SOVIET PHYSICS JETP VOLUME 12, NUMBER 2 FEBRUARY, 1961

ON THE PROBLEM OF THE KNIGHT SHIFT IN SUPERCONDUCTORS

A. A. ABRIKOSOV and L. P. GOR'KOV

Institute for Physical Problems, Academy of Sciences, U.S.S.R.

Submitted to JETP editor March 23, 1960

J. Exptl. Theoret. Phys. (U.S.S.R.) **39**, 480-483 (August, 1960)

The problem of the Knight shift in superconductors of small size is discussed. It is shown that the derivation of a finite value of the shift at absolute zero obtained in the papers of Schrieffer[3] and of Anderson[4] is incorrect.

RECENTLY a number of papers[1-4] has been devoted to the theory of the so-called Knight shift in superconductors, i.e., the change in the nuclear resonance frequency as compared to dielectrics. The aim of these papers is to explain the experimental data obtained by Reif for superconducting emulsions.[5]

As is well known, the cause of the Knight shift in metals is the paramagnetism of the conduction electrons. Because the electron wave function is anomalously large in the neighborhood of the nucleus, the magnetization of the electrons changes the magnetic field acting on the nucleus. The difference between the effective and the external field has the following form

$$\Delta H = (8\pi/3N_{at})\,|\psi(0)|^2\chi H, \tag{1}$$

where $|\psi(0)|^2$ is the probability density of finding the electron at the position of the nucleus, N_{at} is the number of atoms per unit volume, χ is the paramagnetic susceptibility of the electrons, and H is the external field.

Since the conduction electron states are altered in superconductors, one should expect a change in the magnitude of the Knight shift. Formula (1) is still valid in this case, with the susceptibility evidently undergoing the principal change in comparison with the normal metal. The observation of this effect is made difficult by the fact that the field does not penetrate deeply into a bulky superconductor. A homogeneous field can be produced only in superconductors of dimensions much smaller than δ, the penetration depth for a static field. It is just for this reason that an emulsion is utilized in Reif's experiments.

In Yosida's paper[1] a bulky superconductor in a homogeneous field was considered. Such a formulation of the problem does not correspond to actual experimental conditions. In order to be able to completely leave out of account the effect of the boundary conditions and of the inhomogeneity of the field it is necessary that the depth of penetration of the field and the dimensions of the sample should be large compared to the principal parameter of the theory $\xi_0 \sim \hbar v/kT_c$, the characteristic correlation radius. Only in such a case could Yoshida's results, obtained for an infinite superconductor, be used for the interpretation of Reif's experiments. However, it is well known that for the majority of superconductors δ is considerably smaller than ξ_0. From the formal point of view the calculations of the susceptibility in reference 1 for a bulk sample are of course correct, since in order to calculate the coefficient of proportionality between the magnetic moment and the field (assuming the latter to be homogeneous) it is not necessary to solve the problem of the penetration of the field into the sample. We are here simply discussing the fact that actually the field remains homogeneous at distances smaller than $\delta \ll \xi_0$. The attempt by Martin and Kadanoff[2] to take into account the inhomogeneity of the field in the sample cannot lead to any improvement, since such an inhomogeneity increases first of all the line width.

The problem can be formulated quite correctly for superconducting alloys. If the concentration of the impurities is sufficiently great then the role of the correlation parameter is played by the mean free path l. Under these conditions the situation described by London ($\delta \gg l$) arises in the superconductor, and it becomes possible to regard the field in the sample as homogeneous.

As has been pointed out earlier,[7,8] actual samples of small dimensions are conglomerates of crystallites with dimensions of the order of or smaller than the sample dimensions. Because of this, such samples have properties which are rather close to superconducting alloys with an effective mean free path of the same order of magnitude. The paramagnetic susceptibility of superconducting alloys has been recently investigated by Schrieffer[3] and by Anderson.[4] In particular, in these investigations the conclusion was reached that the presence of impurities leads to a finite Knight shift at $T = 0$ which is in agreement with the extrapolation of Reif's results to $T = 0$. In this note it will be shown that such a conclusion is erroneous.

