

There are several effects of which the theory does not take account.

(a) The resistivity of tungsten does not vary as T but rather as $T^{1.25}$.^{2,3} This fact alone would mean that a T^4 dependence should show up as an $R^{3.2}$ dependence.

(b) Since the filament is not a black body, c_1 is not necessarily independent of temperature. Emission of radiation from tungsten filaments, in fact, follows a $T^{5.3}$ law implying that the emissivity follows a $T^{1.3}$ law.³

(c) Since the filament is not a black body, c_2 is not necessarily independent of filament temperature. Absorption of radiation by tungsten filaments, in fact, follows a $T^{0.9}$ law.³

(d) The thermal conductivity of tungsten (on which c_3 depends) is temperature dependent, decreasing with increasing temperature according to a $T^{-0.3}$ law.⁴

(e) It is not proper to talk of *the* temperature of the filament since the temperature increases along the filament from both ends to the center. Not only does this complicate the radiation and conduction effects⁴ but it also complicates the temperature variation of resistance.

It is perhaps surprising that the simple theory,

² I. Langmuir, Phys. Rev. 8, 302 (1916).

³ Langmuir and Taylor, J. Opt. Soc. Am. 25, 321 (1935).

⁴ Langmuir and Taylor, Phys. Rev. 50, 68 (1936).

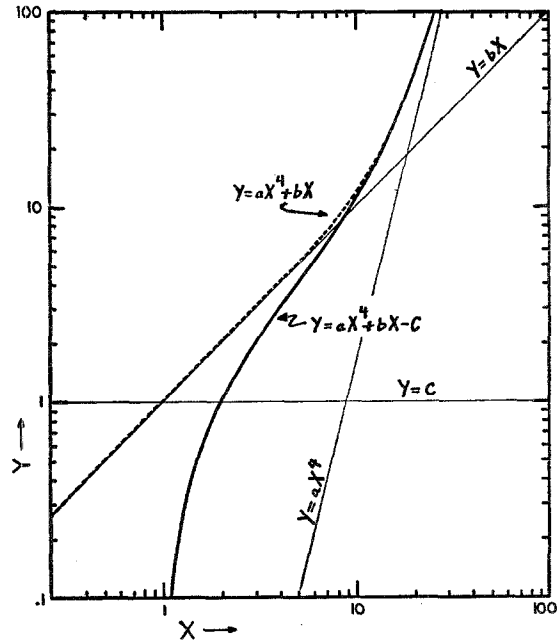


FIG. 2. Curve with a double bend formed by combining a fourth power term plus a first power term minus a constant term.

which ignores the above complications, can lead to a qualitative understanding of the experimental results. It is the purpose of this note to suggest that neither the experimental techniques nor the simple theory are beyond elementary students.

Theory of Superconductivity*

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Some recent developments in the theory of superconductivity are discussed with emphasis on the underlying physical ideas. It is proposed that the electron-phonon interaction produces a strong preference for singlet zero momentum pairs in two-body correlations which can account for superconductivity and related phenomena.

I. INTRODUCTION

IN Professor Boorse's¹ description of the phenomena characteristic of superconductors there is a most striking feature. In spite of the

* Work supported in part by the U. S. Atomic Energy Commission. This paper is the substance of an address delivered at the annual meeting of AAPT in New York on January 31, 1958.

¹H. A. Boorse, Am. J. Phys. 27, 47 (1959).

complexity and the diversity of the metals in which superconductivity occurs, there appears a remarkable simplicity in the way this phenomenon occurs in all metals. This leads us to hope that an explanation, at least of the qualitative features of superconductivity, can be designed without a consideration of the details of metal structure—a possibility for which we can be

grateful since the metals that become superconductors are so complicated.

In what follows we present a picture of a metal divested of all its intricacies and by the same simplification of its individuality. This is perhaps the simplest picture of a metal which contains both the normal and superconducting properties. We do not expect, without further refinement, to obtain those features explicitly dependent on the details of metallic structure, but will be satisfied if we can obtain just those qualitative properties which are associated with the ideal superconductor. Our point of view is that the existence of the superconducting phase is a rather general property of that system which is common to all metals, the dense, highly degenerate interacting electron gas, and that the complications which make up the details of metal structure can be ignored for a qualitative understanding.

The properties of this dense, highly degenerate gas—the valence electrons in a metal—appear to be well understood at ordinary temperatures. The solutions of the Schrödinger equation in the periodic potential produced by the fixed ions in the uniform background of negative charge of the valence electrons give the band structure and the Bloch single particle wave functions. The latter propagate freely through the metal, unless scattered by phonons or impurities, and one can successfully use perturbation theories, beginning with the Bloch wave functions, in most calculations.

At low temperatures, however, in the many metals and alloys which become superconductors this picture seems to break down completely. At a critical temperature there appears the change of phase in which the electrical and thermal properties of these metals which are due to the valence electrons change radically. Although the lattice certainly plays a role in determining the transition temperature, it itself seems to be unchanged in the superconducting transition. The numerous experiments which have been performed to study this superconducting phase have shown that, among other things, one must expect that the electronic wave functions are highly correlated, so that the one-particle Bloch functions no longer give an adequate description. It is further known that the energy of condensation, the energy required to bring the metal from the superconducting back to the normal state is ex-

remely small compared with the Fermi energy of the electrons. The ratio of energy of condensation to the Fermi kinetic energy for a typical metal would be of the order of 10^{-3} .

