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A FUNDAMENTAL THEORY OF SUPERCONDUCTIVITY

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Although phenomenological theories of superconductivity are now well developed, there is still need for an adequate fundamental theory based directly on the quantum behavior of the electrons and the lattice. Recently Schafroth¹ has shown that a Bose gas of charged particles would show the Meissner effect. Also, Bardeen² has shown that a separate particle system where all excited electronic levels are separated from the "surface of the Fermi sea" by a finite energy will show the Meissner effect.

Our analysis of the problem will be more descriptive than mathematical and will be similar in many respects to the theory of liquid helium II.³

The key feature is the finite binding energy of electron pairs or, more precisely, the finite energy required to excite the electronic system in modes other than translational flow of the entire system.

I

Our general knowledge of chemical substances leads us to expect electron pairing. In molecules chemical bonding is strongest for completely paired electrons in all but the rarest cases (such as O₂). We normally find unpaired electrons associated only with atomic inner shells, which are not involved in bonding such as in the rare earths. Metals at room temperature are indeed an exception to this general situation (although the fraction of unpaired electrons is infinitesimal). Simple theories of metals which are successful in many other respects fail to predict superconductivity; however, these theories fail to take adequate account of coulombic repulsion of electrons and make the assumption of a perfect lattice of stationary nuclei.

It is known⁴ that lattice distortions tend to produce breaks in the energy-level bands. If a single distortion lowers the electronic energy sufficiently (more than the energy of zero-point vibration in the corresponding mode), then permanent distortion occurs. Even for a lattice which is perfect in the mean location of the atoms, however, the total energy must be averaged over the various distortions which arise from zero-point vibration. Thus, while the electronic state with com-

plete pairing of spins may be stable by only an infinitesimal margin for a perfect lattice, this margin may be expected to become finite when averaged over the distortions of the lattice.

Let us also discuss this question in terms of Pauling's⁵ theory of metallic binding. One notes that there are a number of locations in the lattice that are appropriate for chemical bonds, i.e., the shortest distances occurring between atoms. In a metal the number of these bond sites exceeds the number of bonding electron pairs. This is in contrast to a crystal such as diamond where the number of sites is precisely equal to the number of bonding electron pairs.

In addition to the bond sites, one must consider the available atomic orbitals suitable for bonding electrons. While almost always a pair of suitable orbitals can be found for each bond site, there are limitations on the number and arrangement of orbitals which may be occupied simultaneously. Thus in graphite, while the 2p orbital perpendicular to the plane is appropriate for the formation of a π bond in any one of the three bond sites adjacent to the atom, only one of these bonds can be formed at a given time. This limitation is important and, while less restrictive in true metals, must be kept in mind. It will be more restrictive in metals where the ratio of electrons to valence-shell orbitals is high. Many such metals show superconductivity, while those with a low ratio of electrons to orbitals do not.

Pauling now constructs wave functions in which the electrons occupy these bond sites and bond orbitals either in pairs or singly. Coulombic repulsion between electrons is very strong; consequently the set of sites occupied in a low-energy wave function must maintain uniform charge density. The true wave function is taken as the optimum linear combination of these component functions (in the manner of quantum-mechanical resonance). The lowest energy is obtained if the electrons, which occupy orbitals singly in one component function, have spins paired, because the resonance may then include other functions with these electrons in a single bond orbital.

Such a system of electrons is free to move collectively through the lattice and thus conduct electricity. Symbolically one may write a possible wave function for a flowing metallic electronic system:

$$\Psi = \Phi \exp i\mathbf{k} \cdot (\sum_i \mathbf{R}_i), \quad (1)$$

where Φ is the wave function of the system in the absence of flow and the \mathbf{R}_i vectors locate the electrons. Feynman³ discusses this type of function more fully in connection with He II. The question of resistance, i.e., energy loss, from such a flow will be considered later.

Now let us recognize that the lattice is vibrating with zero-point amplitude supplemented by any lattice thermal excitation. As the lattice oscillates, some bond sites will become of more nearly ideal length than others. Also, the angles change, and it will be more favorable in terms of atomic orbitals to occupy certain sets of bond sites than others. The electrons will tend at all times to occupy the more favorable bond sites for a large fraction of the time.

We now consider the change when one electron spin is reoriented so that there are two more spins of one sign than of the other. These two electrons now require separate orbitals at all times, whereas before they could occupy a single orbital.

Even in a perfect, stationary lattice it seems likely that this change may sometimes cause the use of a less favorable orbital and a finite increase in energy. But in a distorted lattice the new state clearly requires the use of a less favorable orbital, because, in order to maintain uniform charge distribution, the additional orbital must be selected within a very limited region of space. Thus we conclude that unpairing two electron spins will cause a finite increase in energy in a vibrating lattice.

