Early work on solids, mainly in the thirties*

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The interest in the 1920s in solid-state physics, and particularly in the physics of metals, was motivated less by the possible practical applications than by the many glaring contradictions that resulted from applying classical physics to metals, and on which the old Bohr-Sommerfeld quantum theory was no help. One example was the absence of an electronic specific heat, while the Thomson effect, which in some sense measured the specific heat of the conducting electrons, agreed with the classical expectation. The electron mean free path was in many metals greater than the atomic distance, and, in pure metals, was inversely proportional to the temperature, for which there was no explanation. The magnetic properties also were mysterious. The discovery of the electron spin provided a qualitative explanation of the paramagnetism, but predicted a greater magnitude and a temperature variation according to Curie's law. This last problem offered the first breakthrough. Fermi had applied Pauli's exclusion principle not only within one atom, but to all the electrons in an electron gas, and Pauli used the Fermi statistics to explain the constant and low value of the paramagnetism. The ball now passed to Sommerfeld, who showed that Fermi statistics could also explain the absence, at normal temperatures, of an electronic specific heat. In his positive and optimistic approach he applied the new insight to all phenomena of electric and thermal conduction in metals, with little success. One encouraging result was that the Wiedemann-Franz ratio, which depends on the ratio of electric and thermal conductivity, came out similar to the classical result, but with a different numerical coefficient, which gave a better fit to the data.

Houston and Eckart were visiting postdoctorals in Sommerfeld's group, who collaborated in this work, and Houston came close to explaining the conductivity by pointing out that the scattering of electrons by a lattice is similar to the scattering x rays, which rises with temperature because of the lattice vibrations. However, the x-ray scattering does not extrapolate to zero at zero temperature, because of the zero-point vibration of the lattice; and this remained a difficulty.

At that time (1926–1928) I was a student in Munich under Sommerfeld and absorbed all this new knowledge, but could not yet contribute—I there completed only my fifth semester of study and was still absorbing basic physics and quantum mechanics. In the spring of 1928 Sommerfeld went on sabbatical leave and sent me to Heisenberg in Leipzig, where Felix Bloch was then completing his electron theory of metals. He not only worked out the theory of electron bands, particularly clearly for the limit of tight binding, he also solved the problem of the absence of zero-temperature resistance. He saw that the dominant process was the absorption or emission of a phonon by an electron. At low temperature there are few phonons, and the electrons do not have enough spare energy to create many.

Heisenberg suggested that I look at the problem of what was then called the "anomalous" Hall effect. In some metals the sign of the effect was opposite to that expected, as if the current was being carried by positive carriers. Today the explanation is almost trivial: if the conduction band is nearly filled, the current is carried by the remaining empty places, or holes; and a hole, as the absence of an electron, indeed carries a positive charge.

But it did not look that simple at the time. I started from the fact that in the upper part of the Bloch band the electron velocity decreased with increasing wave vector. I also proved to myself that in an electric field the wave vector would increase as for a free electron. Hence such electrons would be accelerated in a direction opposite to the electric force on them. At first sight this was worrisome because it suggested that it might lead to a negative conductivity. This was soon disposed of by noting that the majority of electrons at lower energy would always give a positive contribution—in the worst case, for a full band, the total current would just cancel. I did not use the term "holes" at the time, but I showed a sketch of the Fermi surface for a nearly full band in a square lattice in two dimensions; the Fermi surface (or Fermi "line" in that case) consists of four circular arcs around the corners, and these empty corners are responsible for the current.

I remember a conversation with Heisenberg, in which he said that the situation was similar to that in atomic spectroscopy, where the spectrum of an atom with one electron missing from a closed shell was similar to that of an atom with one electron in that shell. Unfortunately I cannot remember when this conversation took place. If it was at the beginning, when he suggested the problem, then he knew the answer all along, and I only had to work out the details. If it was when I presented my result to him, it merely shows how quickly he appreciated the situation. I believe the second is likely to be true, but cannot prove it.