In what follows we shall attempt to present the motivating ideas, and some of the structure and consequences of a theory of superconductivity recently proposed by J. Bardeen, J. R. Schrieffer, and the author.² We shall attempt further to indicate at least qualitatively the explanation for some of the phenomena described by Professor Boorse.¹

II. NORMAL METAL

In the Bloch theory of the normal metal,³ the conduction electrons are independent of one another. Bloch's theorem states that in the periodic potential produced by the lattice and the conduction electrons themselves, the single electron wave functions will be modulated plane waves:

$$\varphi_K(\xi) = U_{\mathbf{k}}(\xi) e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (1)$$

where $K \equiv \mathbf{k}, \sigma$; \mathbf{k} is the wave vector of the electron; σ is its spin state; $\xi = \mathbf{r}, s$ are the space and spin coordinates; and $U_{\mathbf{k}}(\xi)$ is a spinor with the lattice periodicity. According to the Pauli exclusion principle, the many electron wave function must be antisymmetric in all of its coordinates. This means that no two electrons can be in the same Bloch state $\varphi_K(\xi)$, or that the many electron wave function can be written as

$$\Phi_N = \frac{1}{\sqrt{N!}} \sum_{\text{permutations of } \xi_1 \dots \xi_N} (-1)^P \times \varphi_{K_1}(\xi_1) \dots \varphi_{K_N}(\xi_N). \quad (2)$$

The energy of the entire system is then

$$W = \sum_{i=1}^N \mathcal{E}_i, \quad (3)$$

where \mathcal{E}_i is the Bloch energy of the i th single electron state. The lowest energy for the system is obtained when the lowest N Bloch states are "filled" by single electrons. This can be pictured in momentum space as the filling in of a Fermi sphere. In our simplest possible model of a metal

² Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957).

³ F. Bloch, Z. Physik **52**, 555 (1928).

we will imagine that the Fermi surface is isotropic and that it is far from the top of any band. With the ground-state wave function Eq. (2) there is no correlation between electrons of opposite spin, and only a statistical correlation of electrons of the same spin. [The only way that electrons are correlated with others is through the general antisymmetry requirement on the total wave function.]

There are an enormous number of single particle excitations of very low energy. These will be given by wave functions identical to the ground state except that a single one electron state $k_i < k_F$ is replaced by another $k_j > k_F$. This can be pictured in momentum space as opening a vacancy below the Fermi surface and placing an excited electron above. [See Fig. 1.] The energy difference between the ground state Φ_0 and the excited state $\Phi_{i,j}$ is

$$E = \mathcal{E}_j - \mathcal{E}_i = \epsilon_j - \epsilon_i = |\epsilon_j| + |\epsilon_i|, \quad (4)$$

where for later convenience we define ϵ as the energy measured relative to the Fermi energy, $\epsilon_i = \mathcal{E}_i - \mathcal{E}_F$. Since there are a large number of such excitations with very small energy, the electronic specific heat (which is a measure of the number of ways a given amount of energy can be distributed among the electrons) goes to zero as a linear function of the temperature, as mentioned by Professor Boorse.¹

To understand a phenomenon like resistance, we recall that any deviation from the perfect lattice assumed in deriving the Bloch states will provide a perturbation from which the Bloch waves may be scattered. Such deviations fall conveniently into two categories: static and dynamic. Static deviations are produced by impurities or lattice defects while the dynamic deviations are caused by the vibrations of the lattice ions about their equilibrium positions.

The number of impurities or lattice defects is temperature-independent and contributes a term to the electrical resistance which is also independent of the temperature. The lattice vibrations on the other hand depend upon the temperature of the lattice and thus contribute a temperature-dependent term in the electrical resistance. When these lattice vibrations are put into normal modes or quantized, they can be characterized as sound waves or phonons—they

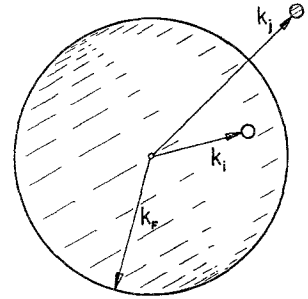


FIG. 1. An excited state of the normal metal is produced by filling the one electron state k_j , $k_j > k_F$, and leaving the vacancy k_i , $k_i < k_F$.

are essentially a wave of pressure variation traveling through the metal. The interaction of the phonons with the conduction electrons is often spoken of as the electron-phonon interaction.

Either of the above scattering mechanisms produces resistance in the same way. They provide a process whereby single electrons can be scattered from one momentum state to another. Thus any current carrying state, in the absence of the field that produced it, is quickly randomized. The essential property of a superfluid (electron fluid or otherwise) is that such single particle processes are severely inhibited, so that ordered states, such as current carrying states, persist even in the absence of external fields.

III. ELECTRON CORRELATIONS AND THE INTERACTION THAT PRODUCES SUPERCONDUCTIVITY

If we ask: What is the probability of finding an electron with spin down a distance r from another electron with spin up: $\rho \uparrow \downarrow (r)$, in the normal metal, we find that

$$\rho \uparrow \downarrow (r) = \frac{1}{4} n^2, \quad (5)$$

where n is the density of electrons. Thus, the probability of finding the electron $2 \uparrow$ a distance r from electron $1 \downarrow$ without any consideration of where electrons 3 to N may be, is just the density of electrons of spin \uparrow , or there is no correlation at all between electrons of opposite spin in the normal metal. For parallel spin there is a correlation, but this is due solely to the fact that no two electrons can be in the same single particle state, and we will not concern ourselves further with this. The properties of the normal metal can be deduced from the single particle uncorrelated electron functions.

