KNIGHT SHIFT IN SUPERCONDUCTORS*

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(Received September 2, 1959)

Although the theory proposed by Bardeen, Cooper, and Schrieffer[1] has been strikingly successful in explaining most properties of superconductors, the measurements of electron spin susceptibilities are supposed to present it with a serious dilemma. The BCS theory introduces strong coupling between pairs of particles with opposite spin and momentum, and therefore tends to prevent the electron spin reorientation necessary for low-temperature paramagnetism. However, observations of the electron spin paramagnetism, by the nuclear hyperfine interaction[2,3] (the Knight shift) in superconducting samples small enough to permit magnetic field penetration, indicate a substantial spin susceptibility. At absolute zero, the spin susceptibility observed in tin and mercury is approximately three quarters of the free electron value.

The purpose of this Letter is to suggest a mechanism for illuminating the Knight shift within the BCS framework. This mechanism occurs in consequence of the relative magnitude at low temperatures of the typical magnetic field wavelength, $\lambda = 1/k$ (approximately 10^{-5} to 10^{-6} cm), and the typical coherence distance, ξ_0 (approximately 10^{-4} to 10^{-5} cm). As these numbers indicate, the magnetic field contains Fourier components with wavelengths small compared to the size of the bound pairs. These components tend to polarize the pairs and thereby eliminate their compensation of the free electron spin susceptibility. Indeed, as the typical magnetic field wavevector increases, the paramagnetic spin susceptibility approaches the Pauli free electron value, $\chi^0=3n\mu^2/mv^2$. (In this expression μ and m are the electron moment and mass, n is the electron density, and v the Fermi velocity.)

In the first paper of a series on many-particle systems,[4] methods for determining thermal and electromagnetic properties of quantum mechanical systems have been developed. In a second, in preparation, these techniques will be shown to yield, for superconductors, the BCS solution with minor modifications which do not destroy the gap.[5] Using this approach, we have investigated the electromagnetic properties of superconductors, obtaining results which agree with the infrared absorption experiments on thin films,[6] and with the calculations of others.[7] We have also applied these methods to the electron spin paramagnetism of a superconductor in a static but spatially varying magnetic field, $\vec{H}$. In such a field, the spin magnetization, $\vec{M}$, is characterized by a nonlocal susceptibility, χ, which satisfies

$$\vec{M}(\vec{r}) = \int \chi(\vec{r} - \vec{r}')\vec{H}(\vec{r}')d\vec{r}'. \tag{1}$$

The Fourier transform of this spin susceptibility, $\chi(\vec{k})$, has been evaluated in terms of the attenuation parameter, $a = \frac{1}{2}\hbar vk/\Delta(\beta)$, the half energy gap, $\Delta(\beta)$, and the inverse of the absolute temperature in units of the energy, β. The result, derived by integrating the time-dependent correlation functions of the BCS model, may be expressed as

$$R(a,\beta) = 1 - \frac{\pi^2}{4a}\tanh(\tfrac{1}{2}\beta\Delta) + \frac{1}{2a}\int_0^\infty \frac{dx}{x}\ln\left|\frac{a+x}{a-x}\right| \frac{\tanh[\frac{1}{2}\beta\Delta(1+x^2)^{1/2}]}{(1+x^2)^{1/2}}, \tag{2}$$

where R is the ratio, $\chi(k)/\chi^0$.

In the large-attenuation or Pippard limit ($a \gg 1$), and at low temperatures, this ratio becomes

$$R(a \gg 1, \beta \to \infty) \approx 1 - \pi^2/4a = 1 - \pi\lambda/2\xi_0. \tag{3}$$

The experimental results are fit by taking $a \approx 10$ in (3). This value agrees qualitatively with estimates for a in bulk samples. (In bulk tin, for example, the coherence length is 2.5×10^{-5} cm and the penetration depth 5×10^{-6} cm, so that a is approximately eight.) A more quantitative comparison with (2) is hardly appropriate since its derivation employs the correlation functions of bulk material. In a detailed analysis the correlation functions of the small sample would have to be determined and the magnetic field variation then derived. (We note that if the boundary of the sample could be treated as incoherently scattering electrons, the effect of finite size would be more important than magnetic field variation in diminishing the correction to the free electron spin susceptibility. Specifically, if the size, or mean free path, l, were less than $\frac{3}{4}\pi\lambda$, R would become[8] $1 - \frac{2}{3}l/\xi_0$. While this treatment of the boundary is known to be unsatisfactory,[9] and the use of bulk correlation functions is not justified, the argument underscores the possible magnitude of size-dependent corrections.)

In the small-attenuation or London limit ($a \ll 1$), the ratio (2) reduces to the form previously calculated by Yosida[10]:

$$R(0,\beta)=2\int_0^\infty dy\,\frac{\exp[y^2+(\beta\Delta)^2]^{1/2}}{\{1+\exp[y^2+(\beta\Delta)^2]^{1/2}\}^2}. \qquad (4)$$

This limit, which predicts a rapidly decreasing Knight shift with decreasing temperature, is appropriate only very near the critical temperature, $1/\beta_c$, where it reduces to

$$R(0,\beta\approx\beta_c)\approx 1-0.60[\Delta(\beta)/\Delta(0)]^2. \qquad (5)$$

We are thus led by (2) to predict tentatively the following behavior for the spin susceptibility as the temperature is decreased: a sharp drop according to (5) immediately below the critical temperature, followed, perhaps, by a rise on entering the Pippard region, and then a smooth decrease to the asymptotic value (3). Observations of a similar structure have been reported by Knight,[11] but his preliminary data suggest that the sharp valley lies immediately above the critical temperature.

We therefore conclude that the Knight shift experiments are not at variance with the BCS theory. Furthermore, although the effects of size may be significant, the predictions for bulk samples agree qualitatively with the observations on small samples.

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*The research was supported in part by the Office of Scientific Research of the U. S. Air Force.

†A. P. Sloane Foundation Fellow.

‡National Science Foundation predoctoral fellow.

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KNIGHT SHIFT IN SUPERCONDUCTORS

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(Received September 3, 1959)

The experimental values of the Knight shift found by Reif[1] on superconducting mercury colloids and by Androes and Knight[2] on evaporated tin plates when extrapolated to $T=0°$K show that the electronic spin susceptibility $\chi_s(0)$ does not vanish for the superconducting ground state. These experiments are in disagreement with the calculation of Yosida[3] based on the BCS theory of superconductivity[4] which predicts an exponentially vanishing susceptibility near $T=0°$K for a uniform magnetic field due to an energy gap $2\epsilon_0(0)$ for the creation of a pair of quasi-particles with total magnetic moment $2\mu_B$. Anderson[5] and Rickayzen[6] have generalized Yosida's calculation to include the effects of a space-varying magnetic field and they find a nonlocal susceptibility which is finite at $T=0$. Heine and Pippard[7] have suggested an alternative form for the matrix elements which enter the theory such that a finite Knight shift is obtained for a uniform field; however, no one has been able to construct wave functions which lead to these matrix elements.