiss nur als ganz provisionel anzusehen ist – so gelangt man auf Grund der entwickelten Statistik zu einen wenigstens qualitativen theoretischen Verständnis der Tatsache, dass trotz des Vorhandenseins des Eigenmomentes des Elektrons viele Metalle in ihrem festen Zustand keinen oder nur einen sehr schwachen und annähernd temperaturunabhängigen Paramagnetismus zeigen.

This paper was largely taken up by a discussion of the difference between Einstein-Bose and Fermi-Dirac statistics, and, except for the derivation of the paramagnetic susceptibility, contained very little of physical interest. It will be seen that in this paper Pauli is far from insisting that the conduction electrons in a metal should definitely be treated as a degenerate gas, but anyone really familiar with the Drude-Lorentz theory of metallic conduction could have seen in a combination of Fowler's and Pauli's papers a key to the solution of the difficulties that had beset the theory. The most outstanding stumbling block (there were many more) was, on the one hand, the necessity for the number of the conduction electrons to be of the order of one per atom, and, on the other hand, for the number to be negligibly small. The first requirement arose from the magnitude of the Hall coefficient, while the second was the basis for one explanation of the fact that the specific heat per atom was the same for insulators and conductors. These requirements could now be reconciled, but it was not until a year later (1928) that Sommerfeld published his paper 'Zur Elektronentheorie der Metalle auf Grund der Fermischen Statistik', which is the real starting point for the major developments that were to follow.

Why had it taken so long to arrive at this point? So far as Fermi and Dirac are

concerned the answer probably is that they were much more interested in general theory than in specific applications. But Fowler and Pauli were interested in applications but missed the main one. I knew Fowler well, but I only met Pauli once – in Copenhagen in April 1931. When I brought the subject up with Fowler, he said ‘I had the thing right under my nose but I couldn’t see it was there. I kick myself whenever I think of it.’ Pauli was more explicit. He had been engaged over many years in dealing with various magnetic problems by means of the old quantum theory, with varying success. Some problems could be solved satisfactorily, others yielded to a mixture of sound theory and currently unfounded conjectures, while others were quite intractable. One of the problems of the third kind was the weak paramagnetism of the alkali metals. But he had left this somewhat narrow field behind him for the more exciting developments which led to the birth of the new quantum mechanics. However, when the papers of Fermi and Dirac appeared, it occurred to Pauli in a flash that here was the solution to a minor problem which had long been troubling him. But once he had written his paper, solid state magnetic problems were to him a completed chapter, and it never occurred to him that there might be another more exciting chapter on a related theme. His main interest was to establish his theory of the spinning electron.

To revert to Sommerfeld, he took over Lorentz’s theory in its entirety, but with the free electrons obeying the Fermi–Dirac statistics instead of the classical, Maxwellian, statistics. It was therefore essentially a phenomenological theory depending upon two parameters,  $n$ , the number of free electrons per unit volume, and  $l$ , the mean free path of the electrons. Since the specific heat of the electrons was negligible compared with that of the lattice vibrations, except at very low temperatures,  $n$  and  $l$  could be deduced purely from the conduction phenomena.

The theory of the Hall effect showed that  $n$  must be of the same order of magnitude as the number of atoms per unit volume, and, to obtain the correct value of the conductivity, for example for silver at room temperature, the mean free path  $l$  had to be of the order of 100 interatomic distances and be proportional to  $1/T$ . This behaviour of the mean free path was inexplicable on any classical collision theory, and the correct explanation was given by F. Bloch in 1928 by a thoroughgoing application of quantum theory, on the assumption that a single-electron theory was adequate for this purpose.

It was shown by G. Floquet in 1883 that the fundamental solutions of any linear differential equation  $L[f] = 0$ , with one independent variable  $x$ , whose coefficients are periodic functions of  $x$  with period  $2\pi$ , are of the form  $f(x) = e^{\mu x}u(x)$ , where the exponent  $\mu$  is either complex or purely imaginary and where  $u(x) = u(x + 2\pi)$ . Now the potential energy of an electron moving in a crystal lattice must have the same periodicity characteristics as those of the lattice, and Bloch generalized Floquet’s theorem to show that the wavefunction of such an electron must be of the form  $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r})$ , where  $u_{\mathbf{k}}(\mathbf{r})$  has the periodicity of the lattice. In other words, provided that  $\mathbf{k}$  is real, the wave function of an electron in a crystal lattice is a modulated plane wave spread over the whole crystal, and a conduction electron

can be conveniently described as a quasi-free electron. Houston (1928) had also arrived at a similar conclusion.

In accordance with the concepts outlined above, a non-zero electrical resistance can only arise in a metal if the atomic lattice is imperfect, the major source of the imperfections being the thermal vibrations of the metal ions. Once this was realized, it was possible to give a physically plausible explanation of the magnitude and temperature variation of the mean free path, and Bloch gave a detailed mathematical derivation of the appropriate formulae.