It is just in this respect that the supercon-

ductor differs. For a description of the superconducting phase we expect that we will need a correlated wave function and, it turns out, that correlations between electrons of opposite spin are the important ones.

We then ask: What is it that will produce correlation between electrons? The answer is that if there is interaction between the electrons, then they will be correlated, e.g., if there was a very strong two-particle repulsion between two electrons, then the two electrons would never get very close to one another. It is these correlations that have been neglected in describing the normal metal and, apparently, one is justified in doing this at ordinary temperatures. On the other hand, at very low temperatures, it is equally apparent that the system can gain energy by going into a highly correlated state, and it is this highly correlated state that we want to find.

What interactions between electrons should then be considered? This has always been a difficult problem, because there are so many interactions between the electrons in a metal, and, in fact, the energy due to most of these interactions, e.g., the Coulomb interaction, is much larger than one actually observes in the superconducting transition. For example, the correlation energy due to the Coulomb repulsion is of the order of one electron volt per atom, while the energy involved in the superconducting transition is of the order of 10^{-8} electron volt per atom. We thus expect that a large amount of the correlation energy is not characteristic of the qualitative change that occurs in the wave function in the transition into the superconducting phase.

As Professor Boorse has said,¹ it was the discovery of the isotope effect⁴ that indicated to theoreticians what interaction it was that was responsible for the phenomenon of superconductivity. It was observed that the transition temperature into the superconducting phase was related to the mass of the ions which made up the lattice by the relation

$$T_c\sqrt{M} = \text{const.} \quad (6)$$

Why should this be so unless, in some sense, the interaction which produces the superconducting phase is one which involves the dynamics of the

ion motion, or the phonons. From Eq. (6) we can see that the transition temperature would be zero if the mass of the ion was infinite or if the lattice points were really fixed. This suggests strongly that the nonzero transition temperature is a consequence of the finite inertia of the ions. Fröhlich⁵ and Bardeen⁶ pointed out that since electrons could interact with lattice vibrations to cause resistance, the electrons should also interact with the virtual lattice vibrations, a self-energy of electrons in a metal. This self-energy, they pointed out, would be proportional to an average phonon energy squared, and thus would give the isotope effect. However, calculating the effect of this self-energy, they were not successful in finding a phase which had the qualitative properties of superconductors.

It turns out that it is the interaction of the electrons with the lattice vibrations which produces superconductivity. But it is an interaction between two electrons via the lattice vibrations which does this. When an electron collides with a vibrating lattice point, or with a lattice wave, it may be scattered and this scattering produces resistance. At $T=0$, there are no lattice vibrations and the phonon part of the resistance goes to zero. However, it is still possible for an electron to excite a lattice wave virtually. This virtual lattice wave can interact with another electron, producing an interaction between electrons.

In the language of field theory one can say that if there is an interaction between electrons and the free phonons of a phonon field (to produce resistance), there will also be an interaction between electrons, due to the exchange of virtual phonons, even at the absolute zero and independent of the number of free phonons present. This is analogous to the situation in quantum electrodynamics. There, a photon can be scattered by an electron and, of course, in order to produce this effect, it is necessary to shine light, photons, on electrons. On the other hand, the Coulomb potential between two electrons, which is independent of the presence of free photons, is the result of the exchange of virtual photons.

The interaction between electrons, via the exchange of virtual phonons, can be thought of classically in the following way. When an electron

⁴E. Maxwell, Phys. Rev. 78, 477 (1950); Reynolds, Serin, Wright, and Nesbitt, Phys. Rev. 78, 487 (1950).

⁵H. Fröhlich, Phys. Rev. 79, 845 (1950).

⁶J. Bardeen, Phys. Rev. 79, 167 (1950).

moves through a lattice, if the lattice points are not rigidly fixed or infinitely heavy, the lattice will be distorted or polarized. Another electron moving through the polarized lattice will feel not the original periodic potential used to derive the Bloch wave functions, but rather the distorted potential due to the fact that the lattice is polarized. The potential distortion is a function of position and time and shows up as a retarded interaction between two electrons. This interaction would disappear if the spring constant were very large, or if the mass of the ions were infinite. Further, whether this interaction is attractive or repulsive, will depend upon the relative phase of the two electrons. (See Figs. 2, 3, and 4.)

Another interaction between electrons in a metal, which turns out to be of importance in the theory of superconductivity, is the short-range

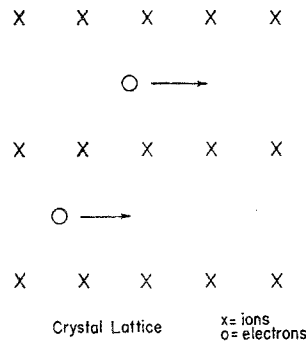


FIG. 2. Two electrons move, undisturbed, through a perfect lattice whose ions are infinitely heavy or rigidly fixed.

Coulomb repulsion. Long-range Coulomb forces tend to be screened out by the other electrons, as indicated in the work of Bohm and Pines.⁷ At very short distances, when the two electrons face one another, so to speak, with no others between them, there is felt the Coulomb repulsion, e^2/r . It is these two interactions between electrons in a metal that have been omitted in forming a zero-order picture which we will use to construct the correlations between electrons.

In considering the kind of correlations that will be produced by the electron-electron interactions mentioned above we make the further step of limiting ourselves to two-body correlations, ignoring three, four, and many electron correlations. This is not because we believe these other correlations do not exist, but rather, that limiting ourselves to two-body correlations is the next

⁷ D. Bohm and D. Pines, Phys. Rev. 92, 609 (1953).