It is interesting that the idea that a full band did not conduct, and that insulators were substances with all filled bands, was not generally appreciated. A. H. Wilson reports that Bloch refused to believe it when Wilson

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made that point to him. (Bloch confirmed that to me.) Of course we now know from the work of Mott and Anderson that not all insulators are of that type.

The work on the Hall effect led in 1928 to my first paper, which understandably gave me some pride. There remained, however, a nagging doubt. The result depended on the shape of the energy spectrum of the Bloch band; in particular, on the fact that the energy surface had a horizontal tangent normal to the zone boundary. This had been shown only for the case of tight binding, which is not very realistic. So had I built the whole theory on false foundations?

The resolution came more than a year later, when I looked at the extreme opposite, the case of nearly free electrons in a weak periodic potential. The potential is then a small perturbation, which does not greatly affect the electron states, except near the zone boundaries, where the matrix elements of the potential connect states of almost the same energy. When the matrix element is of the same order as the energy difference of the states involved, one has to use perturbation theory for almost degenerate states. This device was well known, used, for example, in the theory of the Zeeman effect. But I did not know it and had to invent it for myself. In this way it became evident that the periodic potential would cause energy gaps at the zone boundaries, and that the energy surface acquired a zero slope at the boundary. In other words, the behavior was qualitatively the same for weakly as for strongly bound electrons and therefore could be believed generally. I worked this out only for the case of one dimension, which was enough to dispose of my worry. Brillouin wrote the general theory, that of the Brillouin zones.

By this time I had left Leipzig, since Heisenberg, in turn, had gone on sabbatical leave, and I was working with Pauli at the ETH in Zurich. Pauli had become interested in lattice vibrations. This was a field in which much progress had been made already with the use of the old quantum theory. Through the work of Einstein, of Born and von Kármán, and of Debye, the specific heat of nonmetals was quite well understood. Debye had also pointed out that the thermal conductivity of nonmetals depended on the nonlinear or "anharmonic" effects in the lattice dynamics, which were also responsible for the absorption of sound waves. He had also made a theory of thermal conductivity. Pauli had attempted to describe the absorption of sound waves, but got mixed up. (A summary of a talk by him at a meeting is, I believe, the only incorrect published statement in Pauli's name.) He asked me to look at the problem of anharmonicity and showed me his notes, from which I eventually realized what had gone wrong.

It was clear that for the anharmonic effects a crucial part was played by the conservation of pseudomomentum (or "quasimomentum" or wave vector), which in a uniform medium would be exact, but which in a crystal allows transitions, such as Bragg reflections, in which the pseudomomentum changes by a given amount. For such transitions in the anharmonic regime, I used the term "umklapp processes." In their absence the heat conductivity of a perfect crystal would become infinite, since a stream of phonons could not be arrested by their anharmonic interactions any more than a stream of gas in a smooth tube is stopped by the collisions between the molecules. Umklapp processes require the participation of fairly short-waved phonons, and as these are exponentially rare at low temperature, the thermal conductivity of a perfect crystal should increase exponentially at low temperatures. This is indeed true, but it was not found experimentally until 1951.

Part of this delay was due to my disgracefully failing to realize that "perfect" for this purpose means also isotopically pure, since different isotopes differ in their mass and hence in their response to vibrations; they scatter phonons like impurities. Pomeranchuk made this point about 1943, but we did not see this paper until much later.

These results were in fundamental disagreement with the theory of Debye, which had predicted a finite thermal conductivity even for a continuous medium. The reason is that, in his usually ingenious way of choosing simple but powerful approximations, he had treated the effect as the scattering of sound waves by density fluctuations caused by the phonons, which, because of the nonlinear effects, give fluctuations in the sound velocity, i.e., the refractive index for sound waves. This is analogous to the scattering of light by density fluctuations, and Debye used the standard result for that phenomenon. In doing so, he overlooked the fact that the standard theory assumes static density fluctuations, which is perfectly good for light scattering, because the fluctuations move so much more slowly than light. It does not work for sound, because the density fluctuations are due to phonons, whose velocities are, of course, of the order of the sound velocity.