The most difficult part of the calculation was the determination of the eigenvalues of the quasi-free electrons. For, whereas Floquet's theorem gives precise information about the form of the eigenfunctions, it only gives qualitative and not quantitative information about the eigenvalues. Bloch therefore had recourse to the following approximate method.

If, for simplicity, we consider a perfect simple cubic lattice with lattice constant  $a$ , a conduction electron moves in a field in which its potential energy is of the form

$$V(\mathbf{r}) = \sum_{\mathbf{g}=-\infty}^{\infty} U(\mathbf{r} - \mathbf{g}a), \quad \mathbf{g} = (g_1, g_2, g_3), \quad (5)$$

where the  $g$ 's are integers. Bloch assumed that the wave functions were of the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{g}=-\infty}^{\infty} C_{\mathbf{g}} \phi(\mathbf{r} - \mathbf{g}a), \quad (6)$$

and he made the further assumption that the integral

$$J(\mathbf{g}, \mathbf{h}) = \int \{V(\mathbf{r}) - U(\mathbf{r} - \mathbf{g}a)\} \phi(\mathbf{r} - \mathbf{g}a) \phi(\mathbf{r} - \mathbf{h}a) d\mathbf{r} \quad (7)$$

is only non-zero for  $\mathbf{g} = \mathbf{h}$  or when one of  $g_1, g_2$  and  $g_3$  differs from  $h_1, h_2$  and  $h_3$  by unity. That is, when the electron can, in the zero approximation, be considered to be tightly bound to the atom  $\mathbf{g}$ , and in the first approximation to have a small probability of moving to the vicinity of the six neighbouring atoms. With these approximations, Bloch deduced that the ground state energy level  $E_0$  of an isolated atom gave rise to  $G^3$  energy levels in a metal containing  $G^3$  atoms, and that these energy levels were given by the formula

$$E_{\mathbf{k}} = E_0 - \alpha - 2\beta (\cos ak_1 + \cos ak_2 + \cos ak_3), \quad (8)$$

where  $\alpha = J(\mathbf{g}, \mathbf{g})$  and  $\beta = J(g_1, g_2, g_3; g_1 + 1, g_2, g_3)$ , (9)

the  $C_{\mathbf{g}}$  being given by  $C_{\mathbf{g}} = \exp(i\mathbf{k} \cdot \mathbf{g}a)$ . (10)

Bloch further showed that the velocity  $\mathbf{v}$  of an electron with the wavefunction  $\psi_{\mathbf{k}}(\mathbf{r})$  is given by  $\hbar\mathbf{v} = \text{grad}_{\mathbf{k}} E_{\mathbf{k}}$ . For tightly bound electrons with the energy spectrum (8), the current is given by

$$v_i = (2\beta a / \hbar) \sin ak_i. \quad (11)$$

The next major contribution was made by Peierls in 1929 in a paper entitled 'Zur Theorie der galvanomagnetische Effekte'. In order to calculate the electrical conductivity of his model, Bloch had shown that the mean wavevector  $\bar{k}$  of a wave packet was connected with the applied electric field  $\mathcal{E}$  by the relation

$$d\bar{k}/dt = (-e/\hbar)\mathcal{E}, \quad (12)$$

where  $-e$  is the electronic charge, and hence that, with  $v$  given by (11), the acceleration of an electron due to a field  $(\mathcal{E}, 0, 0)$  is

$$\frac{dv_1}{dt} = \frac{dv_1}{dk_1} \frac{dk_1}{dt} = -\frac{2\beta a^2}{\hbar} e\mathcal{E} \cos ak_1. \quad (13)$$

Commenting on the physical significance of this last equation Peierls stated, 'Diese Gleichung hat folgende merkwürdige Konsequenz: Für  $k_i > \frac{1}{2}\pi/a$  nimmt mit wachsendem  $k_i$  der Strom ab, das heisst im Felde wird ein solches Elektron verzögert, statt beschleunigt zu werden. Diese Tatsache ist so unanschaulich dass es notwendig erscheint ihre Richtigkeit möglichst ohne Vernachlässigungen und Annahmen zu beweisen.' Peierls succeeded in this, and he went on to use (13) to explain the existence of anomalous (that is, positive) Hall coefficients. If the conduction electrons were such that the wave numbers  $k_1 = k_2 = k_3 = k_0$  of the highest filled energy level were less than  $\frac{1}{2}\pi/a$ , the Hall coefficient would be negative. If, on the other hand,  $k_0$  lay in the range  $(\frac{1}{2}\pi/a, \pi/a)$ , the Hall coefficient would be positive.

This discovery gave a rational explanation of the existence of both negative and positive Hall coefficients, and completely cleared up a major mystery, to account for which more than twenty implausible theories had been advanced since 1879.