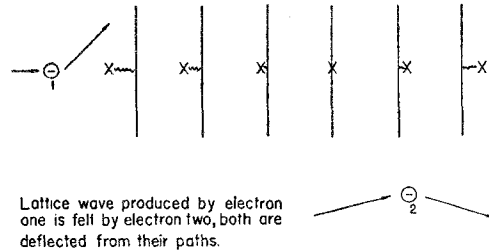


FIG. 3. Two electrons interact in a lattice whose ions have finite inertia and are not rigidly fixed.

simplest step after no correlation at all, and we hope that perhaps two-body correlations will be sufficient to introduce the qualitative features of superconductivity, just as the completely uncorrelated wave function was sufficient to account for the properties of the normal metal.

What then will be the nature of the two-body correlation produced by the interactions we have just described? Suppose we write the antiparallel correlation function, which was a constant for the normal metal, in the form

$$\rho \uparrow\downarrow = \frac{1}{4}n^2 + f(\mathbf{r}, \mathbf{K}), \quad (7)$$

where $f(\mathbf{r}, \mathbf{K})$ is the extra correlation produced by the interactions between electrons, \mathbf{r} is the relative coordinate of the two electrons involved, and \mathbf{K} is the total momentum of the two electrons.

In order to understand why some electrons are strongly correlated while others are not, we return to our description of the normal-state wave function in momentum space. For simplicity we now let the Bloch functions $\varphi_{\mathbf{K}}(\xi)$ be plane waves.

We saw that, for the ground state, single particle states are filled to the Fermi surface. It is the

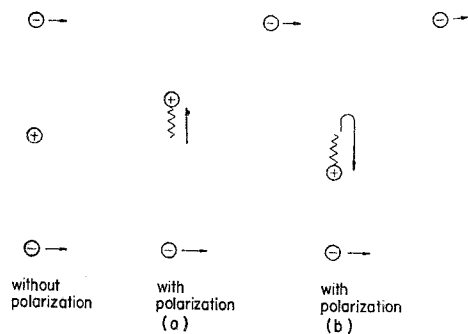


FIG. 4. The interaction between two electrons due to the polarization of the lattice can be attractive or repulsive depending upon the relative phase of the two electrons. In case (a) the interaction is repulsive while in case (b) it is attractive.

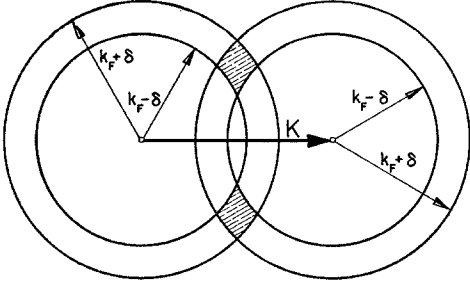


FIG. 5. The shaded area is a cross section of the phase space available for scattering, with conservation of the total momentum K , of a pair of electrons with individual momenta restricted to the shell $k_F - \delta \leq k \leq k_F + \delta$. The volume of available phase space has a sharp maximum when $K=0$.

nature of the electron-electron interactions described above that they seem to be both weak and slowly varying over the Fermi surface. This and the fact that the energy involved in the transition into the superconducting state is small leads us to guess that the correlated states will involve single particle excitations, only in a small shell near the Fermi surface. If we restrict ourselves to pair correlations, we will be interested in the interaction which takes a pair of electrons from one state to another state in this shell near the Fermi surface. Since the total momentum of the pair must be conserved, it is clear that the amount of phase space available for transition from one state to another state, of given total momentum, is a strong function of the total momentum (see Fig. 5) and becomes maximum when the total momentum $K=0$. It turns out, further, that due to exchange terms in the electron-electron matrix element the effective interaction between electrons of singlet spin is much stronger than that between electrons of triplet spin—thus our preoccupation with singlet spin correlations. One finds further that if all the pair correlations have the same total momentum, one gets the maximum correlation of the entire wave function. This gives an interesting coherence to the wave function. For a combination of dynamical and statistical reasons there is a strong preference for momentum zero, singlet spin correlations while for statistical reasons alone there is an equally strong preference that all of the correlations have the same total momentum.

The basic approximation of the BCS theory of superconductivity rests in their assumption that

it is the two-body correlations that are responsible for the qualitative features of superconductivity and that of the two-body correlations there is a very strong preference for singlet zero momentum pairs—so strong that one can get an adequate description of superconductivity by treating these correlations alone.

IV. GROUND STATE OF THE SUPERCONDUCTOR

Within this approximation one is able to write down the *extra energy* due to the pair correlations introduced into the wave function. This is given by

$$W_c = 2 \sum_{-\hbar\omega < \epsilon < 0} |\epsilon| (1 - h(\epsilon)) + 2 \sum_{\hbar\omega > \epsilon > 0} \epsilon h(\epsilon) - V \sum_{|\epsilon|, |\epsilon'| \leq \hbar\omega} [h(\epsilon)(1 - h(\epsilon))h(\epsilon')] \times (1 - h(\epsilon'))^{\frac{1}{2}}, \quad (8)$$

where $h(\epsilon)$ is the probability that the pair state ϵ is occupied (see Fig. 6), 2ϵ is the energy of the pair measured relative to the Fermi surface, $\epsilon = \mathcal{E} - \mathcal{E}_F$, and V is the matrix element between the Bloch pair state of relative momentum \mathbf{k} and \mathbf{k}' . Here we have made the simplifying but not essential assumption that the interaction matrix element $\langle k' | H_1 | k \rangle$ between the pair states of relative momentum \mathbf{k}' and \mathbf{k} is the constant $-V$,