The experience with pseudomomentum conservation made me think how this applied to the electric conduction in metals. In some circumstances, depending on the size and shape of the Fermi surface, there should also be a shortage of umklapp processes in the interaction of electrons and phonons. But there was no sign of this in the data, which seemed to agree perfectly well with the theory of Bloch, which assumed that the distribution of phonons was always kept in statistical equilibrium. This remained a mystery for me for many years, until I realized that the figures given for the electric resistivity of perfect metals were not measured directly, but derived from data on the unavoidably impure specimens by relying on Matthiessen's rule, which states that the ideal resistivity and the "residual" resistivity due to impurities are additive. There is no theoretical reason for this rule, and, in fact, the presence of impurities can ensure that the excess pseudomomentum is disposed of. So, extremely pure metals should at low temperatures show a deviation from the simple Bloch-formula-plus-a-constant law. This "phonon-drag" effect was indeed found in the 1970s.

One problem that caused great headaches to people concerned with electric conductivity was the magne-

toresistance. Sommerfeld had tried to estimate this in formulating his version of the electron theory of metals, but the calculated effect was too small by four orders of magnitude. Bloch, who tried to invoke spin paramagnetism, failed by a similar margin. I produced a theory that predicted a form for the variation of the resistance with magnetic field that would be closer to the data than previous theories, and was going to present this to a conference, when I discovered, on the day before the conference, that the coefficient in front of my law would be zero.

The mystery was solved, independently by Hans Bethe and myself, by the remark that if all electrons carrying the current have the same effective mass and the same mobility, the effect of the magnetic field cancels out identically. In fact, even in a single conduction band there are variations in the mobility for electrons moving in different directions. This seemed at first surprising, because one tried to associate it with lack of isotropy of the Fermi surface; yet the alkalis, whose Fermi surface is spherical with spectacular accuracy, show magnetoresistance of the same order as other metals. The answer lies in the lack of isotropy of the phonons. The effective mass of the electrons is, at least for small wave vectors, a tensor of the second rank, and, in a cubic crystal, must therefore be isotropic. The kinematics of the phonons depends on the elastic constants which form a fourth-rank tensor, and are therefore anisotropic even with cubic symmetry. These ideas could explain the magnitude of the effect, but not the linearity, over a wide range, of the resistance as a function of the magnetic field. This puzzle was solved only many years later by the brilliant work of I. M. Lifshitz and his group.

Landau had made an elegant theory of the diamagnetism of free electrons. It seemed a challenge to extend this to real electrons in a metal, in the presence of the lattice potential and of collisions. For a long time I was stuck with the fact that the perturbations from the free-electron picture were much greater than the small spacing between the magnetic levels. It took me some time to understand that, while perturbation theory may be invalid for individual eigenstates, it can still be applied to the partition function, provided only that the perturbation is less than kT. This gave me the tool required to discuss diamagnetism in general. One conclusion from this was that the diamagnetic susceptibility depends on the energy function at the Fermi surface, and this eventually helped to explain the high susceptibility of bismuth.

It was clear that at low temperatures the picture would be more complicated, and when I went back to the free-electron gas, I saw that there would be a tendency to oscillations, evenly spaced in $1/B$. This was exactly what was found in Bi by de Haas and van Alphen. I was happy with this "discovery," but, in fact, I had failed to notice that the result was already given in Landau's basic paper. He did not regard it as of practical interest because he had been assured by Kapitza that the effect was too small to be observed. He did not know of the de Haas–van Alphen effect.