The writer does not claim to have proved rigorously this essential point, but he does believe that the best available theoretical arguments strongly indicate the correctness of this finite excitation energy. Also, he is aware of no disproof.

While we shall not discuss the transition to the normal state in any detail, it seems safe to assume that the transition temperature is of the order of magnitude ϵ/k , where ϵ is the energy required to unpair the first spin. We shall give some explicit support for this relationship later. For a rigid perfect lattice we believe that this energy may still have a nonzero value ϵ_∞ in at least some substances. In all cases, however, we expect the electronic energy to rise quadratically with lattice distortion and to rise slightly more steeply when a spin is unpaired. Thus we expect a term $\epsilon(M)$ proportional to the square of the amplitude of the lattice vibrations or to $M^{-1/2}$ if M is the atomic mass.

Thus we have

$$kT_c \cong \epsilon = \epsilon_\infty + \epsilon(M) = \epsilon_\infty + (\text{const.}) M^{-1/2}. \quad (2)$$

If ϵ_∞ is negligible, one expects T_c to vary with $M^{-1/2}$, as was observed for mercury.⁶ In the case of tin⁷ the reported exponent of M is -0.462 ± 0.014 , which deviates from $1/2$ by about three times the stated error. This offers some indication that ϵ_∞ may be significant for tin.

Thus the isotope effect is satisfactorily explained in this theory. It is also interesting to note that these energy terms are very small in comparison with the total zero-point energy of lattice vibration. Consequently no large difference in lattice constant, elastic constants, or lattice specific heat is expected between normal and superconductive states.

II

Next let us consider the possibilities of low-energy thermal excitation of the completely paired electronic system. Pines and Bohm⁸ have shown that density oscillations of the usual phonon type have a very high energy in fluid of electrically charged particles and that they will not be excited in the electronic system of metals at low temperatures. The phonons in a metal are to be regarded as lattice motions. The accompanying electronic adjustment for lattice phonon motion is exactly similar to that for lattice zero-point oscillations. The electronic system is still in its ground state.

We have already mentioned the possibility of translational motion of the entire electronic system with respect to the lattice. This requires, of course, that the superconductor be appropriately connected for current flow. There is also the possibility of nonuniform flow, provided the flow rate varies only slowly.

Since all density oscillations are of high frequency and high energy, we may conclude that, as long as all electrons are paired, the only low-energy motion is the translational flow just mentioned. This is such an important point, however, that we shall attempt to show more explicitly the absence of other low-energy states.

By complete electron pairing we mean, of course, that there are equal numbers of electrons with positive and with negative spin. Moreover, we expect that the wave function will be large only for electron locations which constitute an essentially uniform distribution of electrons of each spin as well as uniform distribution of total electronic charge.

Now let us suppose that an electron of positive spin moves slowly from a region A to another region B. In order to maintain uniform charge density (in the absence of net flow), another electron must be transferred from B to A. If the second electron also has positive spin, we do not have an experimentally distinguishable state. We have merely the exchange of two electrons, which leaves the wave function unchanged except for a reversal of sign. This is just the property of the ground state; we have no new state.

The other possibility is that the charge compensation occurs through the motion from B to A of an electron of negative spin. Now we have in region B an excess of two positive spins and in region A an excess of two negative spins. Provided that regions A and B are sufficiently far apart, this is clearly a new state. Its wave function can be orthogonal to that of the ground state. But its energy will exceed that of the normal state by approximately twice the energy of spin unpairing together with any excess electronic kinetic energy. Consequently it is not a low-energy state in the sense of having lower energy than that required to unpair spins.

It is difficult to predict whether there will be states of the type just described where the energy is not sufficient to "dissociate" the regions A and B of excess positive and negative spin. However, detailed consideration indicates that the energies of such states almost certainly must exceed that of a state with a single pair of electrons of parallel spin. Consequently this question is of secondary importance.

We now conclude that in the first approximation the low-energy excited electronic states (other than those for current flow) may be described in terms of unpaired electron spins. If the spin of one electron is reversed, then in the region immediately around it there will be an excess of two electrons of a given spin. These two electrons may then separate to form two regions with single excess spin. Each region may move through the lattice. Thus the location and motion of each region of excess spin comprise observable features which can characterize a large array of excited states.

