MICROSCOPIC QUANTUM INTERFERENCE EFFECTS IN THE THEORY OF SUPERCONDUCTIVITY

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by

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It is an honor and a pleasure to speak to you today about the theory of superconductivity. In a short lecture one can no more than touch on the long history of experimental and theoretical work on this subject before 1957. Nor can one hope to give an adequate account of how our understanding of superconductivity has evolved since that time. The theory (1) we presented in 1957, applied to uniform materials in the weak coupling limit so defining an ideal superconductor, has been extended in almost every imaginable direction. To these developments so many authors have contributed (2) that we can make no pretense of doing them justice. I will confine myself here to an outline of some of the main features of our 1957 theory, an indication of directions taken since and a discussion of quantum interference effects due to the singlet-spin pairing in superconductors which might be considered the microscopic analogue of the effects discussed by Professor Schrieffer.

NORMAL METAL

Although attempts to construct an electron theory of electrical conductivity date from the time of Drude and Lorentz, an understanding of normal metal conduction electrons in modern terms awaited the development of the quantum theory. Soon thereafter Sommerfeld and Bloch introduced what has evolved into the present description of the electron fluid. (3) There the conduction electrons of the normal metal are described by single particle wave functions. In the periodic potential produced by the fixed lattice and the conduction electrons themselves, according to Bloch's theorem, these are modulated plane waves:

$$\varnothing_{\boldsymbol{K}}(\boldsymbol{r}) = \mathrm{u}_{\boldsymbol{K}}(\boldsymbol{r})\, \mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}},$$

where $\mathrm{u}_k(\mathbf{r})$ is a two component spinor with the lattice periodicity. We use $\mathbf{K}$ to designate simultaneously the wave vector $\mathbf{k}$, and the spin state $\sigma: K \equiv k, \uparrow$; $-K \equiv -k, \downarrow$. The single particle Bloch functions satisfy a Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_0(\boldsymbol{r})\right]\varnothing_{\boldsymbol{K}} = \varepsilon_{\boldsymbol{K}}\varnothing_{\boldsymbol{K}}$$

where $V_o(\mathbf{r})$ is the periodic potential and in general might be a linear operator to include exchange terms.

The Pauli exclusion principle requires that the many electron wave function be antisymmetric in all of its coordinates. As a result no two electrons can be

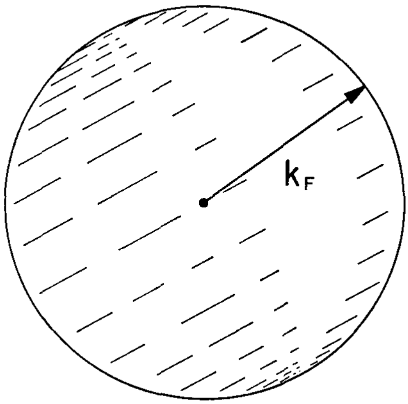


Fig. 1.
The normal ground state wavefunction, Φ_0, is a filled Fermi sphere for both spin directions.

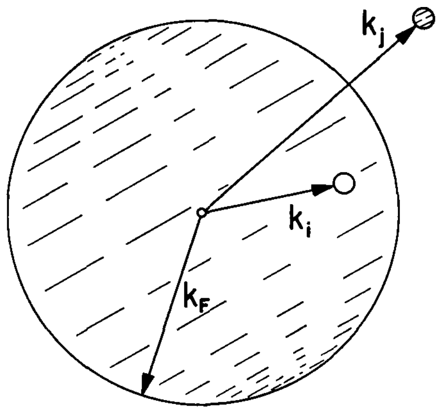


Fig. 2.
An excitation of the normal system.

in the same single particle Bloch state. The energy of the entire system is

$$W = \sum_{i=1}^{2N} \mathcal{E}_i$$

where $\mathcal{E}_i$ is the Bloch energy of the i^{th} single electron state. The ground state of the system is obtained when the lowest N Bloch states of each spin are occupied by single electrons; this can be pictured in momentum space as the filling in of a Fermi sphere, Fig. 1. In the ground-state wave function there is no correlation between electrons of opposite spin and only a statistical correlation (through the general anti-symmetry requirement on the total wave function) of electrons of the same spin.

Single particle excitations are given by wave functions identical to the ground state except that one electron states $k_i < k_F$ are replaced by others $kj < k_F$. This may be pictured in momentum space as opening vacancies below the Fermi surface and placing excited electrons above, Fig. 2. The energy difference between the ground state and the excited state with the particle excitation k_j and the hole excitation k_i is

$$\mathcal{E}_j - \mathcal{E}_i = \mathcal{E}_j - \mathcal{E}_F - (\mathcal{E}_i - \mathcal{E}_F) = \varepsilon_j - \varepsilon_i = |\varepsilon_j| + |\varepsilon_i|$$

where we define ε as the energy measured relative to the Fermi energy

$$\varepsilon_i = \mathcal{E}_i - \mathcal{E}_F.$$

When Coulomb, lattice-electron and other interactions, which have been omitted in constructing the independent particle Bloch model are taken into account, various modifications which have been discussed by Professor Schrieffer are introduced into both the ground state wave function and the excitations. These may be summarized as follows: The normal metal is described by a ground state Φ_0 and by an excitation spectrum which, in addition to the various collective excitations, consists of quasi-fermions which satisfy the usual anticommutation relations. It is defined by the sharpness of the Fermi surface, the finite density of excitations, and the continuous decline of the single particle excitation energy to zero as the Fermi surface is approached.

ELECTRON CORRELATIONSTHAT PRODUCE SUPERCONDUCTIVITY

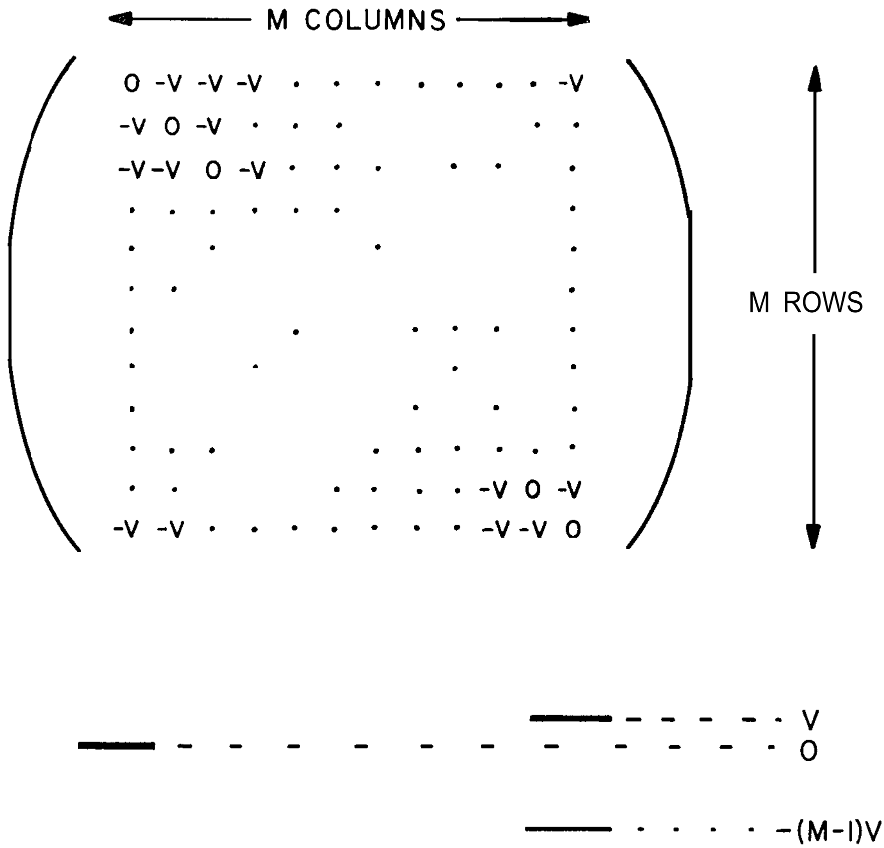
For a description of the superconducting phase we expect to include correlations that are not present in the normal metal. Professor Schrieffer has discussed the correlations introduced by an attractive electron-electron interaction and Professor Bardeen will discuss the role of the electron-phonon interaction in producing the electron-electron interaction which is responsible for superconductivity. It seems to be the case that any attractive interaction between the fermions in a many-fermion system can produce a superconducting-like state. This is believed at present to be the case in nuclei, in the interior of neutron stars and has possibly been observed (4) very recently in He^3. We will therefore develop the consequences of an attractive two-body interaction in a degenerate many-fermion system without enquiring further about its source.