The method for the study of superconductors containing impurities has been developed by us previously.[7,8] In the present case it is necessary to evaluate the spin magnetic moment of the system of electrons in a homogeneous magnetic field. It is given by

$$\mathbf{M} = \mu_0 \operatorname{Sp}\left[\exp\left(\frac{\Omega + \hat{N}\mu - \hat{\mathscr{H}}}{T}\right) \psi_\alpha^+(x)\, \boldsymbol{\sigma}_{\alpha\beta}\, \psi_\beta(x)\right], \qquad (2)$$

where μ_0 is the Bohr magneton and $\boldsymbol{\sigma}$ are the Pauli matrices. The Hamiltonian for the interaction between the electron spins and the magnetic field has the form

$$\hat{\mathscr{H}}_1 = -\mu_0 \int \psi_\alpha^+(\mathbf{x})\, (\boldsymbol{\sigma}_{\alpha\beta}\mathbf{H})\, \psi_\beta(\mathbf{x})\, d^3\mathbf{x}. \qquad (3)$$

By utilizing the techniques used in quantum field theory at finite temperatures[8,9] and by restricting ourselves to terms of the first order in H we obtain

$$\mathbf{M} = -\mu_0^2 \lim_{\substack{\tau' \to \tau + 0 \\ x' \to x}} \int_0^{1/T} d\tau_y \int d^3\mathbf{y} \operatorname{Sp}\left[\exp\left(\frac{\Omega + \hat{N}\mu - \mathscr{H}_0}{T}\right) \times T_\tau\left(\psi_\beta(x)\, \psi_\gamma^+(y)\, \psi_\delta(y)\, \psi_\alpha^+(x')\right) \boldsymbol{\sigma}_{\alpha\beta} (\boldsymbol{\sigma}_{\gamma\delta}\mathbf{H})\right] \qquad (4)$$

In this formula the operators ψ are not free, but include the interaction with the impurities:

$$\hat{\mathscr{H}}_2 = \int \psi_\alpha^+(\mathbf{x})\, \psi_\alpha(\mathbf{x}) \sum_a V(\mathbf{x} - \mathbf{x}_a)\, d^3\mathbf{x}, \qquad (5)$$

where $\mathbf{x}_a$ is the position vector of the impurity atom.

Further calculations have been carried out in complete analogy with the way this was done in references 7 and 8. It was shown there that averaging over the coordinates of the impurity atoms leads to the introduction of a special diagram technique. Each impurity line in a diagram arises from averaging two factors corresponding to scattering by one of the impurity atoms. It is sufficient to retain only the non-intersecting lines in order to obtain a result which differs from the correct one by small terms only. If we apply this procedure to formula (4) then the calculation of the magnetic moment obviously reduces to the evaluation of the sum of loops with two spinor vertices $\sigma_{\alpha\beta}$ and with all the nonintersecting impurity lines.

In averaging over the impurity coordinates we must take into account the fact that, for example, $\overline{G(\mathrm{x, y})\, G(\mathrm{y, x})}$ is not equal to $\overline{G(\mathrm{x, y})} \cdot \overline{G(\mathrm{y, x})}$. In the opposite case this expression would simply be given by

$$G_0(x - y)\, G_0(y - x) \exp(-|\mathbf{x} - \mathbf{y}|/l),$$

where l is the mean free path, while $G_0(x - y)$ is the Green's function for the pure superconductor. This incorrect assumption is the one made in Schrieffer's note[3] and leads to an erroneous result.

If we denote by $\Pi_{\beta\alpha}^1(\mathbf{p}, \omega_n)$ the Fourier component of

$$\int_0^{1/T} d\tau_y \int d^3\mathbf{y} \operatorname{Sp}\left[\exp\left(\frac{\Omega + \hat{N}\mu - \hat{\mathscr{H}}_0}{T}\right) \times T_\tau\left(\psi_\beta(x)\, \psi_\gamma^+(y)\, \psi_\delta(y)\, \psi_\alpha^+(x')\right) \boldsymbol{\sigma}_{\gamma\delta}\right],$$

we can easily relate this quantity by means of appropriate equations to Fourier components of three other similar quantities:

$$\int d^4 y\, \overline{[\psi_\beta(x)\, \psi_\gamma^+(y)\, \psi_\delta(y)\, (\psi(x')\, \hat{g})_\alpha]}\, \boldsymbol{\sigma}_{\gamma\delta},$$

$$\int d^4 y\, \overline{[(\hat{g}\psi^+(x))_\beta\, \psi_\gamma^+(y)\, \psi_\delta(y)\, \psi_\alpha(x')]}\, \boldsymbol{\sigma}_{\gamma\delta},$$

$$\int d^4 y\, \overline{[(\hat{g}\psi^+(x))_\beta\, \psi_\gamma^+(y)\, \psi_\delta^+(y)\, (\psi(x')\, \hat{g})_\alpha]}\, \boldsymbol{\sigma}_{\gamma\delta},$$

where

$$\hat{g} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}.$$

The magnetic moment is expressed in terms of $\Pi_{\beta\alpha}^1$ by means of the relation

$$\mathbf{M} = -\mu_0^2\, \boldsymbol{\sigma}_{\alpha\beta}\, T \sum_n (2\pi)^{-3} \int \mathbf{H}\Pi_{\beta\alpha}^1(\omega_n, \mathbf{p})\, d^3\mathbf{p}, \qquad (6)$$

where $\omega_n = \pi T(2n + 1)$.

