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CURRENT PROBLEMS IN RESEARCH

Superconductivity: A Solved Problem?

Modern theoretical physics has come close to explaining this hitherto baffling phenomenon.

H. W. Lewis

In the first quarter of the 20th century, there was no shortage of phenomena of low-energy atomic, molecular, or solid-state physics which defied rational explanation in terms of the physical theories of the time. To be sure, a major breakthrough had occurred with the explanation of the spectrum of the hydrogen atom in terms of the old quantum theory, but efforts to extend this theory to systems involving more than one electron met with only limited success.

This situation changed dramatically in the middle and late 1920's with the development and exploitation of wave-mechanics, and problem after problem fell before the magnificent new theory. Indeed, it was soon apparent that there was no phenomenon in the area of atomic and molecular physics which would not be correctly explained by the new quantum mechanics, were we only able to solve the relevant equations. This was, of course, no small matter, but as the approximations improved, the agreement with experiment improved, and there was no substantial body of opinion which doubted that we were, at last, dealing with the correct theory.

Against this background of success, however, there stood, more and more isolated, two gross macroscopic phenomena that defied even qualitative understanding, although one was sure that they must be explicable in terms of quantum mechanics. These were superfluidity of helium, and superconductivity. Each represented an abrupt change in the flow or transport properties of matter at extremely low temperatures: in the case of helium, the complete disappearance of viscosity at about 2 degrees of absolute temperature, and in the case of superconductivity, the complete disappearance of electrical resistance in a large number of materials at temperatures ranging from a fraction of a degree up to 18 degrees absolute. Eighteen degrees, for an intermetallic compound of niobium and tin, is now the highest known superconducting transition temperature. We will omit here further reference to the problem of superfluidity, although great progress has also been made during the past few years toward an understanding of this problem.

Properties of Superconductors and Metals

What, then, are the properties of superconductors, and what do we have to understand? The principal properties of a superconductor are that, below its transition temperature, it offers no resistance to the flow of electrical current (circulating currents in a superconducting ring continue without observable decay for as long as it has been possible to keep the samples cold), and that it behaves as a perfect diamagnet—that is, it excludes magnetic fields from its interior. Both of these properties can be destroyed by the application of a sufficiently strong magnetic field, the critical field, and the critical field is itself a function of temperature, varying from zero at the transition temperature to a maximum at absolute zero. Some believe that the diamagnetism is a more fundamental property of a superconductor than its lack of resistance, but, in fact, a theory of superconductivity must account for both phenomena.

To see why there is difficulty in explaining the absence of resistance in some metals, it is, of course, necessary to begin by asking why metals exhibit electrical resistance in the first place. Electric currents in metals are carried by electrons, which, in a perfect crystal, would be able to pass unhindered through the body of the crystal, without resistance. Resistance appears only when the electrons are impeded or scattered in their progress through the crystal, and there are two main sources of such scattering.

In the first place, the crystal may not be perfect. Such imperfections may involve granular structure, dislocations of various sorts, or impurities in the metal, all of which can serve as scattering centers and can lead to electrical resistance. Such structural defects are normally independent of temperature and are responsible for the resistance of most materials at absolute zero.

The second main source of resistance is somewhat more esoteric, but, as we shall see, more closely connected with superconductivity. This is the emission and absorption of sound waves by the electrons. This is a necessarily elegant way of saying that the atoms in a solid metal are always involved in thermal agitation, and that this thermal agitation

The author is on the staff of the department of physics, University of Wisconsin, Madison.

also destroys the perfect periodicity of the crystal, leading to scattering of the electrons, hence to electrical resistance. The quantum-mechanical version of this statement is that the ordered motion of the atoms in a solid is called a sound wave, that any irregular motion of the atoms can be described in terms of these sound waves, and that an electron which is scattered by these irregular motions exchanges energy with the sound waves. Thus, we say that the electron has emitted or absorbed a sound wave in much the same way that electrons can emit or absorb light. Since the amount of thermal agitation of the atoms in a metal is dependent on the temperature, this part of the resistance is expected to be temperature-dependent. In particular, it should vanish at absolute zero, leaving only the impurity and defect resistance. The remarkable fact about superconductors is that *all* the resistance vanishes at a finite temperature, different from absolute zero. Thus, in particular, although nothing happens to the impurities, they cease, for some reason, to be able to scatter the electrons. The explanation of this extraordinary immobilization of the scattering centers is one of the major problems of the theory. The other is to connect this property, somehow, with the unwillingness of the metal to harbor a magnetic field—its property of perfect diamagnetism, otherwise known as the Meissner effect. There have been many abortive attempts to solve these problems. We will only consider here the modern developments, which began about 1950.