The fundamental qualitative difference between the superconducting and normal ground state wave function is produced when the large degeneracy of the single particle electron levels in the normal state is removed. If we visualize the Hamiltonian matrix which results from an attractive two-body interaction in the basis of normal metal configurations, we find in this enormous matrix, sub-matrices in which all single-particle states except for one pair of electrons remain unchanged. These two electrons can scatter via the electron-electron interaction to all states of the same total momentum. We may envisage the pair wending its way (so to speak) over all states unoccupied by other electrons. [The electron-electron interaction in which we are interested is 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 only single particle excitations in a small shell near the Fermi surface play a role. It turns out, further, that due to exchange terms in the electron-electron matrix element, the effective interaction in metals between electrons of singlet spin is much stronger than that between electrons of triplet spin-thus our preoccupation with singlet spin correlations near the Fermi surface.] Since every such state is connected to every other, if the interaction is attractive and does not vary rapidly, we are presented with submatrices of the entire Hamiltonian of the form shown in Fig. 3. For purposes of illustration we have set all off diagonal matrix elements equal to the constant-V and the diagonal terms equal to zero (the single particle excitation energy at the Fermi surface) as though all the initial electron levels were completely degenerate. Needless to say, these simplifications are not essential to the qualitative result.

Diagonalizing this matrix results in an energy level structure with M-1 levels raised in energy to $E = + V$ while one level (which is a superposition of all of the original levels and quite different in character) is lowered in energy to

$$E = -(M-1)V.$$

Since M, the number of unoccupied levels, is proportional to the volume of the container while V, the scattering matrix element, is proportional to l/volume, the product is independent of the volume. Thus the removal of



For V = 0,
M levels
at E = 0

For V > 0, M — 1 levels at
E = V and one level
at E = —(M—1) V

Fig. 3

the degeneracy produces a single level separated from the others by a volume independent energy gap.

To incorporate this into a solution of the full Hamiltonian, one must devise a technique by which all of the electrons pairs can scatter while obeying the exclusion principle. The wave function which accomplishes this has been discussed by Professor Schrieffer. Each pair gains an energy due to the removal of the degeneracy as above and one obtains the maximum correlation of the entire wave function if the pairs all have the same total momentum. This gives a coherence to the wave function in which 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.

In what follows I shall present an outline of our 1957 theory modified by introducing the quasi-particles of Bogoliubov and Valatin. (5) This leads to a formulation which is generally applicable to a wide range of calculations

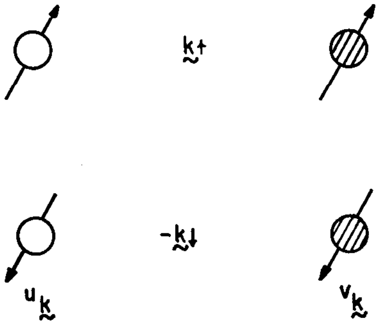


Fig. 4.
The ground state of the superconductor is a linear superposition of states in which pairs (k↑- k↓) are occupied or unoccupied.

in a manner analogous to similar calculations in the theory of normal metals.

We limit the interactions to terms which scatter (and thus correlate) singlet zero-momentum pairs. To do this, it is convenient to introduce the pair operators :

$$b_k = c_{-K} c_K$$
$$b_k^* = c_K^* c_{-K}^*$$

and using these we extract from the full Hamiltonian the so-called reduced Hamiltonian

$$H_{\text{reduced}} = \sum_{k<k_f} 2|\varepsilon| b_k b_k^* + \sum_{k>k_f} 2\varepsilon b_k^* b_k + \sum_{kk'} V_{k'k} b_{k'}^* b_k$$

where $V_{k'k}$ is the scattering matrix element between the pair states k and k'.

GROUND STATE

As Professor Schrieffer has explained, the ground state of the superconductor is a linear superposition of pair states in which the pairs (k↑, k↓) are occupied or unoccupied as indicated in Fig. 4. It can be decomposed into two disjoint vectors - one in which the pair state k is occupied, ϕ and one in which it is unoccupied, $\phi_{(k)}$:

$$\psi_0 = u_k \emptyset_{(k)} + v_k \emptyset_k.$$

The probability amplitude that the pair state k is (is not) occupied in the ground state is then $v_k(u_k)$. Normalization requires that $|u|^2 + |v|^2 = 1$. The phase of the ground state wave function may be chosen so that with no loss o generality u_k is real. We can then write

$$u = (1-h)^{1/2}$$
$$v = h^{1/2} e^{i\varphi}$$

where

$$0 \leqslant h \leqslant 1.$$

A further decomposition of the ground state wave function of the superconductor in which the pair states k and k' are either occupied or unoccupied Fig. 5 is:

$$\psi_0 = u_k u_{k'} \emptyset_{(k),(k')} + u_k v_{k'} \emptyset_{(k),k'} + v_k u_{k'} \emptyset_{k,(k')} + v_k v_{k'} \emptyset_{k,k'} \ .$$

This is a Hartree-like approximation in the probability amplitudes for the occupation of pair states. It can be shown that for a fermion system the wave

