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THEORY OF DIRTY SUPERCONDUCTORS

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Abstract—A B.C.S. type of theory (see BARDEEN, COOPER and SCHREIFFER, *Phys. Rev.* **108,** 1175 (1957)) is sketched for very dirty superconductors, where elastic scattering from physical and chemical impurities is large compared with the energy gap. This theory is based on pairing each one-electron state with its exact time reverse, a generalization of the k up, $-k$ down pairing of the B.C.S. theory which is independent of such scattering. Such a theory has many qualitative and a few quantitative points of agreement with experiment, in particular with specific-heat data, energy-gap measurements, and transition-temperature versus impurity curves. Other types of pairing which have been suggested are not compatible with the existence of dirty superconductors.

ONE of the most striking experimental facts about superconductivity is that it is often insensitive to enormous amounts of physical and chemical impurities. For one example, several substances in essentially an amorphous state have been shown to be superconductors, such as bismuth and beryllium films laid down at liquid-helium temperatures.[1] As another example, there are disordered alloy systems with 20–50 per cent of chemical scattering centers, but with transition temperatures comparable with those of pure elements.[2] These quantities of crystal imperfections are large enough to scatter the electrons at an extremely rapid rate. In fact, if we were to take the mean free time before scattering for the electron as a measure of the electrons' uncertainty in energy, that uncertainty in energy is large compared not only with the energy gap ϵ_0, but with the Debye energy $\hbar\omega_D$. Plane-wave states for the electrons definitely have this very large degree of energy uncertainty.

On the other hand, the experiments of SERIN *et al.*[3] have shown that, starting with a pure single crystal of a superconducting material, there is usually a rather sharp initial drop in the superconducting transition temperature as the first small percentage of chemical imperfection is added. They show that this initial drop is proportional to the extra resistivity caused by these imperfections, and therefore proportional to the amount of scattering. If the impurities which are introduced are magnetic ions rather than ordinary chemical impurities, MATTHIAS *et al*[4] have shown that this initial sharp drop continues, and superconductivity is very soon destroyed. On the other hand, for ordinary impurities the sharp drop stops rather soon and is replaced by a more gradual behavior, which seems to be determined primarily by the fact that the impurity adds or subtracts electrons from the band, changes the density of states, and in various ways gradually varies the parameters of the free electrons. Thus we may divide superconductivity into two regions: (1) the region of relatively pure superconductors where scattering has a rather sharp effect on superconducting transition temperatures; and (2) the region of very imperfect superconductors, where additional scattering has very little effect. It is the purpose of the present paper to give a theory of this region of the "dirty" superconductor.

The fundamental assumption we will make is that in this region the problem of the electron wave functions is best solved by first diagonalizing the scattering interaction between the electrons and the impurities, and then calculating the phonon interactions between electrons. Finally, one calculates from this the superconducting properties. That is, we find a new set of one-electron wave functions for the electrons, and then solve the problem of the interactions of the electrons in terms of these, rather than in terms of ordinary

plane-wave functions, such as are appropriate in the region of the pure superconductor. All of this, of course, assumes that the scattering is perfectly elastic, as it is from any form of chemical or physical imperfection. (At the low temperatures where superconductivity is important, inelastic phonon scattering does not play an important role.) So what we do is simply to assume that somebody has solved for us the extremely difficult problem of the wave functions of the electrons in the presence of the scatterers, and write down the resulting wave function $\psi_{n\sigma}$:

$$\psi_{n\sigma} = \sum_{k} (n|k)\phi_{k\sigma}, \tag{1}$$

where $\phi_{k\sigma}$ are the Bloch waves and $(n|k)$ the unitary transformation solving the scattering problem. (We give ψ_n a spin index σ; this may not be valid in heavy elements because of spin-orbit coupling, but the theory is still valid there.)

The basic observation which we make is that if $\psi_{n\sigma}$ is such an exact one-electron wave function in the presence of scatterers, and if the scatterers are nonmagnetic, the time-reversed wave function, $(\psi_{n\sigma})^*$, is also an exact wave function of the one-electron Hamiltonian. What is more, $(\psi_{n\sigma})^*$ has the same energy as $\psi_{n\sigma}$ itself. We shall call this energy E_n. The time-reversed wave function $(\psi_{n\sigma})^*$ is:

$$(\psi_{n\sigma})^* = \sum_{k} (n|k)^*\phi_{-k-\sigma}. \tag{2}$$

Now, having the correct one-electron wave functions, we proceed to derive the phonon interaction between these electrons. It is not at all correct simply to transform the B.C.S. interaction[5] directly into the interaction between these new wave functions $\psi_{n\sigma}$; the reason for this is that $\psi_{n\sigma}$ contains plane wave functions which have quite different energies, and in particular, in the presence of strong scattering contains wave functions from outside of the region where the B.C.S. electron interaction is attractive. Therefore, this method would lead us to the conclusion that the interaction between electrons is altered rather seriously. Actually, it is correct instead to write down the interaction between these new scattered-electron wave functions and the phonons, and then to do the second-order perturbation theory which gives us the interaction between the electrons caused by the phonons. When the calculation is done this way, the energy denominators in the second-order perturbation theory contain the energies not of the initial plane-wave states, E_k, but rather the energies E_n of the scattered one-electron states. Whether or not the interaction is attractive depends primarily on what these energy denominators are. Therefore, we find that the attractiveness or not of the interaction is now a function not of E_k, the energy of the plane-wave states, but of E_n, the energy of the scattered-electron states. Without going into excessive detail, we simply write down the part of the interaction which corresponds to the B.C.S. truncated Hamiltonian:[5]

$$\mathscr{H}_{\text{red.}} = -\sum_{n,n'} V_{nn'} c_n^* c_{-n}^* c_{-n'} c_{n'},$$

$$V_{nn'} = \sum_{k,k'} \frac{|(n|k)|^2|(n'|k')|^2|M_{k-k'}|^2\hbar\omega_{k-k'}}{(\hbar\omega_{k-k'})^2-(E_n-E_{n'})^2}. \tag{3}$$

Here c_n^* and c_{-n}^* are creation and destruction operators for electrons in state $\psi_{n\sigma}$ and $(\psi_{n\sigma})^*$, $M_{k-k'}$ and $\hbar\omega_{k-k'}$ have the usual meaning, and $(n|k)$ is defined in equation (11).

This interaction is summed over all the plane wave functions which are contained in the scattered function n, with a coefficient which is given by the square of the amount of the state contained in the state n. Normalization requires the following equation:

$$\sum_{k} |(n|k)|^2 = 1. \tag{4}$$

Because of equation (4), if the parameters entering in the interaction were constants, as was assumed by B.C.S., the interaction would be exactly the same for the scattered state as it was for the plane-wave state. As it is, the interaction is not a constant, but at best only roughly so, and expression (3) picks out of the total interaction only the constant part. That is, the interaction (3) is strictly the average interaction over all the states going to make up the scattered state n. Since the states which make up this scattered state are, at least under conditions of strong scattering, taken more or less randomly from all the regions of the Fermi surface, we conclude that the interaction will be (aside

from a smooth energy dependence) a constant, averaged over the entire Fermi surface.

The rest of the interaction, the part which was removed in the truncated Hamiltonian of B.C.S., is changed in a very radical way. In the pure substance the rest of the interaction can be thought of as an interaction between pairs which do not have exactly zero total momentum but rather some finite momentum. However, under conditions of strong scattering this part of the interaction does not take this form at all; each individual matrix element is smaller by a number of the order of the total number of electrons. This is because the momentum selection rule no longer holds, so that there is no reason why any individual matrix element should vanish. This increases the total number of matrix elements and must therefore decrease their magnitude. Thus, in the scattered state the B.C.S. part of the interaction, or rather the transformed B.C.S. part, plays a much more obviously unique role than it does in the pure superconductor.

One final comment about this interaction: obviously if the scattering is strong enough the procedure which we have followed, of first diagonalizing the one-electron Hamiltonian including scattering, and then introducing the electron–phonon interaction and the interaction between the electrons which results from it, is correct. When we ask the question: at what degree of scattering is this no longer the correct procedure? the first guess would be that one should find some average amount of electron–phonon interaction and when the scattering becomes less than that the procedure is no longer correct. However, it is fairly easy to convince oneself that this is not the correct way, but that the diagonalization of the one-electron part of the Hamiltonian is correct at very much smaller amounts of scattering. As a matter of fact, the procedure we have followed seems to be correct until the actual interaction *between* the electrons caused by the electron–phonon interaction begins to come in to play. That is, it is correct until $\hbar/\tau$ becomes comparable with the energy gap, which is a reasonable measure of the electron–electron interaction. This is, in fact, the experimental criterion for the transition from the region of strong scattering, as here defined, to the region of weak scattering.[3]

Now we shall draw some physical conclusions from these ideas. First we should observe that it is possible to solve the B.C.S. integral equation and derive a theory of superconductivity just as well as in the new situation with the new averaged interaction and the scattered wave functions ψ_n as it was in the old situation with the old interaction and the plane-wave functions ψ_k. A general result, which is fairly easy to prove, is that the energy gap, and therefore the transition temperature, will always be slightly smaller for the scattered states than they would be in the pure case, essentially because the average taken in the scattered case is not as favorable as one gets in the pure case. This explains why it is that in the pure superconductor region the transition temperature drops so radically, and yet stops dropping after one gets into the region of strong scattering; and at the same time it explains why this drop is relatively small, because one does not expect the difference between the two energy gaps to be very large. Thus, we see that these ideas explain fairly satisfactorily the general features of SERIN's results. It is also clear that when the time-reversal transformation cannot be made, that is, when the energy of the state ψ_n is not the same as the energy of ψ_{-n}, all this cannot be done, and the transition temperature will continue to drop as the degree of magnetic scattering increases.