Experimentally, it is not known, and can never be known, whether all metals become superconductors at a sufficiently low temperature. All that can be said is that, at the lowest temperatures obtainable, some metals are, and some are not, superconducting. With this qualification, it had been known for a long time that there seemed to be an inverse correlation between a metal's conductivity at ordinary temperatures and its tendency to become a superconductor at very low temperatures. The very good conductors, like silver, copper, and gold, do not become superconductors, while the bad ones, like lead and tin, are superconducting at quite high temperatures. However, if one made a metal into a bad conductor, by, for example, adding impurities, this did not appreciably affect its superconducting properties. Thus, the correlation appeared to be with that part of the resistivity due to the phonon or sound-wave interaction.

Isotope Effect

With this background, the stage was set for the development of a theory of superconductivity, but still no substantial progress was made until 1950, when the great breakthrough occurred. In this year, both experimental confirmation that superconductivity was connected with the phonon interactions and the rudimentary beginnings of a theoretical explanation were achieved.

The former was accomplished by the discovery of the isotope effect—that the superconducting transition temperature of a material depended upon its isotopic constitution, with the heavier isotopes exhibiting lower transition temperatures. This is a most remarkable result, and it is important to understand just what it means, independently of any detailed theory of superconductivity. As we know, a high temperature is characterized by a great deal of agitation of the atoms of a material, and a low temperature, by the fact that the atoms are nearly quiescent. Further, at a given temperature, heavier atoms (or isotopes) are considerably less agitated than the lighter atoms, because it takes more energy to agitate a heavy atom. Indeed, at the very low temperatures characteristic of superconductivity, the atomic thermal agitation has practically ceased. This means that, at very low temperatures, one would not expect the mass of an atom to be important, since the mass affects only the thermal agitation and the latter has practically disappeared. Thus, one's first guess is that superconductivity cannot depend upon the atomic mass. Yet, the isotope effect is evidence that it does, and in a very substantial way. This can only mean that superconductivity depends upon the interaction of the electrons in the metal with the sound waves, and in a way which does not depend upon the thermal agitation of the atoms, or upon thermal excitation of the sound waves. Indeed, since the superconductivity disappears at a sufficiently high temperature, one can conclude that thermal effects are antipathetic to superconductivity.

Phonon-Electron Interaction

What, then, are the possible consequences of an interaction between electrons and phonons that could conceivably lead to a theory of the superconducting phenomenon? Only two pass the test of being thermally independent, or, more specifically, available at absolute zero. Historically, the first to be thought of, in 1950, was the self-energy effect. This is exactly analogous to the corresponding electromagnetic self-energy of an electron, which is, perhaps, more familiar. The latter arises in the following way: We know that the electron acquires energy when it is placed in an electric field, and we know further that an electron serves, like any other charged particle, as the source of an electric field. The energy the electron has by virtue of being inescapably in the field of which it is itself the source is called the self-energy. Similarly, the electron in a metal produces a local phonon field, with which it interacts. The latter may be more easily understandable as a local distortion of the metallic lattice, due to the presence of the electron.

But how can this lead to an effective interaction between electrons, which is what one needs for a theory of superconductivity? The answer to this follows from the observation that electrons are indistinguishable from each other, so that an interaction of an electron with itself inevitably leads to an apparent interaction with other electrons. It was this apparent interaction which served as the basis for both Fröhlich's and Bardeen's 1950 theories of superconductivity. These theories were found wanting because of technical difficulties in their formulation, which we will not go into here, and also because it was never found possible to bridge the gap between the apparent interaction and the phenomenology of superconductors. In short, the self-energy effects led to a theory of something, but that something could never be identified with superconductivity. It is now felt by some that such effects may indeed be appreciable, but that they do not, in fact, distinguish between superconductors and nonsuperconductors.

Electron-Electron Interaction

The next step is, then, to explore the higher-order effects of the interaction between electrons and phonons, and this was done by Bardeen and his collaborators in 1957. This appears to have led to a reasonable picture of the superconducting state, though, at this writing, there is still considerable controversy about the detailed formulation of the theory—controversy which is by no means trivial.

The basic difference between this

theory and theories of the self-energy type can again be most easily understood in terms of the electromagnetic analogy. Again the electron serves as the source of an electromagnetic field, but this time the energy arises from the presence of another electron in the field. Such a description applies to the origin of electric and magnetic forces between electrons, and the analogous effect in metals leads to a phonon-induced interaction between electrons. One electron distorts the metallic lattice, and the other electron is affected by the distortion. Note that the dynamic effects of such an interaction depend upon the isotopic mass of the metal atoms, as they should, so that it is conceivable that the isotope effect can be explained by such a theory.