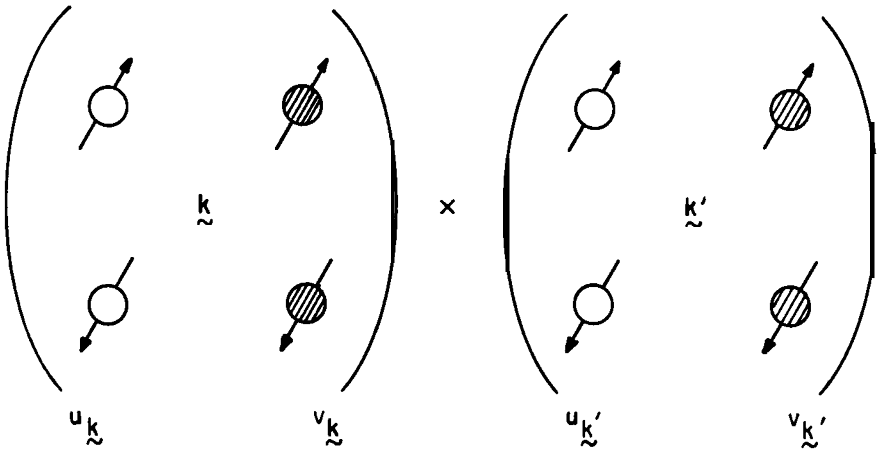


Fig. 5.
A decomposition of the ground state of the superconductor into states in which the pair states k and k' are either occupied or unoccupied.

function cannot have this property unless there are a variable number of particles. To terms of order 1/N, however, this decomposition is possible for a fixed number of particles; the errors introduced go to zero as the number of particles become infinite. (6)

The correlation energy, W_c, is the expectation value of H_{red} for the state ψ_0

$$W_c = (\psi_0, H_{red}\psi_0) = W_c\,[h,\varphi].$$

Setting the variation of W_c with respect to h and φ equal to zero in order to minimize the energy gives

$$h = 1/2\ (1-\varepsilon/E)$$

$$E = (\varepsilon^2 + |\Delta|^2)^{1/2}$$

where

$$\Delta = |\Delta| e^{i\varphi}$$

satisfies the integral equation

$$\Delta(\boldsymbol{k}) = -1/2 \sum_{k'} V_{kk'} \frac{\Delta(\boldsymbol{k'})}{E(\boldsymbol{k'})}.$$

If a non-zero solution of this integral equation exists, $W_c < 0$ and the "normal" Fermi sea is unstable under the formation of correlated pairs.

In the wave function that results there are strong correlations between pairs of electrons with opposite spin and zero total momentum. These correlations are built from normal excitations near the Fermi surface and extend over spatial distances typically of the order of 10^{-4} cm. They can be constructed due to the large wave numbers available because of the exclusion principle. Thus with a small additional expenditure of kinetic energy there can be a greater gain in the potential energy term. Professor Schrieffer has discussed some of the properties of this state and the condensation energy associated with it.

SINGLE-PARTICLE EXCITATIONS

In considering the excited states of the superconductor it is useful, as for the

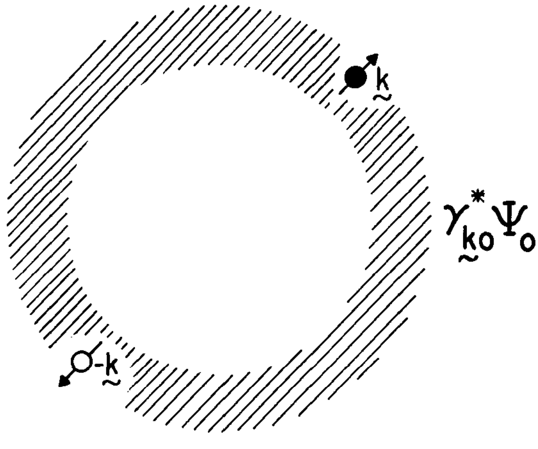


Fig. 6.
A single par icle excitation of the superconduc or in one-to-one correspondent with an excitation of the normal fermion system.

normal metal, to make a distinction between single-particle and collective excitations; it is the single-particle excitation spectrum whose alteration is responsible for superfluid properties. For the superconductor excited (quasi-particle) states can be defined in one-to-one correspondence with the excitations of the normal metal. One finds, for example, that the expectation value of H_{red} for the excitation Fig. 6 is given by

$$E_k = \sqrt{\varepsilon_k^2 + |\Delta|^2}.$$

In contrast to the normal system, for the superconductor even as ε goes to zero E remains larger than zero, its lowest possible value being $E = |\Delta|$. One can therefore produce single particle excitations from the superconducting ground state only with the expenditure of a small but finite amount of energy. This is called the energy gap; its existence severely inhibits single particle processes and is in general responsible for the superfluid behavior of the electron gas. [In a gapless superconductor it is the finite value of $\Delta(r)$, the order parameter, rather than the energy gap as such that becomes responsible for the superfluid properties.] In the ideal superconductor, the energy gap appears because not a single pair can be broken nor can a single element of phase space be removed without a finite expenditure of energy. If a single pair is broken, one loses its correlation energy; if one removes an element of phase space from the system, the number of possible transitions of all the pairs is reduced resulting in both cases in an increase in the energy which does not go to zero as the volume of the system increases.

The ground state of the superconductor and the excitation spectrum described above can conveniently be treated by introducing a linear combination of c* and c, the creation and annihilation operators of normal fermions. This is the transformation of Bogoliubov and Valatin (5):

$$\gamma^*_{k0} = u_k c^*_K - v^*_k c_{-K}$$
$$\gamma^*_{k1} = v^*_k c_K + u_k c^*_{-K}$$

It follows that

$$\gamma_{ki}\psi_0 = 0$$

so that the γ_{ki} play the role of annihilation operators, while the γ_{ki}^* create excitations

$$\gamma_{ki}^* \cdots \gamma_{mj}^* \psi_0 = \psi_{ki}, \ldots_{mj}.$$

The γ operators satisfy Fermi anti-commutation relations so that with them we obtain a complete orthonormal set of excitations in one-to-one correspondence with the excitations of the normal metal.

We can sketch the following picture. In the ground state of the superconductor all the electrons are in singlet-pair correlated states of zero total momentum. In an m electron excited state the excited electrons are in "quasi-particle" states, very similar to the normal excitations and not strongly correlated with any of the other electrons. In the background, so to speak, the other electrons are still correlated much as they were in the ground state. The excited electrons behave in a manner similar to normal electrons; they can be easily scattered or excited further. But the background electrons - those which remain correlated - retain their special behavior; they are difficult to scatter or to excite.

Thus, one can identify two almost independent fluids. The correlated portion of the wave function shows the resistance to change and the very small specific heat characteristic of the superfluid, while the excitations behave very much like normal electrons, displaying 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. [7]

THERMODYNAMIC PROPERTIES, THE IDEAL SUPERCONDUCTOR

We can obtain the thermodynamic properties of the superconductor using the ground state and excitation spectrum just described. The free energy of the system is given by

$$F[h, \varphi, f] = W_c(T) - TS,$$

where T is the absolute temperature and S is the entropy; f is the superconducting Fermi function which gives the probability of single-particle excitations. The entropy of the system comes entirely from the excitations as the correlated portion of the wave function is non-degenerate. The free energy becomes a function of $f(k)$ and h(k), where $f(k)$ is the probability that the state k is occupied by an excitation or a quasi-particle, and $h(k)$ is the relative probability that the state k is occupied by a pair given that is not occupied by a quasi-particle. Thus some states are occupied by quasi-particles and the unoccupied phase space is available for the formation of the coherent background of the remaining electrons. Since a portion of phase space is occupied by excitations at finite temperatures, making it unavailable for the transitions of bound pairs, the correlation energy is a function of the temperature, $W_c(T)$. As T increases, $W_c(T)$ and at the same time Δ decrease until the critical temperature is reached and the system reverts to the normal phase.