#### THE PERIOD 1929-33

By the middle of 1929 the state of knowledge was as follows. By making the heroic assumption that the valency electrons in a perfect crystalline solid were not firmly bound, each to a single atom, but had a non-zero chance of jumping to a neighbouring atom, the electrical properties of metals had for the first time been given a rational explanation. The valency electrons could be considered to be quasi-free, and, surprisingly, the energy spectra of quasi-free electrons were such that they could result either in negative (normal) Hall effects or positive (anomalous) Hall effects. However, a number of substantial criticisms could be levelled at the theory. It is sufficient to give two examples.

In the first place, the problem had only been made tractable by neglecting the electrostatic forces between the valency electrons, except in so far as they could be deemed to give rise to a smeared field having the same symmetry as that due to the atomic nuclei and the core electrons. This meant neglecting the exchange forces between the valency electrons, the dominant effect of which was the basis for the theory of ferromagnetism, first put forward by Heisenberg in 1928.

In the second place, while Bloch's theory, as supplemented by Peierls, gave

satisfying explanations of the electrical and thermal conductivities and the Hall effect both at room temperatures and at low temperatures, it had not had the same success in dealing with the magneto-resistance effect: the increase in the electrical resistance produced by a uniform magnetic field. Various theories had indeed been put forward, but they had not stood up to detailed criticism. Simplifying assumptions had to be made to permit a rudimentary start on these and other problems, and it was not easy to light upon assumptions that were sufficiently plausible.

It was at this stage that I first became interested in the theory of metals, largely because P. Kapitza, who was then working in Cambridge, published a number of papers on the electrical resistance of bismuth crystals in strong magnetic fields (1929). In these pioneering experiments Kapitza used magnetic fields of up to 200 000 G (20 T) and worked at temperatures down to liquid air, and he came to the conclusion that the change in resistance was proportional to the magnetic field, but that this linear behaviour was masked in weak fields by disturbances in the metal that are equivalent to that produced by an inner magnetic field.

I had not got very far in tackling this problem when I was extremely fortunate in receiving the offer of a Rockefeller Travelling Fellowship, and I decided to spend the best part of a year in Leipzig, interspersed with shorter stays in Copenhagen. I arrived in Leipzig in the first week in January 1931, and Heisenberg immediately pressed me into giving a colloquium on magnetic effects in metals, remarking 'Peierls' work is undoubtedly important, but the mathematics is complex and the physical ideas not easy to disentangle. We ought to have a thorough discussion of the whole subject, and, as you have more free time than the rest of us, would you agree to give the first talk?' I had studied Peierls's papers and had not found them too easy, and though I thought I had understood them well enough for my own purposes, to give a colloquium on them, and in German, was a formidable task. I had to find ways of shortening and simplifying the arguments. I was unsuccessful for a couple of weeks, but just at the end of January it suddenly occurred to me that the Bloch-Peierls theories could be enormously simplified and made intuitively more plausible if one assumed that quasi-free electrons, like valency electrons in single atoms, could form either open or closed shells.

Bloch's theory had in fact proved too much. Before his paper appeared it was difficult to understand the existence of metals. Afterwards it was the existence of insulators that required explanation. This problem had been by-passed because it had been taken for granted that insulators were merely bad conductors rather than non-conductors, the difference between metals and insulators being a quantitative and not a qualitative one. This concept I now challenged.

I went to see Heisenberg the next day and told him that I wanted to change and broaden the subject for the colloquium which was scheduled to take place two weeks later. I expounded my thoughts to Heisenberg who grasped the significance of them at once and fetched in Bloch from the adjoining room to take part in the discussion. Bloch was highly sceptical and stuck to the view that insulators were substances for which the overlap integral  $J(\mathbf{g}, \mathbf{h})$  (defined in (7) above) was negligibly



small. As a refutation of my hypothesis, he pointed out that it would entail the monovalent elements being metals while the divalent alkaline earth elements would be insulators.

The discussion ended there for that day, but it was resumed on the following morning, by which time I had marshalled arguments against Bloch's views, which had depended upon the energy spectra of one-dimensional and three-dimensional lattices being qualitatively similar. I pointed out that, whereas in one dimension the number of states in each energy band is equal to the number of atoms, a similar result does not necessarily obtain in three dimensions; the energy levels split up into bands, but the bands can overlap. It therefore followed that an elemental solid (that is, composed of atoms, not molecules) with an odd valency had to be a metal, whereas elements with an even valency might produce either a metal or an insulator.

Bloch was eventually convinced, but the arrangements for the colloquium were changed, the reason being that the experimental physicists in Leipzig were far from certain what the real differences were between metals, semi-metals and insulators. In the end, two colloquia were held, some 3 months apart, the second of which was attended by a large contingent from Erlangen, headed by B. Gudden.