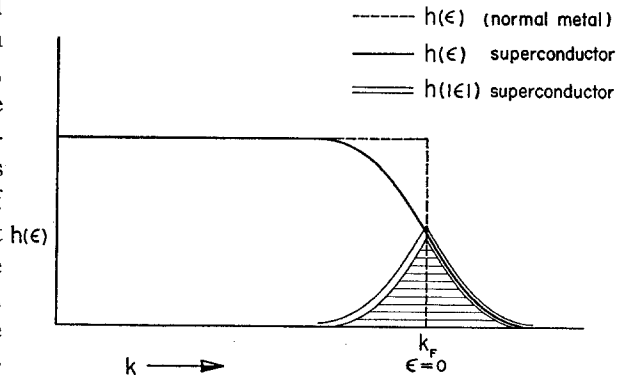


FIG. 6. The probability, $h(\epsilon)$, that the pair state of energy ϵ is occupied in the ground-state wave function. For the normal metal all states below the Fermi energy are occupied, while those above are empty. In the superconducting ground state there are vacancies below the Fermi surface and occupied states above; $h(|\epsilon|)$ gives the symmetrical probability of electron pairs above k_F and vacancy pairs below. The extra kinetic energy due to the mixing in of these pair states can be written

$$T_c = 2 \sum_{|\epsilon| \geq \hbar\omega} |\epsilon| h(|\epsilon|).$$

for $|\epsilon|, |\epsilon'| < \hbar\omega$ (an average phonon energy), and zero elsewhere. This implies that the Fermi surface is isotropic so that h is a function of ϵ alone.

The first two terms give the increase in kinetic energy due to the fact that single particle states with $k > k_F$ have been included in the wave function, while the third term gives the change in potential energy due to the correlations that have been introduced. This energy is now minimized with respect to h . If it can be made smaller than zero then the correlated state has the lower energy. There is an obvious solution which makes $W_c = 0$ (no correlation energy), that is,

$$\begin{aligned} h &= 0 & \epsilon > 0, \\ h &= 1 & \epsilon < 0. \end{aligned} \quad (9)$$

But this is just the normal state; there all the Bloch states below the Fermi surface are occupied while those above are empty.

Setting the variation of W_c with respect to h equal to zero, one finds the following relations:

$$\begin{aligned} h &= \frac{1}{2}(1 - \epsilon/E), \\ E &= (\epsilon^2 + \epsilon_0^2)^{\frac{1}{2}}, \end{aligned} \quad (10)$$

and

$$\epsilon_0 = \frac{V}{2} \sum_{|\epsilon| < \hbar\omega} \frac{\epsilon_0}{(\epsilon^2 + \epsilon_0^2)^{\frac{1}{2}}}.$$

The last equation for ϵ_0 is the basic nonlinear integral equation which determines whether or not a superconducting solution exists. We see immediately that this equation has no nonzero solutions for ϵ_0 if $V < 0$. This provides a criterion for the potentials that will produce a superconducting state, since the electron-electron interaction due to phonon exchange is attractive, while the screened Coulomb interaction is repulsive. The criterion

$$V = -(k' |H_1| k) > 0 \quad (11)$$

will be satisfied roughly if the electron-phonon interaction is large enough. This provides a resolution of an often noted paradox—that good conductors (copper, silver, gold) do not become superconductors. A large electron-phonon interaction which means a large resistance in the normal state is conducive to the formation of the resistanceless superconducting phase.

If $V > 0$ we have (changing the summation to

an integration)

$$1 = N(o) V \int_0^{\hbar\omega} \frac{d\epsilon}{(\epsilon^2 + \epsilon_0^2)^{\frac{1}{2}}}, \quad (12)$$

or

$$\epsilon_0 = \hbar\omega / \sinh \frac{1}{N(o) V},$$

where $N(o)$ is the density per unit energy of electrons of one spin at the Fermi surface. In the weak coupling limit [$N(o) V \ll 1$], which seems to be the region of interest empirically,

$$\epsilon_0 \simeq 2\hbar\omega e^{-1/N(o)V}. \quad (13)$$

The energy difference between the normal and superconducting states becomes (again in the weak coupling limit)

$$W_S - W_N = W_c = -2N(o)(\hbar\omega)^2 e^{-2/N(o)V}. \quad (14)$$

The dependence of the correlation energy on $(\hbar\omega)^2$ gives the isotope effect while the exponential factor reduces the correlation energy from the dimensionally expected $N(o)(\hbar\omega)^2$ to the much smaller observed value. The correlation function between two electrons of opposite spin is now given by the following expression:

$$\begin{aligned} \rho_{\uparrow\downarrow}(\mathbf{r}) &= \left(\frac{1}{4} n^2 \right) \\ &+ \left| \left(\frac{1}{2\pi} \right)^3 \int d\mathbf{k} h^{\frac{1}{2}} (1-h)^{\frac{1}{2}} e^{i\mathbf{k}\cdot\mathbf{r}} \right|^2. \end{aligned} \quad (15)$$

It thus turns out that in the superconducting ground-state wave function there are strong correlations between pairs of electrons with opposite spins and zero total momentum. These correlations are built from single particle Bloch state excitations, near the Fermi surface, and extended over spacial distance of the order of 10^{-4} cm (see Fig. 7). The reason that these correlations can be constructed is that even the noninteracting electrons have very large wave numbers available, due to the exclusion principle. Thus with a small additional expenditure of kinetic energy given by first two terms in W_c there can be a great gain in the potential energy term.