Since the excitations of the superconductor are independent and in a one-to-one correspondence with those of the normal metal, the entropy of an excited configuration is given by an expression identical with that for the normal metal except that the Fermi function, $f(k)$, refers to quasi-particle excitations. The correlation energy at finite temperature is given by an expression similar to that at $T = 0$ with the available phase space modified by the occupation functions $f(k)$. Setting the variation of F with respect to h, φ, and f equal to zero gives:

$$h = 1/2\ (1-\varepsilon/E)$$
$$E = \sqrt{\varepsilon^2 + |\Delta|^2}$$

and

$$f = \frac{1}{1 + \exp(E/k_B T)}$$

where

$$\Delta = |\Delta| e^{i\varphi}$$

is now temperature-dependent and satisfies the fundamental integral equation of the theory

$$\Delta_k(T) = -1/2 \sum_{kk'} V_{kk'} \frac{\Delta_{k'}(T)}{E_{k'}(T)} \tanh\left(\frac{E_{k'}(T)}{2k_B T}\right).$$

The form of these equations is the same as that at $T = 0$ except that the energy gap varies with the temperature. The equation for the energy gap can be satisfied with non-zero values of Δ 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 $E(k)$ is bounded below by $|\Delta|$. In this region the system has properties qualitatively different from the normal metal.

In the region $T > T_c$, $\Delta = 0$ and we have in every respect the normal solution. In particular f, the distribution function for excitations, becomes just the Fermi function for excited electrons $k > k_F$, and for holes $k < k_F$

$$f = \frac{1}{1 + \exp(|\varepsilon|/k_B T)}.$$

If we make our simplifications of 1957, (defining in this way an 'ideal' superconductor)

$$V_{k'k} = -V \qquad |\varepsilon| < \hbar\omega_{av}$$
$$= 0 \qquad \text{otherwise}$$

and replace the energy dependent density of states by its value at the Fermi surface, $N(0)$, the integral equation for Δ becomes

$$1 = N(0)\, V \int_0^{\hbar\omega_{av}} \frac{d\varepsilon}{\sqrt{\varepsilon^2 + |\Delta|^2}} \tanh\left(\frac{\sqrt{\varepsilon^2 + |\Delta|^2}}{2k_B T}\right).$$

The solution of this equation, Fig. 7, gives $\Delta(T)$ and with this f and h. We can then calculate the free energy of the superconducting state and obtain the thermodynamic properties of the system.

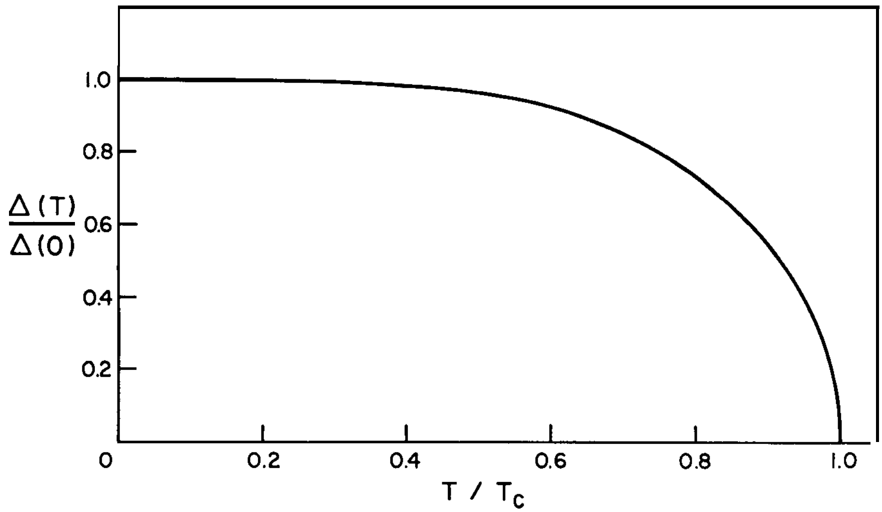


Fig. 7.
Variation of the energy gap with temperature for the ideal superconductor.

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) and a discontinuity in the specific heat. At very low temperatures the specific heat goes to zero exponentially. For this ideal superconductor one also obtains a law of corresponding states in which the ratio

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

where

$$\gamma = 2/3\pi^2 N(0) k_B^2.$$

The experimental data scatter about the number 0.170. The ratio of A to $k_B T_c$ is given as a universal constant

$$\Delta / k_B T_c = 1.75.$$

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

$$k_B T_c = 1.14\, \hbar\omega_{av} e^{-1/N(0)V}.$$

At the absolute zero

$$\Delta = \hbar\omega_{av}/\sinh\left(\frac{1}{N(0)V}\right).$$

Further, defining a weak coupling limit [N(O) $V \ll 1$] which is one region of interest empirically, we obtain

$$\Delta \simeq 2\hbar\omega_{av} e^{-1/N(0)V}.$$

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

$$W_s - W_n = W_c = -2N(0)(\hbar\omega_{av})^2\, e^{-2/N(0)V}.$$

The dependence of the correlation energy on $(\hbar\omega_{av})^2$ gives the isotope effect, while the exponential factor reduces the correlation energy from the dimensionally expected $\mathcal{N}(0)(\hbar\omega_{av})^2$ to the much smaller observed value. This, however, is more a demonstration that the isotope effect is consistent with our model rather than a consequence of it, as will be discussed further by Professor Bardeen.

The thermodynamic properties calculated for the ideal superconductor are in qualitative agreement with experiment for weakly coupled superconductors. Very detailed comparison between experiment and theory has been made by many authors. A summary of the recent status may be found in reference (2). When one considers that in the theory of the ideal superconductor the existence of an actual metal is no more than hinted at (We have in fact done all the calculations considering weakly interacting fermions in a container.) so that in principle (with appropriate modifications) the calculations apply to neutron stars as well as metals, we must regard detailed quantitative agreement as a gift from above. We should be content if there is a single metal for which such agreement exists. [Pure single crystals of tin or vanadium are possible candidates.]

To make comparison between theory and experiments on actual metals, a plethora of detailed considerations must be made. Professor Bardeen will discuss developments in the theory of the electron-phonon interaction and the resulting dependence of the electron-electron interaction and superconducting properties on the phonon spectrum and the range of the Coulomb repulsion. Crystal symmetry, Brillouin zone structure and the actual wave function (S, P or D states) of the conduction electrons all play a role in determining real metal behavior. There is a fundamental distinction between superconductors w ich always show a Meissner effect and those (type II) which allow magnetic field penetration in units of the flux quantum.

When one considers, in addition, specimens with impurities (magnetic and otherwise) superimposed films, small samples, and so on, one obtains a variety of situations, developed in the years since 1957 by many authors, whose richness and detail takes volumes to discuss. The theory of the ideal superconductor has so far allowed the addition of those extensions and modifications necessary to describe, in what must be considered remarkable detail, all of the experience actually encountered.