The momentum associated with such excitations can interact with the lattice phonons of appropriate wave length. Thus the electronic specific heat of the superconductor will be in thermal equilibrium with the lattice. On the other hand, there does not appear to be any mechanism whereby lattice oscillations can directly create such electron-spin excitations. They must be created at a surface or an interior defect or may be transferred into a superconductive region from a nonsuperconductive region of the metal. This picture is in accord, in general features at least, with the observed facts on the kinetics of the phase transition in superconductivity.⁹

The superconductive properties arise because the infinitesimal energy quanta of translation of the entire electronic system are unable to excite either phonons or electron excitations of the spin-unpairing type. For electronic motion to excite phonons the force exerted on the lattice atoms must vary from atom to atom with

appropriate wave length. This flow of the entire electronic system will exert a uniform nonoscillating force and hence cannot excite phonons. In order to create new electron-spin excitations, a larger energy is required than a single quantum of translation can provide, unless the velocity of the general motion is high. The final possible source of resistance is a transfer of energy of general electron motion to the existing electron-spin excitations. Here, as in the case of the phonons, the force on the excitation must vary in space, whereas the general electron motion yields only a uniform force. These energy-transfer prohibitions are similar to those operating for the superflow in liquid He II.

We conclude that there is no mechanism for transfer of the energy of a slow motion of the entire electronic system. Thus we have the infinite conductivity without any conflict with the Bloch theorem, which requires the state with current flow to have higher energy than the state of zero current.

We have already noted the proof by Bardeen² that an energy-level system of this type will show the Meissner effect.

Recently Corak and collaborators¹⁰ showed that the electronic heat capacity of superconductors at temperatures below follows T_c the exponential equation

$$C = \gamma T_c a e^{-bT_c/T}, \quad (3)$$

where the constants a and b have values near 9.17 and 1.50, respectively, for several metals. The energy-level pattern given by our theory yields just this type of equation with $\epsilon = bkT_c$. This is evidence for our earlier assumption that the transition temperature is proportional to the energy of excitation ϵ .

Since our energy term $\epsilon \cong kT_c$ depends primarily on conduction electron-lattice interactions which are the cause of resistance in the normal metal, we may conclude that T_c will be roughly proportional to the resistance for metals with equal densities of conduction electrons. While superconductors generally have high resistance in the normal state, one cannot claim that any such quantitative relationship holds. The variety of complicating conditions, however, is such that lack of quantitative agreement is not surprising.

We should note that, in contrast to the proposals of Frohlich and Bardeen,¹¹ our theory gives no minimum magnitude of lattice interaction below which the metal will fail to become superconducting even at 0° K. We predict merely that T_c will be much lower for metals with small lattice interaction. However, there is another source of interference with superconductivity which will prevent some metals from attaining that state even at absolute zero. This is atomic magnetic moment from inner electron shells or possibly even nuclear magnetic moment. If the effective magnetic field from this source exceeds the critical field for superconductivity, then no superconductivity occurs. This effect eliminates ferromagnetic (also probably antiferromagnetic) metals from the list of possible superconductors. Since the critical field H_0 is roughly proportional to ϵ (and to T_c), even the nuclear magnetic moment might prevent superconductivity in cases where ϵ is very small. However, tests for superconductivity have not been pushed to low enough temperatures and external fields to make the nuclear moment an important criterion yet.

We believe that we have here the basis for a theory of superconductivity. It yields the observed properties of the superconductive state near 0° K. At a later

date we hope to discuss the nature of the transition to the normal state and, if possible, to add some more quantitative aspects to the general theory.

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¹ M. R. Schafroth, *Phys. Rev.*, **96**, 1149, 1954; **100**, 463, 1955.

² J. Bardeen, *Phys. Rev.*, **97**, 1724, 1955.

³ See the treatment of Feynman, in C. J. Gorter (ed.), *Progress in Low Temperature Physics* (Amsterdam: North Holland Publishing Co., 1955), chap. ii.

⁴ See, for example, R. E. Peierls, *Quantum Theory of Solids* (London: Oxford University Press, 1955), p. 108.

⁵ L. Pauling, *Nature of the Chemical Bond* (2d ed.; Ithaca, N.Y.: Cornell University Press, 1945), p. 402; *Proc. Roy. Soc. London, A*, **196**, 343, 1949.

⁶ C. A. Reynolds, B. Serin, and L. B. Nesbitt, *Phys. Rev.*, **84**, 691, 1951.

⁷ J. M. Lock, A. B. Pippard, and D. Shoenberg, *Proc. Cambridge Phil. Soc.*, **47**, 811, 1951.

⁸ D. Pines, *Phys. Rev.*, **92**, 626, 1953; see also D. Bohm and D. Pines, *Phys. Rev.*, **85**, 338, 1952; **92**, 609, 1953.

⁹ See T. E. Faber and A. B. Pippard, in C. J. Gorter (ed.), *Progress in Low Temperature Physics* (Amsterdam: North Holland Publishing Co., 1955), chap. ix.

¹⁰ W. S. Corak, B. B. Goodmann, C. B. Satterthwaite, and A. Wexler, *Phys. Rev.*, **102**, 656, 662, 1956.

¹¹ J. Bardeen, *Revs. Mod. Phys.*, **23**, 261, 1951, and references there cited, including H. Fröhlich, *Phys. Rev.*, **79**, 845, 1950.