It is also possible to build a similar correlated wave function giving the singlet pairs the same nonzero total momentum. This corresponds to a

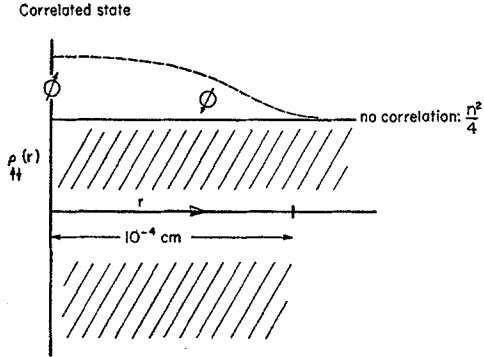


FIG. 7. The envelope of the antiparallel correlation function in the superconducting state.

current-carrying state. The energy of this current-carrying state is higher than the energy of the ground state.

It is a typical property of these correlated wave functions that not a single pair can be broken up nor can a single element of phase space be removed without a finite expenditure of energy. If a single pair correlation is broken up, one loses its correlation energy which is finite. If one removes an element of phase space from the system, the number of possible transitions of all of the pairs is reduced causing again a finite change in the energy. Thus, compared to the situation in a normal metal, one finds that one can produce single particle excitations from this correlated wave function only with the expenditure of a small but finite amount of energy, and this amounts to the introduction of an energy gap into the single particle spectrum. The energy difference between this correlated phase and the normal phase is, in fact, very small, but the nature of the wave function, qualitatively, is entirely different. The correlated wave function has a high degree of coherence and a great resistance to any kind of change, whereas in the normal metal, it is very easy through normal perturbations to change the electronic part of the wave function.

V. EXCITED STATES

In considering the excited states of the superconductor, it is useful to distinguish single particle excitations from collective excitations such as plasmons or the current carrying states mentioned in the previous section. It is the single particle excitation spectrum whose alteration is

responsible for superfluid properties. The collective modes of excitation can remain quite similar for the normal and superconducting states.

For the normal metal, we recall that for the ground state, single particle states are occupied up to the Fermi momentum. A single particle excitation is obtained by occupying a single particle state \mathbf{k}_1 above k_F , leaving a vacancy \mathbf{k}_2 below k_F . The energy of this excited state, measured with respect to the ground state, is

$$\begin{aligned} \mathcal{E}_1 - \mathcal{E}_2 &= (\mathcal{E}_1 - \mathcal{E}_F) - (\mathcal{E}_2 - \mathcal{E}_F) \\ &= \epsilon_1 - \epsilon_2 = |\epsilon_1| + |\epsilon_2|, \end{aligned} \quad (16)$$

which can be made as small as desired for a macroscopic sample.

For the superconductor excited states (quasi-particle states) can be defined in a one-to-one correspondence with the excitations of the normal metal.⁸ One then finds that the excitation energy (again measured from the ground state) for the excitation corresponding to the normal one whose energy is given by Eq. (16) is

$$E_1 + E_2 = (\epsilon_1^2 + \epsilon_0^2)^{1/2} + (\epsilon_2^2 + \epsilon_0^2)^{1/2}. \quad (17)$$

In contrast to the normal excitation energy for the superconductor even as ϵ_1 and ϵ_2 go to zero, $E_1 + E_2$ remains larger than zero; in fact the lowest possible excitation energy is given by

$$E_1 + E_2 = 2\epsilon_0. \quad (18)$$

Thus one says that there is an energy gap between the ground state and the lowest single particle excitations. This energy gap inhibits severely single particle processes and is responsible for the superfluid behavior of the electron gas.

We can draw the following picture of the excited states. In the ground state of the superconductor all the electrons are in singlet pair correlated states of zero total momentum. In an n electron excited state n electrons are in "quasi-particle" states—these let us say are the normal single particle Bloch states—they are not strongly correlated with any of the other electrons. These excited electrons exist against a background of all the other electrons which are still correlated—very much as they were in the ground state. The

⁸ An equivalent but simplified method of constructing the single particle excitations has been given by N. N. Bogolyubov, *Nuovo cimento* **7**, 794 (1958) and J. G. Valatin, *Nuovo cimento* **7**, 843 (1958).

excited electrons behave very much like normal electrons; they can be easily scattered or excited further. On the other hand, the background electrons—those which remain correlated—behave still like a superfluid and are very hard to scatter or to excite. Thus, one can identify two almost independent fluids. The correlated portion of the wave function has the properties of the superfluid: the resistance to change, the very small specific heat, whereas the excitations behave very much like normal electrons, and have an almost normal specific heat and resistance. When a steady electric field is applied to the metal the superfluid electrons short out the normal ones, but with higher frequency fields the resistive properties of the excited electrons can be observed.⁹

VI. THERMAL PROPERTIES

We are now able to deduce the thermal properties of the superconductor using the ground state and excitation spectrum previously described. The free energy of the system is given by

$$F = W_c(T) - TS, \quad (19)$$

where T is the absolute temperature and S is the entropy. The entropy of the system comes entirely from the excitations as the correlated portion of the wave function is nondegenerate. The free energy turns out to be a function of $f(\mathbf{k})$ and $h(\mathbf{k})$ where $f(\mathbf{k})$ is the probability that the state of momentum \mathbf{k} is occupied by an excitation or a quasi-particle, and $h(\mathbf{k})$ is the relative probability that the state \mathbf{k} is occupied by a pair given that it is not occupied by a quasi-particle. Thus

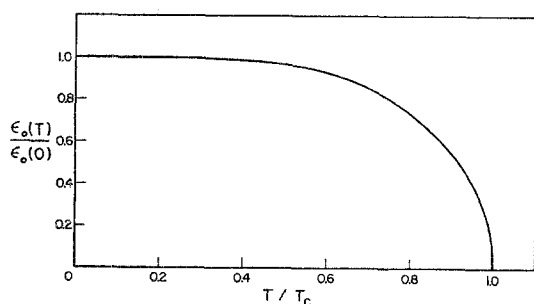


FIG. 8. Ratio of the energy gap for single particlelike excitations to the gap at $T=0^\circ\text{K}$ vs temperature.