The most recent survey of the conductivity of solids had been written by E. Grüneisen (1928) for the *Handbuch der Physik*, in which solids were classified as metals, semi-metals and insulators according to the shapes of their resistance-temperature curves. He defined a semiconductor as a metallic conductor, the resistance of which was high at low temperatures but which diminished with increasing temperature until a minimum was reached, whereafter it increased. As examples of such substances he cited boron, silicon, titanium, zirconium, germanium, selenium, graphite and various alloys. However, more recent work had tended to show that the peculiar shapes of the resistance curves of the above substances might well be due to the presence of poorly conducting oxide layers, and, if they could be purified sufficiently, they would be found to be metals.

The first colloquium failed to clarify the situation, and I therefore wrote a paper for the Royal Society giving details of my theory of the difference between metals and insulators, but leaving open whether true semiconductors existed, that is, whether there were insulators with so small an energy gap that, at room temperature, electrons could be thermally excited from a full band to the next higher one.

The next colloquium was much more fruitful, largely because Heisenberg had drawn my attention to Gudden's view (1930) that no pure substance was ever a semiconductor, and that the conductivity of such conductors is due to the presence of impurities. These impurities could be either electropositive or electronegative according as they gave rise to negative or positive Hall effects. In other words, the impurities could act either as donors or acceptors of electrons. The mechanism by which free electrons could be produced in an otherwise empty energy band, or free holes in an otherwise full energy band, could readily be explained by a simple expansion of my theory, and this was given in a second paper.

Subsequent developments are either well known or would be better described by others. I shall therefore conclude my personal reminiscences by posing two questions, namely why were my discoveries not made earlier, and why was so little done in the 1930s to follow them up?

As regards the first question, both Bloch and especially Peierls might well have forestalled me, and they may be able to remember why they did not do so. The only clue that I can offer is a remark made by Peierls in his paper of 1930 on electrical and thermal conductivity in which he states: 'Die Eigenfunktionen sind in zwei Fällen bekannt: erstens in dem Grenzfall freier Elektronen, ... und zweitens in dem Grenzfall stark gebundener Elektronen, wo man sie nach Bloch durch ein Störungsverfahren aus den Eigenfunktionen des einzelnen Atoms verhalten kann ... Von dem zweiten Grenzfall (stark gebundenen Elektronen) weiss man wegen seinen Konsequenzen für die magnetische Suszeptibilität dass er praktisch nie realisiert ist.' With the concept of nearly free electrons uppermost in his mind, it is understandable that Peierls did not give much attention to insulators.

As regards opportunities missed or seized during the remainder of the 1930s I can speak only about Cambridge with first-hand knowledge. On my return there in October 1931 considerable interest was shown in my discoveries, but, when I suggested that germanium might be a very interesting substance to study in detail, the silence was deafening. However, I eventually got J. D. Bernal to consider the project, though he saw little hope in it. In a paper published in 1927, H. J. Seemann had investigated the temperature coefficient of the resistance of ten single crystals of silicon between  $-80^{\circ}\text{C}$  and room temperature. He found that not only was it positive but that it was of the same order of magnitude as for normal metals. (This was confirmed by Schulze in 1931.) In view of this fact, that silicon, in its pure state and freed from oxide films, was a metal, germanium would also be a metal and of no more interest than grey tin. But, since Bernal possessed a large single crystal of silicon of outstanding purity, he agreed to examine its properties. After some six months Bernal told me that he thought that Seemann was probably right, though he did not reveal his grounds for saying so. It is likely that he was merely being polite, and that the subject held no interest for him.

The canard that silicon is a good metal continued to be believed in many circles for a long time. For example, in the *Handbuch der Metallphysik*, published in 1935, both U. Dehlinger and G. Borelius stressed that all the elements which had at one time or another been classed as semiconductors were, in the pure state, true metals. Borelius ends his review ruling out the existence of semiconductors with the following statement (p. 354): 'Man kann qualitativ nur zwischen metallischen Leitern (Elektronenleiter) und elektrolytischen Leitern (Ionenleiter) unterscheiden.'

Whether anything interesting would have emerged from a proper study of germanium in the 1930s is extremely doubtful. Methods of purification would almost certainly not have been established because there were no incentives, either academic or industrial, to do so, and impure germanium is one of the least interesting of substances.

To conclude, one further gaffe is perhaps worth mentioning. For many years cuprous oxide was the most interesting semiconductor as an object both of academic study and for commercial applications. When I first discussed it in 1931(*a, b*) it was deemed to be an 'excess conductor' in which the current is carried by electrons derived from excess donor copper atoms. In 1935 it was discovered by Schottky & Waibel that in all previous measurements the Hall coefficient had been given the wrong sign, and that the current is in fact carried by holes produced by excess acceptor oxygen atoms.

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*General*

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