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H. H. Nickle: NONVANISHING PARAMAGNETIC SUSCEPTIBILITY SUPERCONDUCTORS AT ABSOLUTE ZERO. -

The Barden-Cooper-Schrieffer (BCS) theory(1) of superconductivity predicts(2) that a weak uniform magnetic field cannot polarize the superconducting electron spins and, hence no Knight shift should occur at zero temperature. However, the experimentally observed Knight shifts in nuclear magnetic resonance experiments on mercury(3), tin(4), and vanadium(5) contradict this prediction.

A number of authors have proposed possible explanations of this puzzle(6). We wish to suggest a much simpler explanation. If the phenomenological BCS "effective potential" is attractive only near the Fermi surface, say from $k_F - (1/a)$ to $k_F + (1/a)$, then the electron states inside the sphere of radius $R = k_F - (1/a)$ can be completely filled at absolute zero with unpaired "normal" electrons, which give a nonvanishing contribution(7),

(1) $$\chi_s(0) = 2\mu_0^2 \, N(E_F - \hbar\Omega)$$

to the paramagnetic susceptibility of the superconductor. If, for simplicity, we assume that the effective electron mass is a scalar, then $N(E) \propto E^{1/2}$, and the ratio of the superconducting susceptibility to the normal susceptibility is

(2) $$\chi_s(0)/\chi_n(0) = \left\{1 - (\hbar\Omega/E_F)\right\}^{1/2} .$$

Equation (2) means that the extrapolated experimental value of $\chi_s(0)$ is essentially a measure of the density of states at the surface of $\underline{k}$-space where the attractive pairing interaction (responsible for superconductivity) vanishes.

A simple mathematical formulation of this conjecture may help to clarify the situation. In the presence of a constant magnetic field $\underline{B}$, the BCS Hamiltonian is(8)

(3) $$H = \sum_{\underline{k}} (\epsilon_k - \mu_0 B)\, n_{\underline{k}\uparrow} + \sum_{\underline{k}} (\epsilon_k + \mu_0 B)\, n_{\underline{k}\downarrow} - \sum_{\underline{k},\underline{k}'} V_{\underline{kk}'}\, b^{+}_{k'}\, b_k \quad ,$$

except for an unessential additive constant due to the fact that the Bloch energies, $\epsilon_k$, are measured relative to the Fermi energy. Here we have assumed that $\underline{B}$ is in the same direction as the axis of quantization of the electron spins. It is also convenient to regard $\underline{k}$-space as consisting of three regions: $\underline{k} \in N \Rightarrow 0 \leq k \leq k_F - (1/a)$; $\underline{k} \in S \Rightarrow k_F - (1/a) < k < k_F + (1/a)$; $\underline{k} \in E \Rightarrow k \geq k_F + (1/a)$.

The well-known BCS ground state solution for the probability, $h_k$, that pair state $k = (\underline{k}\uparrow, -\underline{k}\downarrow)$ is occupied is

$$(4) \qquad h_k = 1/2 \left\{ 1 - (\epsilon_k / E_k) \right\}^{1/2} \quad ,$$

where

$$(5) \qquad E_k = (\epsilon_o^2 + \epsilon_k^2)^{1/2} \quad .$$

If we assume $\epsilon_o = 0$ for $|\epsilon_k| \geq \hbar\Omega$, the BCS solution becomes(9) $h_k = 1$ for $\underline{k} \in N$. However, electrons in region N do not "realize" they are inside the Fermi surface of a superconductor. Another way of arriving at the same conclusion is to realize that the variational solution for $h_k$ in region S does not hold for regions N or E when an external magnetic field is present, because the expectation value of the pairing interaction Hamiltonian is nonvanishing only in region S. It is clear from an inspection of the Hamiltonian (3) that (at absolute zero) one can obtain a state of lowest energy by aligning the spins of the electrons (in region N) parallel to $\underline{B}$.

The usual expression for the paramagnetic susceptibility of a normal metal is(10)

$$(6) \qquad \chi_n(T) = -2\mu_o^2 \sum_{\underline{k}} \frac{\partial f(\epsilon_k)}{\partial \epsilon_k} \quad ,$$

where

$$(7) \qquad f(\epsilon_k) = \left[ \exp(\epsilon_k / k_B T) + 1 \right]^{-1} \quad .$$

Changing to an integral over energy (measured relative to the Fermi energy), Eq. (6) becomes

$$(8) \qquad \chi_n(T) = -2\mu_o^2 \int \frac{\partial f(\epsilon)}{\partial \epsilon} N(\epsilon) d\epsilon \quad ,$$

where the lower and upper limits can usually be taken to be $-\infty$ and $+\infty$, respectively, without serious error. We have seen that the derivative of the Fermi-Dirac distribution function for the unpaired "normal" electrons (present in a superconductor at absolute zero) has a $\delta$-function singularity at $\epsilon = -\hbar\Omega$, i. e.,

$$\frac{\partial f(\epsilon)}{\partial \epsilon} = -\delta(\epsilon + \hbar\Omega)$$

which yields Eq. (1) immediately.

Speaking in terms of a two-fluid model, one might be tempted to say that part of the superconductor remains normal even at absolute zero. However, it is important to realize that these unpaired "normal" electrons are constrained (by the fact that all available states with $0 \leq k \leq k_F - (1/a)$ must be filled at absolute zero) in such a way that the ground state solution propo- sed here still exhibits an energy gap in the single electron spectrum. Thus the only way to excite one of these "normal" electrons is to put it into either (a) a state $\underline{k}$ in the region S or else (b) into a state $\underline{k}$ in region E. Alterna- tive (b) obviously requires the expenditure of a finite amount of energy. Al- ternative (a) also requires the expenditure of a finite amount of energy, be- cause it eliminates the pair state k and thereby increases the total energy of the system by the product of the pair interaction energy (between any other pair and the pair k) times the total number of pairs which could have inte- racted with pair state k.