At first sight it might appear, from what has been said earlier about the fundamental indistinguishability of electrons, that the two interactions we have described—of an electron with itself and with another electron—are really the same. It is in fact true that the distinction between them is a matter of convenience and is more a matter of different methods of calculation than of different theories. In the end, what is hoped for is a theory of a many-electron system in a metal, in interaction with the phonons of the lattice, and such a theory must incorporate all the phenomena involved. Nonetheless, it is possible to start writing down theories with different areas of emphasis, and, as each is refined, they should tend to reveal the common truth. This is a situation not solely characteristic of the theory of superconductivity.

The most important single feature of this electron-electron interaction is that it induces transitions between degenerate states—that is, between states which have the same energy. To see this, consider a pair of electrons that have equal and opposite momenta, so that the total momentum of the state under consideration is zero. When these electrons scatter each other (because of the phonon-induced interaction) the conservation of momentum tells us they will still have equal and opposite momenta, though in different directions, and the conservation of energy tells us that the momentum of each will have the same magnitude as before the scattering. Hence, their directions of motion will simply have been rotated through a certain angle, and their state will have been transformed into another equivalent state. Note that this is only necessarily true if they start with equal and opposite momenta.

Now it is a fact that if, in a quantum-mechanical calculation, a variety of degenerate states are present, and transitions are induced between them by the forces present in the problem, then all these states must be treated together in determining the state of the system. The problem is not trivial in the case of the phonon interaction, but this can, to a certain extent, be accomplished. We will make no effort here to go into the mathematical details, but only to describe those physical consequences of the theory, on which most of the active workers in the field are agreed.

The upshot of the treatment is that the ground state of the metal is not quiescent but involves large numbers of excited electron pairs (equal-and-opposite-momenta pairs, as described above), interacting with each other through the electron-phonon interaction. Thus, each pair is continually being scattered and rescattered into the other available pair states, and the ground state is a seething mass of such pairs.

The recognition that such a state, so dramatically different from the ground state of a nonsuperconductor, can be formed is half the battle. The other half is to show that a metal in such a state exhibits the well-known properties of a superconductor, and it is here that there still exist some ambiguities in the theory. Once one has settled on the ground state described above, it is necessary, in order to determine the further properties of the material, to learn something about the spectrum of excited states. The only predictions one can make on the basis of the ground state alone are the identity of the superconducting metals and, via a thermodynamic argument, the critical magnetic field at absolute zero. Both of these predictions seem to agree tolerably well with experiment, and from the latter there emerges the isotope effect, as observed.

The Energy Gap

The basic feature of the spectrum of excited states, which leads to the characteristic superconducting properties, is the energy gap. By this we mean that it takes a finite amount of energy to excite the lowest-lying excited state above the ground state. This is a prediction of the theory, as well as a prediction that this energy gap should be a function of temperature, largest at absolute zero and decreasing to zero as the temperature is increased to the transition temperature at zero field. It is not easy to see why the energy gap should lead to perfect diamagnetism or to perfect conductivity, so let us first concern ourselves with the question of whether the gap exists. The most direct evidence that it does arises from experiments on the absorption of electromagnetic radiation in superconductors. In these experiments, a superconductor is exposed to radiation of a given frequency, and the amount of radiation absorbed by the superconductor is measured. It is found that, roughly speaking, only radiation above a given frequency is absorbed. This is exactly what one expects from an energy-gap model, where there is a minimum energy of excitation of the electrons, since the energy of a photon is connected to its frequency by Planck's constant. Indeed, there is even some recent evidence that the energy gap may vary with temperature, as expected. There are other types of evidence, such as the specific heat, and, all in all, we are quite sure that the energy gap exists. But why does it lead to the properties of a superconductor?

It was pointed out long ago by London that, if the wave functions of the electrons were, for some reason, unusually rigid, this might account for the diamagnetism of a superconductor. What has been shown by Bardeen and his collaborators is that the energy gap induces a peculiar stability in the electronic wave functions, so that the conditions for perfect diamagnetism are, in fact, fulfilled. We will not go into the many details of this argument here.

In summary we can say that the many successes of this physically simple, but mathematically still obscure, theory leave no doubt that a major success has been scored in the quest for a theory of superconductivity. While there are a number of questions still to be resolved, it is clear to everyone in the field that we stand, for the first time, within reach of a real understanding of this heretofore baffling problem.