MICROSCOPIC INTERFERENCE EFFECTS

In its interaction with external perturbations the superconductor displays remarkable interference effects which result from the paired nature of the wave function and are not at all present in similar normal metal interactions. Neither would they be present in any ordinary two-fluid model. These "coherence effects" are in a sense manifestations of interference in spin and momentum space on a microscopic scale, analogous to the macroscopic quantum effects due to interference in ordinary space which Professor Schrieffer discussed. They depend on the behavior under time reversal of the perturbing fields. (8) It is intriguing to speculate that if one could somehow amplify them

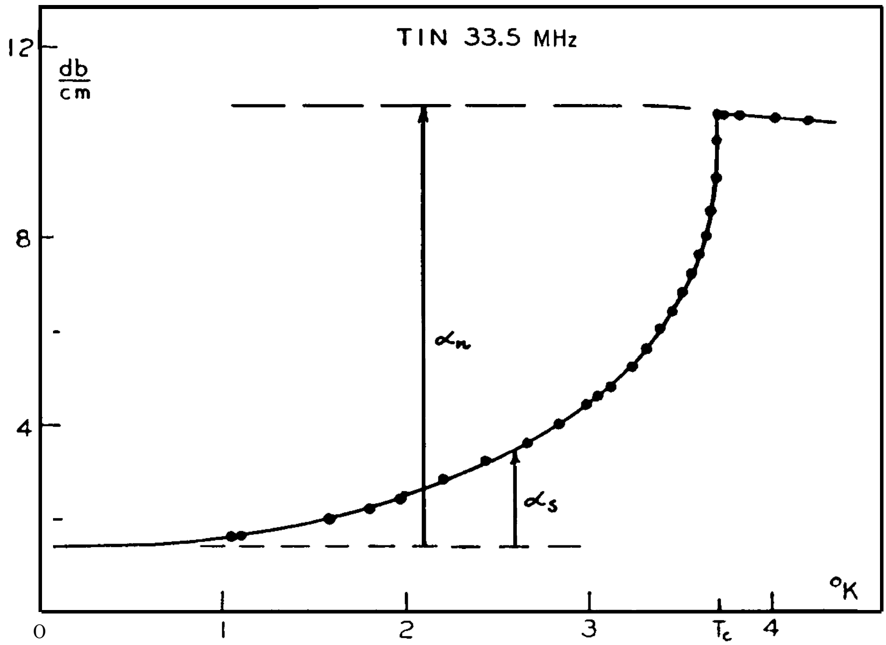


Fig. 8.
Ultrasonic attenuation as a function of temperature across the superconducting transition as measured by Morse and Bohm.

properly, the time reversal symmetry of a fundamental interaction might be tested. Further, if helium 3 does in fact display a phase transition analogous to the superconducting transition in metals as may be indicated by recent experiments (4) and this is a spin triplet state, the coherences effects would be greatly altered.

Near the transition temperature these coherence effects produce quite dramatic contrasts in the behavior of coefficients which measure interactions with the conduction electrons. Historically, the comparison with theory of the behavior of the relaxation rate of nuclear spins (9) and the attenuation of longitudinal ultrasonic waves in clean samples (10) as the temperature is decreased through T_c provided an early test of the detailed structure of the theory.

The attenuation of longitudinal acoustic waves due to their interaction with the conduction electrons in a metal undergoes a very rapid drop (10a) as the temperature drops below T_c. Since the scattering of phonons from "normal" electrons is responsible for most of the acoustic attenuation, a drop was to be expected ; but the rapidity of the decrease measured by Morse and Bohm (10b) Fig. 8 was difficult to reconcile with estimates of the decrease in the normal electron component of a two-fluid model.

The rate of relaxation of nuclear spins was measured by Hebel and Slichter (9a) in zero magnetic field in superconducting aluminum from 0.94 K to 4.2 K just at the time of the development of our 1957 theory. Redfield and Anderson (9b) confirmed and extended their results. The dominant relaxation mechanism is provided by interaction with the conduction electrons so that one would expect, on the basis of a two-fluid model, that this rate should decrease below the transition temperature due to the diminishing density of "normal" electrons. The experimental results however show just the reverse. The relaxation rate does not drop but increases by a factor of more than two just below the transition temperature. Fig 13. This observed increase in the nuclear spin relaxation rate and the very sharp drop in the acoustic attenuation coefficient as the temperature is decreased through T_c impose contradictory requirements on a conventional two-fluid model.

To illustrate how such effects come about in our theory, we consider the transition probability per unit time of a process involving electronic transitions from the excited state k to the state k′ with the emission to or absorption of energy from the interacting field. What is to be calculated is the rate of transition between an initial state $|i>$ and a final state $|f>$ with the absorption or emission of the energy $\hbar\omega_{|\boldsymbol{k}'-\boldsymbol{k}|}$ (a phonon for example in the interaction of sound waves with the superconductor). All of this properly summed over final states and averaged with statistical factors over initial states may be written:

$$\omega = \frac{2\pi}{\hbar} \frac{\sum_{i,f} \exp(-W_i/k_B T)\left| <f|H_{\text{int}}|i> \right|^2 \delta(W_f - W_i)}{\sum_i \exp(-W_i/k_B T)}$$

We focus our attention on the matrix element $<f|H_{\text{int}}|i>$. This typically contains as one of its factors matrix elements between excited states of the superconductor of the operator

$$B = \sum_{\boldsymbol{K}\,\boldsymbol{K}'} B_{\boldsymbol{K}'\boldsymbol{K}} c^*_{\boldsymbol{K}'} c_{\boldsymbol{K}}$$

where $c^*_{\boldsymbol{K}'}$ and c_K are the creation and annihilation operators for electrons in the states K′ and K, and *Bk1,,* is the matrix element between the states *K'* and *K* of the configuration space operator *B(r)*

$$B_{\boldsymbol{K}'\boldsymbol{K}} = <\boldsymbol{K}'|B(\boldsymbol{r})|\boldsymbol{K}>.$$

The operator *B* is the electronic part of the matrix element between the full final and initial state

$$<f|H_{\text{int}}|i> = m_{fi} <f|B|i>.$$

In the normal system scattering from single-particle electron states *K* to *K'* is independent of scattering from -K′ to -K. But the superconducting states are linear superpositions of *(K,* -K) occupied and unoccupied. Because of this states with excitations $\boldsymbol{k}\uparrow$ and $k'\uparrow$ are connected not only by $c^*_{\boldsymbol{k}'\uparrow} c_{\boldsymbol{k}\uparrow}$ but also by $c^*_{-\boldsymbol{k}\downarrow} c_{-\boldsymbol{k}'\downarrow}$; if the state $|f>$ contains the single-particle excitation $k'\uparrow$ while the state $|i>$ contains $\boldsymbol{k}\uparrow$, as a result of the superposition of occupied and unoccupied pair states in the coherent part of the wave function, these are connected not only by $B_{\boldsymbol{K}'\boldsymbol{K}} c^*_{\boldsymbol{K}'} c_{\boldsymbol{K}}$ but also by $B_{-\boldsymbol{K}-\boldsymbol{K}'} c^*_{-\boldsymbol{K}} c_{-\boldsymbol{K}'}$.