⁹ R. E. Glover and M. Tinkham, Phys. Rev. **108**, 243 (1957); Biondi, Forrester, Garfunkel, and Satterthwaite, Revs. Modern Phys. **30**, 1109 (1958). (See Sec. V, in particular, where further references will be found.)

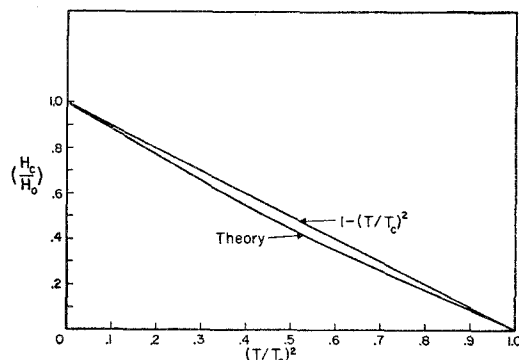


FIG. 9. Ratio of the critical field to its value at $T=0^\circ\text{K}$ vs $(T/T_c)^2$. The upper curve is the $1 - (T/T_c)^2$ law of the Gorter-Casimir theory and the lower curve is that of the idealized BCS theory in the weak coupling limit. Experimental values generally lie between the two curves.

some states are occupied by quasi-particles according to $f(\mathbf{k})$; then the remaining phase space is available for the formation of coherent states of the remaining electrons.

Setting the variation of F with respect to f and h equal to zero yields the following relations:

$$\begin{aligned} h &= \frac{1}{2}(1 - \epsilon/E), \\ f &= \frac{1}{1 + e^{\beta E}}, \\ E &= [\epsilon^2 + \epsilon_0^2(T)]^{\frac{1}{2}}, \end{aligned} \quad (20)$$

and

$$\epsilon_0(T) = N(0) V \epsilon_0(T) \int_0^{\hbar\omega} \frac{d\epsilon}{E} \tanh\left(\frac{E}{2kT}\right). \quad (21)$$

The form of these equations is the same as that at $T=0$, except that ϵ_0 , the energy gap, varies with the temperature. The variation of ϵ_0 with T is given by Eq. (21) and plotted in Fig. 8. There we see that the equation for $\epsilon_0(T)$ can be satisfied with nonzero values of $\epsilon_0(T)$ only in a restricted temperature range. The upper bound of this temperature range is defined as T_c , the critical temperature. For $T < T_c$, singlet spin zero momentum electrons are strongly correlated, there is an energy gap associated with exciting electrons from the correlated part of the wave function and $E(\mathbf{k})$ is modified according to Eq. (20). In this region the system has properties qualitatively different from the normal metal.

In the region $T > T_c$, $\epsilon_0 = 0$ and we have in every respect the normal solution. In particular

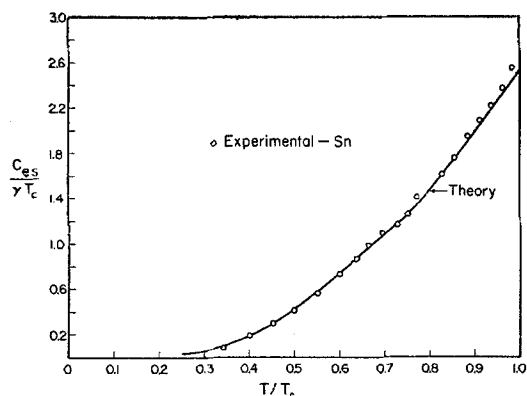


FIG. 10. Ratio of the electronic specific heat in the superconductor to its value in the normal state at T_c vs T/T_c . Experimental values for tin are shown for comparison.

f , the distribution function for excitations, becomes just the Fermi function for excited electrons $k > k_F$, and for holes $k < k_F$:

$$f = \frac{1}{1 + \exp(|\epsilon|/kT)} \quad (22)$$

Using f , and h as given by Eq. (20), we can calculate the free energy of the superconducting state and with this determine all of the equilibrium thermal properties of the system. The results of these calculations for the specific heat and the critical field are given in Figs. 9, 10, and 11.

In particular one finds that at T_c (in the absence of a magnetic field) there is a second-order transition (no latent heat: $W_c = 0$ at T_c) but a discontinuity in the specific heat. At very low temperatures the specific heat goes to zero exponentially. This idealized theory also predicts a law of corresponding states in which the ratio

$$\frac{\gamma T_c^2}{H_0^2} = 0.170,$$

where

$$\gamma = \frac{2}{3} \pi^2 N(0) k^2.$$

The experimental data scatter about the number 0.170. The ratio of ϵ_0 to kT_c is given as a universal constant

$$\epsilon_0/kT_c = 1.75.$$

For actual superconductors both of the above ratios seem to range about the numbers given above. A more realistic choice of the electron-

electron interaction modifies these results somewhat and makes possible a variation of these constants from metal to metal, leaving open the possibility of more detailed agreement of theory with experiment.