Since all these calculations corespond completely to those carried out in reference 7, we shall not dwell on the solution of these equations, and shall simply state the answer:

$$\chi = 2\mu_0^2 (m p_0 / 2\pi^2)(N_n / N) = \chi_n N_n / N, \qquad (7)$$

where χ_n is the susceptibility of the normal metal, and N_n/N is the ratio of the number of "normal" electrons to the total number of electrons given by

$$\frac{N_n}{N_0} = \frac{1}{2T} \int_{\Delta(T)}^{\infty} \frac{\varepsilon\, d\varepsilon}{\sqrt{\varepsilon^2 - \Delta^2(T)} \cosh^2(\varepsilon/2T)}. \qquad (8)$$

The function $N_s = N - N_n$ determines the penetration depth for a pure superconductor of the London type.

Formulas (7) and (8) agree with Yosida's result[1] obtained formally for the case of a bulk of pure superconductor in a homogeneous field. This is explained by the fact that these formulas do not contain the mean free path. We also note that in the case considered here $l \gg 1/p_0$ the size of the gap $\Delta(T)$ agrees with the same quantity for the case of a pure superconductor.

From our results it follows, in particular, that for $T = 0$ the susceptibility χ vanishes, i.e., that no Knight shift should be observed. This conclusion is perfectly natural. In its ground state the superconductor has no magnetic moment, and the excited state is separated from the ground state by an energy gap. This applies not only to pure superconductors, but also to alloys with nonmagnetic impurities. Nevertheless, this result contradicts Reif's experiments,[5] which, as has been noted by Yosida, give values of χ larger than those given by formula (7). The quantity χ does not vanish when we extrapolate to $T = 0$.

In this connection it is necessary to subject to some criticism the interpretation of Reif's experiment. As we have already mentioned, in these experiments emulsions were used, i.e., an aggregate of small spherical samples of different sizes. Apparently at the present time this is the only method for investigating nuclear resonance in superconductors, and it can give rise to no objections if the particles are sufficiently small. In this case they had a diameter d on the average equal to one third of the penetration depth. However, the distribution of particles with respect to size is fairly broad, and since the effectiveness of individual particles is proportional to their volume the most important role is played by the large particles, even though they are less numerous. In such particles the field is inhomogeneous, which is in complete agreement with the large width of the resonance line obtained by Reif at low temperatures.

One other essential circumstance should also be noted. As is well known, the transition from the superconducting to the normal state in particles of dimensions smaller than the penetration depth is a phase transition of the second kind for which the superconducting "gap" in the spectrum vanishes in a continuous manner. This means that particles for which the external magnetic field is only slightly lower than the critical value (we recall that $H_c \sim 1/d$) will be very close in their properties to the normal metal right down to very low temperatures. From this it follows that in the given external field (which, incidentally, was approximately equal to 1000 gauss) the particles cannot be separated into completely normal ones and totally superconducting ones with corresponding resonance frequencies, but give rise to various intermediate values of the resonance frequency.

In view of the foregoing, it appears to us that at the present time it is premature to speak of the existence of a contradiction between theory and experiment.

In conclusion we express our gratitude to Academician L. D. Landau for discussion of this work.

[1] K. Yosida, Phys. Rev. **110**, 769 (1958).

[2] P. Martin and L. Kadanoff, Phys. Rev. Letters **3**, 322 (1959).

[3] J. R. Schrieffer, Phys. Rev. Letters **3**, 323 (1959).

[4] P. W. Anderson, Phys. Rev. Letters **3**, 325 (1959).

[5] F. Reif, Phys. Rev. **106**, 208 (1957).

[6] Townes, Herring, and Knight, Phys. Rev. **77**, 851 (1950).

[7] A. A. Abrikosov and L. P. Gor'kov, JETP **35**, 1558 (1958), Soviet Phys. JETP **8**, 1090 (1959).

[8] A. A. Abrikosov and L. P. Gor'kov, JETP **36**, 319 (1959), Soviet Phys. JETP **9**, 220 (1959).

[9] Abrikosov, Gor'kov, and Dzyaloshinskiĭ, JETP **36**, 900 (1959), Soviet Phys. JETP **9**, 636 (1959).

Translated by G. Volkoff
93