For operators which do not flip spins we therefore write:

$$B = \sum_{\boldsymbol{k}\,\boldsymbol{k}'} (B_{\boldsymbol{K}'\boldsymbol{K}} c^*_{\boldsymbol{K}'} c_{\boldsymbol{K}} + B_{-\boldsymbol{K}-\boldsymbol{K}'} c^*_{-\boldsymbol{K}} c_{-\boldsymbol{K}'}).$$

Many of the operators, *B,* we encounter (e.g., the electric current, or the charge density operator) have a well-defined behavior under the operation of time reversal so that

$$B_{\boldsymbol{K}'\boldsymbol{K}} = \pm B_{-\boldsymbol{K}-\boldsymbol{K}'} \equiv B_{\boldsymbol{k}'\boldsymbol{k}}.$$

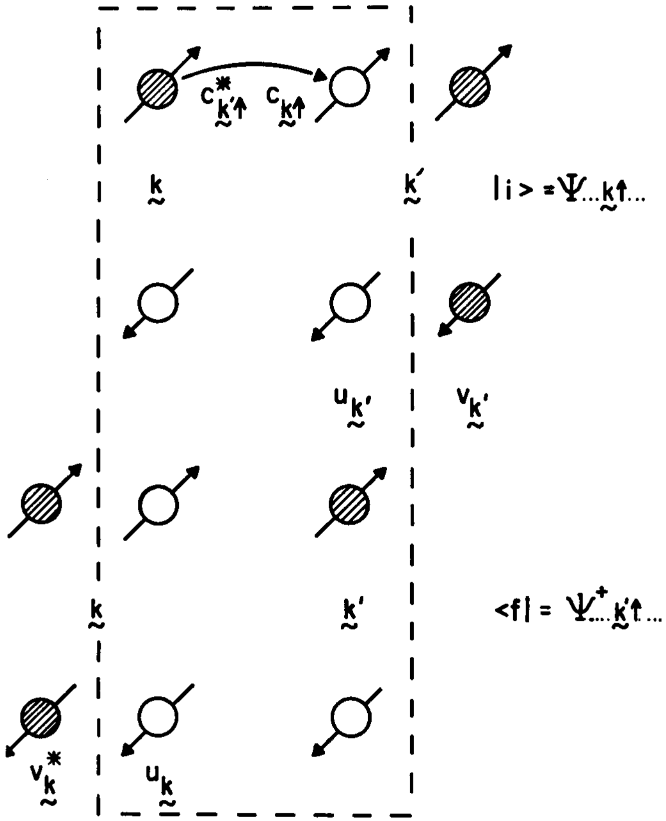


Fig. 9.
The two states $|\, i >$ and $< f \,|$ shown are connected by $c^*_{k'\uparrow}\, c_{k\uparrow}$ with the amplitude $u_{k'}u_k$.

Then B becomes

$$B = \sum_{k\,k'} B_{k'k}\, (c^*_{k'\uparrow} c_{k\uparrow} \pm c^*_{-k\downarrow} c_{-k'\downarrow})$$

where the upper (lower) sign results for operators even (odd) under time reversal.

The matrix element of B between the initial state, $\psi \ldots {}_{k\uparrow} \ldots$, and the final state $\psi \ldots {}_{k'\uparrow} \ldots$ contains contributions from $c^*_{k'\uparrow} c_{k\uparrow}$ Fig.9 and unexpectedly from $c^*_{-k\downarrow} c_{-k'\downarrow}$ Fig. 10. As a result the matrix element squared $|< f \,|\, B \,|\, i >|^2$ contains terms of the form

$$|B_{k'k}|^2 \; |(u_{k'}u_k \mp v_{k'}v^*_k)|^2,$$

where the sign is determined by the behavior of B under time reversal:

upper sign $\quad B$ even under time reversal

lower sign $\quad B$ odd under time reversal.

Applied to processes involving the emission or absorption of boson quanta such as phonons or photons, the squared matrix element above is averaged with the appropriate statistical factors over initial and summed over final states; substracting emission from absorption probability per unit time, we obtain typically

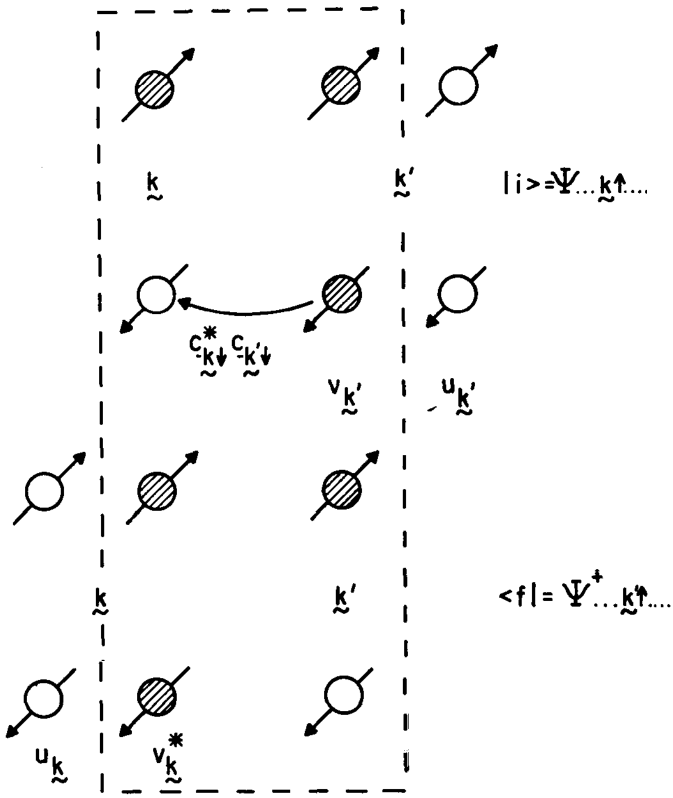


Fig. 10.
The two states $|i>$ and $<f|$ are also connected by $c^*_{k\downarrow}c_{k'\downarrow}$ with the amplitude $v_{k'}v^*_k$.

$$a = \frac{4\pi}{\hbar}|m|^2 \sum_{kk'} \left|(u_{k'}u_k \mp v_{k'}v^*_k)\right|^2 \ (f_{k'}-f_k)\ \delta(E_{k'}-E_k-\hbar\omega_{|k-k'|})$$

where f_k is the occupation probability in the superconductor for the excitation $k\uparrow$or $k\downarrow$,. [In the expression above we have considered only quasiparticle or quasi-hole scattering processes (not including processes in which a pair of excitations is created or annihilated from the coherent part of the wave function) since $h\varpi_{|k'-k|} < \Delta$, is the usual region of interest for the ultrasonic attenuation and nuclear spin relaxation we shall contrast.]

For the ideal superconductor, there is isotropy around the Fermi surface and symmetry between particles and holes; therefore sums of the form $\underset{k}{Z}$ can be converted to integrals over the superconducting excitation energy, E:

$$\sum_k \rightarrow 2\mathcal{N}(0)\int_{\Delta}^{\infty}\frac{E}{\sqrt{E^2-\Delta^2}}\,\mathrm{d}E$$

where N(~~0)~~ $_J$- - - !& = N(O)$_E$-is the density of excitations in the super- E

conductor, Fig. 11.