An interesting question is what size of particles and at what degree of scattering will superconductivity actually cease. The first point is that, as long as the particle size remains fairly large, no quantity of scattering which leaves the substance a metal would seem to be capable of actually destroying superconductivity, because the average which is taken over the Fermi surface does not depend in any important way on the actual amount of scattering. On the other hand, on reducing the particle size, we will begin to get to the point at which the scattered wave functions ψ_n have energies E_n which are separated by discrete energy gaps. That is, their energies must extend over something like the total Fermi energy, which is about 10 eV; and if there were only about a thousand electrons, that would mean that the energy differences between the states would be of the order of 0·01 eV. With such energy differences among the E_n, superconductivity would no longer be possible; in fact, it is fairly easily seen that the energy differences must be less than the energy gap. That means that

particles with fewer than about 10^4–10^5 electrons will begin to be affected. So far no experiments are reported on particles of this order of magnitude of size, although the particles used in REIF's nuclear-resonance experiments are beginning to approach this point.[6]

Another conclusion is that the B.C.S. theory in its original form, assuming a constant interaction, will be more nearly correct in the dirty superconductor region that it will be for pure superconductors; that is, in the impure superconductors the interaction is relatively a constant, and therefore the energy gap itself will be a constant and the thermal and other results of B.C.S. should be nearly exact. On the other hand, in pure single crystals of superconductors, one can very quickly show that the energy gap will be a strong function of the momentum vector on the Fermi surface, because most superconductors have fairly complicated Fermi surfaces, and it would be a miracle if the interactions were sufficiently constant to maintain a constant energy gap. There are two types of experiments which bear on this point. One type of experiment is the electronic specific heat and, in fact, various recent experiments[7] show deviations from the exponential specific-heat curve of the B.C.S. theory in the direction which would be expected if the energy gap were a function of position on the Fermi surface. Experiments on less perfect single crystals have shown less such deviations, as is to be expected. On the other hand, most of the direct experiments, in particular the experiments of TINKHAM and his co-workers[8] on the optical measurement of the energy gap and the experiments of HEBEL and SLICHTER[9] measuring the density of states by the relaxation time in nuclear resonance, are necessarily undertaken in the dirty superconductor region. In the case of TINKHAM's experiments, the measurement is necessarily made near a surface, while the other measurement is made on small particles. Therefore, neither of these types of experiments would have been expected to show any considerable anisotropy of the energy gap. The former do not; the structure observed in the latter experiments[10] is probably a collective excitation.[11] The question of the experimental investigation of the anisotropy is a fascinating one which remains open so far as I know. Our conclusion is that the recent experiments on the detailed investigation of the specific-heat curve must be considered as being more of a confirmation of the B.C.S. theory than vice versa, because they show that the expected anisotropy of the energy gap is actually there.

In conclusion I should like to make a number of acknowledgements and apologies. In the first place various notions about time reversal and superconductivity have appeared independently in a number of places. Most particularly, ABRAHAMS and WEISS at Rutgers have made similar calculations, and BARDEEN and MATTIS[12] have used a related wave function. In the second place, the idea of the anisotropy of the energy gap occurred independently to COOPER and to PIPPARD and HEINE[13]. Thus, the purpose of the present paper is merely to summarize in a physically consistent way all of these ideas, and to show that there is good agreement qualitatively with experiments. I should also acknowledge interesting discussions with C. HERRING and H. SUHL.

A final comment is that the nucleus is itself a dirty superconductor in the sense that the nucleus is a very fine particle with only a very small number of Fermi particles in it. Thus, it is not surprising to find that the theory of nuclei contains a "pairing" concept for $+m_1 - m$ pairs[14] which shows very great similarity to the discussion in this paper.

It is hard to see how any explanation other than time-reversal invariance will explain all these facts; in particular, the suggestions of inexact pairings or pairings of parallel-spin electrons advanced relative to the explanation of Knight shift results[15] certainly fail of agreement with the facts about dirty superconductors. It seems to the author that these considerations represent the strongest arguments that the theory of superconductivity must have some relation to zero-momentum, opposite-spin pairs.

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