We wish to emphasize that we do not disagree with the results of Yo- sida[2] in regard to the paired electrons. As a matter of fact, one can easily modify his result to include the presence of the conjectured "normal" elec- trons at absolute zero. Yosida found

$$\chi_s(T) = -2\mu_0^2 \sum_{\underline{k}} \frac{\partial f(E_k)}{\partial E_k} , \tag{9}$$

where $E_k$ is given by Eq. (5). We shall use Eq. (9) with $E_k = \epsilon_k$ for regions N and E[9]. The states $\underline{k} \in N$ are then completely occupied at $T = 0^\circ$ K because $\epsilon_k < 0$. Hence

$$\chi_s(T) = -2\mu_0^2 \int_{-\infty}^{-\hbar\Omega} \frac{\partial f(\epsilon)}{\partial \epsilon} N(\epsilon)\, d\epsilon - 2\mu_0^2 \int_{-\hbar\omega}^{\hbar\omega} \frac{\partial f(E)}{\partial E} N(E)\, dE - 2\mu_0^2 \int_{\hbar\Omega}^{+\infty} \frac{\partial f(\epsilon)}{\partial \epsilon} N(\epsilon)\, d\epsilon \tag{10}$$

where

$$\hbar\omega \equiv \left[ (\hbar\Omega)^2 + \epsilon_0^2 \right]^{1/2} .$$

As $T \rightarrow 0^\circ$K, the first integral on the right gives the result expressed in Eq. (1), while the other two integrals vanish. As $T \rightarrow T_c$, $\epsilon_0 \rightarrow 0$, and $\chi_s(T) \rightarrow \chi_n(T)$. For $0 < T < T_c$, the graph of Eq. (10) looks very much like Fig. 1 of reference (2) (Yoshida actually plots[11] $\chi_s(T)/\chi_n(0)$ vs. $T/T_c$, and the scale on his axis of ordinates must be multiplied by the factor $\left\{1 - \left[1 - (\hbar\Omega/E_F)\right]^{1/2}\right\}^{-1}$ so that his interval from $\chi_s/\chi_n = 0$ to 1 becomes an interval from $\chi_s/\chi_n = \left[1 - (\hbar\Omega/E_F)\right]^{1/2}$ to 1).

In conclusion, we wish to point out that experimental measurements of $\chi_s(T)$ as $T \rightarrow 0^\circ$K for superconductors possessing markedly different values of the ratio $(k_B\theta/E_F)$ should be able to prove or disprove the pre- sent conjecture, since one would expect some kind of rough correlation bet- ween the magnitude of the Debye temperature $\theta$ and $\hbar\Omega/k_B$. In the inter- pretation of such results, it may be necessary to treat the density of states more realistically than was done in the derivation of Eq. (2).

Also tunneling experiments at very low temperatures on some of the metals which apparently do not become superconducting might prove to be of interest. One can, for example, imagine a crystal in which the electron-lattice interaction produces an attractive "effective potential" over some region in k-space which lies entirely inside the Fermi surface. Then, even at absolute zero, the electron states near $k_F$ will be occupied by normal electrons. However, the presence of the attractive interaction will produce a modified density of states, and this can perhaps be detected in a tunneling experiment. We hasten to add that we cannot derive such an "effective potential" (whose range of attraction does not overlap $k_F$) from basic principles, so there is no theoretical evidence that such metals actually exist in nature.

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(7) - $\chi_s(0)$ denotes the paramagnetic susceptibility at absolute zero, $\mu_0$ is the Bohr magneton, and $N(E_F - \hbar\Omega)$ is the density of states at energy $E_F - \hbar\Omega$. $\hbar\Omega$ is the energy corresponding to wave vector (1/a).

(8) - Our notation is the same as that used in reference (1).

(9) - In the usual BCS solution, $E_k$ is always positive, even in region N when $\epsilon_0 = 0$, i. e., $E_k = -\epsilon_k$. The modification proposed here leads to $h_k = 0$ for regions N and E. Thus the equilibrium distribution of single particles (at arbitrary temperatures) is described by Fermi-Dirac distribution function of argument $(\epsilon_k \pm \mu_0 B)/k_B T$ for regions N and E, and of argument $E_k/k_B T$ for region S. On the other hand, the usual BCS theory leads to a single particle distribution function of argument $E_k/k_B T$, where $E_k = -\epsilon_k$ for region N, $E_k = +\epsilon_k$ for region E. The question of whether this change leads to any other experimentally observable differences (other than the Knight shift) will be discussed in detail in a forthcoming publication. In general, since the proposed modification only affects the Fermi-Dirac distribution function for single electrons in region N, it is not expected to affect any observables which depend on the properties of electrons near the Fermi surface. The Knight shift at absolute zero is an exception, because the paired electrons near the Fermi surface do not respond to the presence of an external magnetic field.

(10) - See, for example, R. A. Smith, Wave Mechanics of Crystalline Solids (John Wiley & Sons Inc., New York, 1961), pp. 376-378.

(11) - $\chi_n(T)$ is essentially independent of temperature and equal to $2\mu_0^2 N(E_F)$.