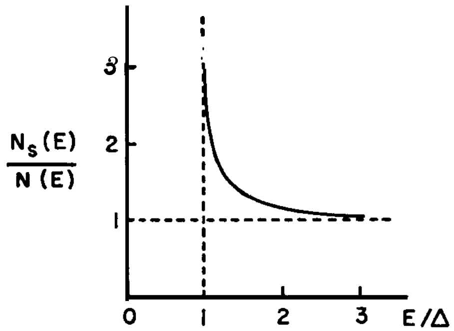


Fig. 11.
Ratio of superconducting to normal density of excitations as a function of E/Δ.

The appearance of this density of excitations is a surprise. Contrary to our intuitive expectations, the onset of superconductivity seems initially to enhance rather than diminish electronic transitions, as might be anticipated in a reasonable two-fluid model.

But the coherence factors $|(u'u \mp v'v^*)|^2$ are even more surprising; they behave in such a way as to sometimes completely negate the effect of the increased density of states. This can be seen using the expressions obtained above for u and v for the ideal superconductor to obtain

$$(u'u \mp v'v)^2 = \frac{1}{2}\left(1 + \frac{\varepsilon\varepsilon' \mp \Delta^2}{EE'}\right).$$

In the integration over k and k' the $\varepsilon\varepsilon'$ term vanishes. We thus define $(u'u \mp v'v)_s^2$; in usual limit where $\hbar\omega_{|k'-k|} \ll \Delta$, $\varepsilon \simeq \varepsilon'$ and $E \simeq E'$, this becomes

$$(u^2 - v^2)_s^2 \rightarrow \frac{1}{2}\left(\frac{\varepsilon^2}{E^2}\right) \qquad \text{operators even under time reversal}$$

$$(u^2 + v^2)_s^2 \rightarrow \frac{1}{2}\left(1 + \frac{E^2}{\Delta^2}\right) \qquad \text{operators odd under time reversal.}$$

For operators even under time reversal, therefore, the decrease of the coherence factors near $\varepsilon = 0$ just cancels the increase due to the density of states. For the operators odd under time reversal the effect of the increase of the density of states is not cancelled and should be observed as an increase in the rate of the corresponding process.

In general the interaction Hamiltonian for a field interacting with the superconductor (being basically an electromagnetic interaction) is invariant under the operation of time reversal. However, the operator B might be the electric current j(r) (for electromagnetic interactions) the electric charge density $\varrho(\boldsymbol{r})$ (for the electron-phonon interaction) or the z component of the electron spin operator, σ_z (for the nuclear spin relaxation interaction). Since under time-reversal

$\boldsymbol{j}(\boldsymbol{r}, \mathrm{t}) \rightarrow -\boldsymbol{j}(\boldsymbol{r}, -t)$ (electromagnetic interaction)
$\varrho(\boldsymbol{r}, \mathrm{t}) \rightarrow +\varrho(\boldsymbol{r}, -t)$ (electron-phonon interaction)
$\sigma_z(t) \rightarrow -\sigma_z(-t)$ (nuclear spin relaxation interaction)

these show strikingly different interference effects.

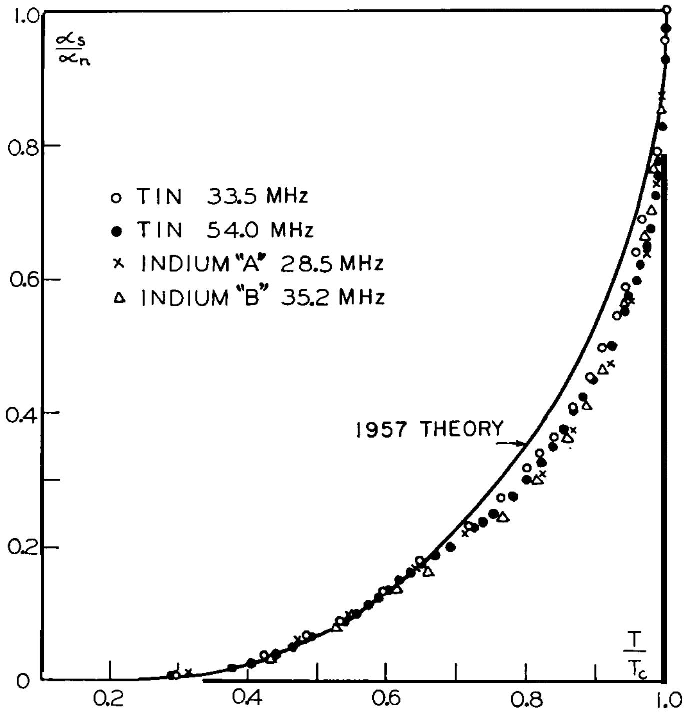


Fig. 12.
Comparison of observed ultrasonic attenuation with the ideal theory. The data are due to Morse and Bohm.

Ultrasonic attenuation in the ideal pure superconductor for $ql \gg 1$ (the product of the phonon wave number and the electron mean free path) depends in a fundamental way on the absorption and emission of phonons. Since the matrix elements have a very weak dependence on changes near the Fermi surface in occupation of states other than k or k' that occur in the normal to superconducting transition, calculations within the quasi-particle model can be compared in a very direct manner with similar calculations for the normal metal, as $B_{k'k}$ is the same in both states. The ratio of the attenuation in the normal and superconducting states becomes:

$$\frac{\alpha_s}{\alpha_n} = -4\int_{\Delta}^{\infty} dE(u^2-v^2)_s^2 \left(\frac{E}{\varepsilon}\right)^2 \frac{df(E)}{dE}.$$

Since $(u^2-v^2)_s^2 \to \frac{1}{2}\left(\frac{\varepsilon}{E}\right)^2$, the coherence factors cancel the density of states giving

$$\frac{\alpha_s}{\alpha_n} = 2f(\Delta(T)) = \frac{2}{1+\exp\left(\frac{\Delta(T)}{k_B T}\right)}.$$

Morse and Bohm (10b) used this result to obtain a direct experimental determination of the variation of Δ with T. Comparison of their attenuation data with the theoretical curve is shown in Figure 12.

In contrast the relaxation of nuclear spins which have been aligned in a magnetic field proceeds through their interaction with the magnetic moment of the conduction electrons. In an isotropic superconductor this can be shown to depend upon the z component of the electron spin operator

$$B_{K'K} = B(c^*_{k'\uparrow}c_{k\uparrow} - c^*_{-k\downarrow}c_{-k'\downarrow})$$

so that

$$B_{K'K} = -B_{-K-K'}.$$

This follows in general from the property of the spin operator under time reversal

$$\sigma_z(t) = -\sigma_z(-t).$$

The calculation of the nuclear spin relaxation rate proceeds in a manner not too different from that for ultrasonic attenuation resulting finally in a ratio of nuclear spin relaxation rates in superconducting and normal states in the same sample:

$$\frac{R_s}{R_n} = -4\int_{\Delta}^{\infty} dE(u^2+v^2)_s^2\left(\frac{E}{\varepsilon}\right)^2 \frac{df(E)}{dE}.$$

But $(u^2+v^2)_s^2$ does not go to zero at the lower limit so that the full effect of the increase in density of states at $E = \Delta$ is felt. Taken literally, in fact, this expression diverges logarithmically at the lower limit due to the infinite density of states. When the Zeeman energy difference between the spin up and spin down states is included, the integral is no longer divergent but the integrand is much too large. Hebel and Slichter, by putting in a broadening of levels phenomenologically, could produce agreement between theory and experiment. More recently Fibich (11) by including the effect of thermal phonons has obtained the agreement between theory and experiment shown in Fig. 13.