For quantitative answers, one required some difficult integrals, and these were worked out numerically with the assistance of Maurice Blackman. Later Landau showed how they could be done analytically.

By this time, in 1933, there were many exciting things happening in physics to tempt me away from metals. I did, however, return to the conduction problems when there appeared a paper by a German physicist, Kretschmann, who attacked much of the current electron theory as invalid. One of his claims was that the use of perturbation theory for the collisions of electrons with phonons or impurities was invalid. I felt annoyed by this attack and sat down to answer his objections, in particular to justify the use of perturbation theory. It came as a shock to find that a condition on the validity of perturbation theory appeared to be that $\hbar/\tau$ (τ=collision time), which is a measure of the strength of the collisions, be small compared to kT. Estimates for real metals showed that the two quantities were roughly of the same order of magnitude: sometimes one was smaller, sometimes the other. The situation was very worrisome until Landau produced an elegant argument showing that the condition was not, in general, necessary, but that it was sufficient for $\hbar/\tau$ to be small compared to the Fermi energy, which is usually all right.

Through contact with Pauli I had become interested also in quantum electrodynamics, and in 1933–1934, when Hans Bethe and I were together in Manchester and in touch with the Cavendish Laboratory in Cambridge, we got excited about nuclear physics. But there was one interlude, which I suppose counts as condensed-matter physics: In W. L. Bragg's laboratory in Manchester there was much interest in superlattices in alloys, which was there handled by what we now call a mean-field approximation, which we did not find convincing. Hans and I spent many hours devising ways of improving the treatment. Eventually he came up with what is now known as the "Bethe method." To show how it worked, he had to cover stacks of paper with counts of configurations—no computers, of course, in 1934. I then applied his method to adsorbed layers and to alloys of varying composition.

I returned again to solid-state theory on two occasions, each time as a reaction to somebody else making a claim with which I disagreed. One was a claim (I do not remember by whom) that thermal expansion made the usual expansion in terms of small displacements of atoms invalid. He had evidently not understood the existence of long-range order in a crystal, and that induced me to think about long-range positional order. I found one could prove its existence in three dimensions, and its absence in one dimension. The case of two dimensions was marginal; I said it also had no positional long-range order, which was technically correct, but practically misleading, since the disorder grows only logarithmically and therefore is immaterial in most practical specimens.

The other occasion was a seminar in which someone reported on Ising's paper, which showed that the Ising model had no long-range order in one dimension. The

speaker then proceeded to give a proof that the same was true in two and three dimensions. I knew this was wrong, but instead of trying to find his error, I decided to prove the opposite, which for two dimensions proved very easy.

My last prewar excursion into problems of solids was at the suggestion of Orowan. He had thought of a model for a dislocation, which might give an estimate of the force required to move it. But he did not want to take the trouble to write down the equations for it and asked me to do so. I found the model led to a nonlinear integral equation, and I had the surprise of my life when I saw that this had an elementary exact solution. I wanted Orowan to sign the paper, but he refused, and, thinking the matter unimportant, I did not insist. Later Nabarro extended the calculation to screw dislocations and, more importantly, corrected a major numerical error in my result. So the result is now called the "Peierls-Nabarro force," but should really have Orowan's name attached.

I am conscious of the fact that this essay concentrates on my own work—it was meant as personal recollections, and it is natural that one's recollections of one's own work are the clearest. It goes without saying that during the thirties many important steps were taken by others. Besides those already mentioned, a balanced summary of the growth of solid-state theory during the period should certainly include at least Mott's many contributions, including the description of the photographic process, A. H. Wilson's work on semiconductors, Bardeen's analysis of the electron-phonon coupling, Fowler and Nordheim's work on cold emission, Néel on antiferromagnetism, and Wigner and Seitz on metal binding energy. The last meant the start of the modern quantitative treatment of solids and disproved the view I had always taken of the field as an area full of interesting and useful qualitative insights to be obtained, but resisting any accurate quantitative approach.