There are no arbitrary parameters in the theory. In the region of empirical interest all the thermal properties are determined by the quantities γ and $\hbar\omega e^{-1/N(0)V}$. The first, γ , is found by observation of the normal specific heat, while the second is found from the critical temperature, given by

$$kT_c = 1.14 \hbar\omega e^{-1/N(0)V}.$$

VII. ELECTRODYNAMIC PROPERTIES AND SUPERFLUIDITY

With ground state and excitation spectrum described above, one can also calculate the electrodynamic properties of the superconductor. As the detailed calculations are quite intricate, we will not reproduce them here. One can refer to the original calculations of BCS. There it is found that the material will expel magnetic fields, giving a Meissner effect¹⁰; also one obtains a

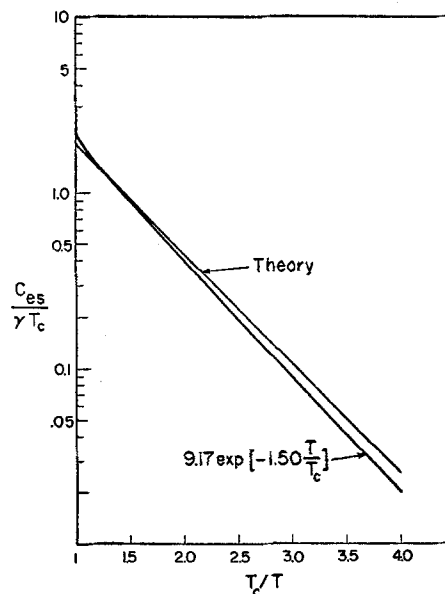


FIG. 11. A logarithmic plot of the ratio of the electronic specific heat to its value in the normal state at T_c vs T_c/T . The simple exponential fits the experimental data for tin and vanadium well for $T_c/T > 1.4$.

¹⁰ For a discussion of problems concerning gauge invariance and collective excitations in the theory of superconductivity one can refer to P. W. Anderson, Phys. Rev. 112, 1900 (1958).

penetration depth, and a variation of the penetration depth with temperature as mentioned by Professor Boorse.¹

Fortunately a qualitative picture of the phenomenon for which superconductivity was named can be easily drawn. To choose the simplest possible situation imagine the metal at absolute zero. In this case, there would be no resistance even for a normal metal other than resistance caused by impurities, since there are no free phonons. We then consider an impure normal specimen at the absolute zero, where the resistance is due to the scattering of Bloch waves from the impurities.

Suppose one places a field on this normal specimen. Then the Fermi sphere is displaced so that the electrons have some total momentum, and there is a current. As long as the field is on, there is a certain equilibrium current, because the acceleration caused by the field is balanced by the deceleration due to scattering of electrons from the impurities. If the field is turned off, the electrons will very rapidly return to a state of no current, as the scattering by impurities will randomize their motion.

We can now contrast this with the situation in the superconducting state. Here the electron wave function is very highly correlated. Each electron near the Fermi surface where the current is flowing is correlated to another with opposite spin. Once this coherent pattern is established, it is very difficult to break up the state via the mechanism of impurity scattering. The reason for this is found in the basic properties of correlated wave functions. To break up correlated pair or to get any single particle excitation requires finite energy. Thus, any single particle scattering process increases the energy of the electron system if the current is not too large in spite of the fact that the total energy is larger than the ground state energy. Unless the extra kinetic energy of the electron due to the current flow is larger than the energy gap, the scattering process

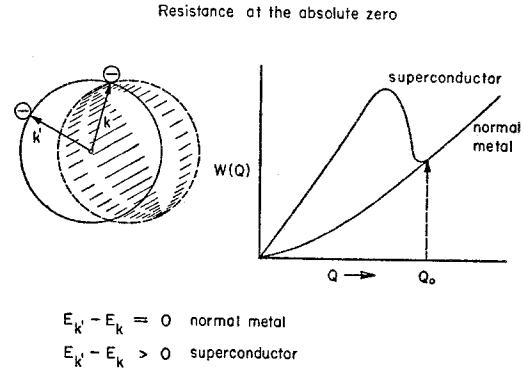


FIG. 12. Persistent currents are maintained in the impure superconductor at $T=0^\circ\text{K}$, even though the energy of the current state is larger than that of the ground state. This is due to the energy gap in the single particle excitation spectrum, which (for small enough currents) prevents the elastic scattering of electrons by the impurities. As elastic scattering by impurities is the mechanism which destroys the current in the normal state, with this mechanism suppressed, the current is metastable and the metal is a superconductor.

will be severely inhibited. At any finite temperature, the situation is very similar. The excitations act as normal electrons against the background of the superfluid. If the system is put into a state of current, the current will be carried entirely by the superfluid electrons (as the normal electrons are shorted out). For a particular current the system is in a minimum of free energy. Single particle excitations can only increase the free energy and the system is metastable (see Fig. 12).

This final illustration again reveals the basic property of the superconducting state wave function: its tremendous coherence and resistance to change via single particle mechanisms, which is essentially the criterion for superfluidity. Since most of the dissipative processes which appear macroscopically as resistance or friction are single particle processes, a system in which such single particle processes are severely inhibited, in spite of the fact that collective motions (such as states of nonzero total momentum in which a current or a fluid flows) are possible, appears macroscopically as a superfluid.