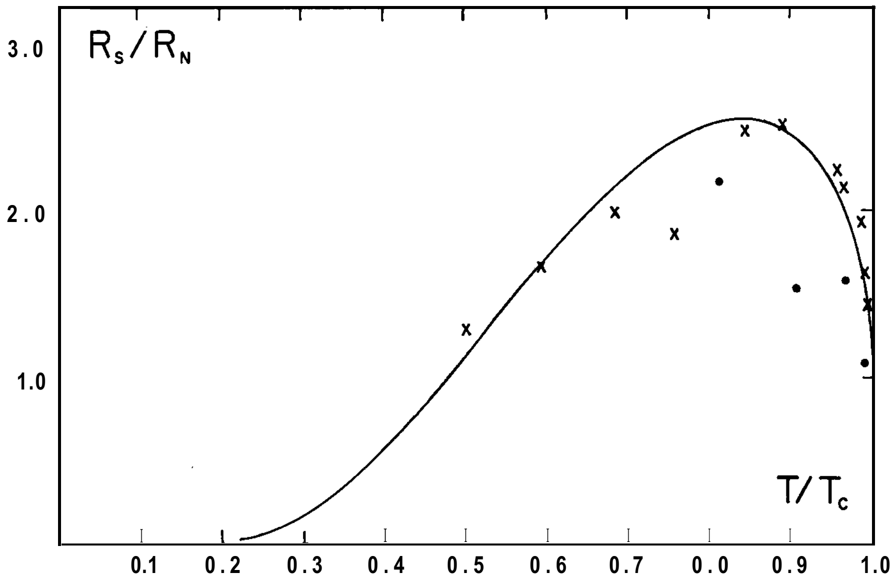


Fig. 13.
Comparison of observed nuclear spin relaxation rate with theory. The circles represent experimental data of Hebel and Slichter, the crosses data by Redfield and Anderson.

Interference effects manifest themselves in a similar manner in the interaction of electromagnetic radiation with the superconductor. Near T_c the absorption is dominated by quasi-particle scattering matrix elements of the type we have described. Near $T = 0$, the number of quasi-particle excitations goes to zero and the matrix elements that contribute are those in which quasi-particle pairs are created from ψ_0. For absorption these latter occur only when $\hbar\omega > 2\Delta$. For the linear response of the superconductor to a static magnetic field, the interference occurs in such a manner that the paramagnetic contribution goes to zero leaving the diamagnetic part which gives the Meissner effect.

The theory developed in 1957 and applied to the equilibrium properties of uniform materials in the weak coupling region has been extended in numerous directions by many authors. Professor Schrieffer has spoken of Josephson junctions and macroscopic quantum interference effects; Professor Bardeen will discuss the modifications of the theory when the electron-phonon interactions are strong. The treatment of ultrasonic attenuation, generalized to include situations in uniform superconductors in which $ql < 1$, gives a surprisingly similar result to that above. (12) There have been extensive developments using Green's function methods (13) appropriate for type II superconductors, materials with magnetic impurities and non-uniform materials or boundary regions where the order parameter is a function of the spatial coordinates. (14) With these methods formal problems of gauge invariance and/or current conservation have been resolved in a very elegant manner. (15) In addition, many calculations (16) of great complexity and detail for type II superconductors have treated ultrasonic attenuation, nuclear spin relaxation and other phenomena in the clean and dirty limits (few or large numbers of impurities). The results cited above are modified in various ways. For example, the average density of excitation levels is less sharply peaked at T_c in a type II superconductor; the coherence effects also change somewhat in these altered circumstances but nevertheless play an important role. Overall one can say that the theory has been amenable to these generalizations and that agreement with experiment is good.

It is now believed that the finite many-nucleon system that is the atomic nucleus enters a correlated state analogous to that of a superconductor. (17) Similar considerations have been applied to many-fermion systems as diverse as neutron stars, (18) liquid He^3, (19) and to elementary fermions. (20) In addition the idea of spontaneously broken symmetry of a degenerate vacuum has been applied widely in elementary particle theory and recently in the theory of weak interactions. (21) What the electron-phonon interaction has produced between electrons in metals may be produced by the van der Waals interaction between atoms in He^3, the nuclear interaction in nuclei and neutron stars, and the fundamental interactions in elementary fermions. Whatever the success of these attempts, for the theoretician the possible existence of this correlated paired state must in the future be considered for any degenerate many-fermion system where there is some kind of effective attraction between fermions for transitions near the Fermi surface.

In the past few weeks my colleagues and I have been asked many times: "What are the practical uses of your theory?" Although even a summary inspection of the proceedings of conferences on superconductivity and its applications would give an immediate sense of the experimental, theoretical and developmental work in this field as well as expectations, hopes and anticipations -from applications in heavy electrical machinery to measuring devices of extraordinary sensitivity and new elements with very rapid switching speeds for computers - I, personally, feel somewhat uneasy responding. The discovery of the phenomena and the development of the theory is a vast work to which many scientists have contributed. In addition there are numerous practical uses of the phenomena for which theory rightly should not take credit. A theory (though it may guide us in reaching them) does not produce the treasures the world holds. And the treasures themselves occasionally dazzle our attention; for we are not so wealthy that we may regard them as irrelevant.

But a theory is more. It is an ordering of experience that both makes experience meaningful and is a pleasure to regard in its own right. Henri Poincart wrote (22):

> Le savant doit ordonner; on fait la science
> avec des faits comme une maison avec des
> pierres; mais une accumulation de faits
> n'est pas plus une science qu'un tas de
> pierres n'est une maison.

One can build from ordinary stone a humble house or the finest chateau. Either is constructed to enclose a space, to keep out the rain and the cold. They differ in the ambition and resources of their builder and the art by which he has achieved his end. A theory, built of ordinary materials, also may serve many a humble function. But when we enter and regard the relations in the space of ideas, we see columns of remarkable height and arches of daring breadth. They vault the fine structure constant, from the magnetic moment of the electron to the behavior of metallic junctions near the absolute zero; they span the distance from materials at the lowest temperatures to those in the interior of stars, from the properties of operators under time reversal to the behavior of attenuation coefficients just beyond the transition temperature.

I believe that I speak for my colleagues in theoretical science as well as myself when I say that our ultimate, our warmest pleasure in the midst of one of these incredible structures comes with the realization that what we have made is not only useful but is indeed a beautiful way to enclose a space.

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