SPIN-ORBIT INTERACTION AND THE KNIGHT SHIFT IN SUPERCONDUCTORS

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A theory of the Knight shift in superconductors is presented. It is shown that the effect can be completely explained if the spin-orbit part of the interaction in the scattering of electrons on the crystal boundaries is taken into account. The agreement between the theory and the experimental data [8] is found to be good.

1. INTRODUCTION

MANY recent papers [1-7] have been devoted to an explanation of the nonvanishing shift in the frequency of the nuclear magnetic resonance in a superconductor at zero absolute temperature. As is known, this so-called Knight shift is proportional to the paramagnetic susceptibility of the conduction electrons, χ:

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

where $|\psi(0)|^2$ is the probability density for finding an electron at the position of the nucleus and N_{at} is the number of atoms in a unit volume.

According to the microscopic theory of superconductivity, the paramagnetic susceptibility of the electrons in the superconducting state vanishes for $T = 0$. This is in contradiction with the nonvanishing Knight shift observed experimentally. The vanishing of χ for $T = 0$ is connected with the fact that the states of a superconductor are classified according to the eigenvalues of the total spin. In the ground state all electrons are paired in Cooper pairs, and the total spin of the system is zero. Excitation of the system requires a finite energy 2Δ, where Δ is the gap in the energy spectrum of the superconductor.

The most natural explanation of the finite Knight shift in superconductors is based on the assumption of Ferrell [5] and Anderson [6] that the spin-orbit interaction plays an important role for electrons in small specimens. Owing to this interaction the electron can change its spin direction when it is scattered at the boundary. The states of such a system can therefore no longer be characterized by the eigenvalues of the spin, and the above-mentioned conclusion is not correct.

A finite shift at $T = 0$ in tin has definitely been observed by Androes and Knight in recent work. [8] The earlier results of Reif [9] on the Knight shift in colloidal mercury are difficult to interpret, since, as noted by the authors, [4] the uncertainty in the size of the particles was so large that an appreciable number of large particles may have gone over into the normal state in fields of the order of a few kilooersted thus simulating a finite shift in the superconducting state.

The experiments of Androes and Knight [8] were performed with stacks of thin films with thickness of 40 Å. The fields used in this work (from 1 to 8 kilooersted) were weaker than the critical fields, which reach a strength of 25 kilooersted. The ratio χ_s/χ_n, extrapolated to $T = 0$, was equal to ~ 0.77.

In the present paper we shall show that the above-mentioned spin-orbit interaction provides a correct quantitative explanation of the phenomenon. For the mathematical formulation of the problem it is important to take into consideration that the thin films as well as all small-sized specimens, have a polycrystalline structure. At the boundaries of the crystallites the electrons are scattered, which leads to a destruction of the correlations between a pair of electrons which were introduced in the transition to the superconducting state. These correlations are thus restricted to distances of the order of the dimensions of the crystallites. The dimensions of the crystallites, therefore, play the role of a mean free path for the electrons. Hence we shall below consider the equivalent problem of the scattering of an electron by impurities in the superconductor, where spin flip can occur on account of the spin-orbit interaction. As will be shown below, the final result

will involve only the mean free path of the electrons with respect to spin flip, $l_{s.o.}$.

The amplitude for the scattering of an electron by an atom of the impurity can be written in the form

$$\hat{f}(\mathbf{p}, \mathbf{p}') = a(\mathbf{p}, \mathbf{p}') + ib(\mathbf{p}, \mathbf{p}')\, p_0^{-2}([\mathbf{p}, \mathbf{p}']\, \hat{\sigma}), \quad (1)^*$$

where $\mathbf{p}$ and $\mathbf{p}'$ are the momenta of the electron before and after the collision, $\hat{\sigma}$ are the Pauli spin matrices, and p_0 is the Fermi momentum. The second term in (1), corresponding to the spin-orbit interaction, is of order $b/a \sim (Ze^2/\hbar c)^2$ and may, in general, be appreciable for heavy elements. To keep the calculations simple, we shall, however, assume that $|b/a|^2 \ll 1$. In other words, we shall assume that the mean free path $l_{s.o.}$ is much larger than the mean free path between collisions of the electrons with the impurities, l, which is determined essentially by the amplitude $a(\mathbf{p}, \mathbf{p}')$ in (1). It was shown in [4] that the scattering does not change the paramagnetic susceptibility of the superconductor in the absence of the spin-orbit interaction, so that there will be a Knight shift of the order of unity at $T = 0$ if

$$l_{s.o.} \sim \xi_0 \sim \hbar v/T_c \sim 10^{-4} - 10^{-5} \text{ cm}.$$

2. CALCULATION OF THE PARAMAGNETIC SUSCEPTIBILITY

The spin magnetic moment of a system of electrons in a uniform magnetic field is equal to [4]

$$\mathbf{M} = -\mu_0^2 \lim_{\substack{\tau' \to \tau + 0 \\ \mathbf{r}' \to \mathbf{r}}} \int_0^{1/T} d\tau_y \int d^3\mathbf{y}\, \mathrm{Sp}\left[\exp\left(\frac{\Omega + \mu N - H_0}{T}\right) \times T_\tau (\psi_\alpha(x)\, \psi_\gamma^+(y)\, \psi_\delta(y)\, \psi_\beta^+(x'))\, \sigma_{\beta\alpha}(\sigma_{\gamma\delta}\mathbf{H})\right]. \quad (2)$$

Here μ_0 is the Bohr magneton. In the following we shall use the thermodynamic formulation [10,11] of perturbation theory, in which the field operators depend on the time parameter τ $(0 < \tau < 1/T)$.

Denoting the average over the Gibbs ensemble by $\langle \ldots \rangle$, we consider the average over the product of four operators appearing in (2):

$$\langle T(\psi_\alpha(x)\, \psi_\gamma^+(y) \psi_\delta(y)\, \psi_\beta^+(x')) \rangle.$$

In a superconductor this average can be written in the form

$$\langle T(\psi_\alpha(x)\, \psi_\gamma^+(y)\, \psi_\delta(y)\, \psi_\beta^+(x')) \rangle = \mathcal{G}_{\alpha\gamma}(x, y)\, \mathcal{G}_{\delta\beta}(y, x') - \mathfrak{F}_{\alpha\delta}(x, y)\, \mathfrak{F}^+_{\gamma\beta}(y, x'), \quad (3)$$

where

$$\mathcal{G}_{\alpha\beta}(x, y) = -\langle T(\psi_\alpha(x)\, \psi_\beta^+(y)) \rangle;$$

$$\mathfrak{F}_{\alpha\beta}(x, y) = \langle T(\psi_\alpha(x)\, \psi_\beta(y)) \rangle;$$

$$\mathfrak{F}^+_{\alpha\beta}(x, y) = \langle T(\psi_\alpha^+(x)\, \psi_\beta^+(y)) \rangle.$$

The diagram corresponding to expression (3) is shown in Fig. 1. The line with both arrows pointing in the same direction represents the function $\mathcal{G}$ and the lines with the arrows pointing both either in or out represent $\mathfrak{F}$ and $\mathfrak{F}^+$.

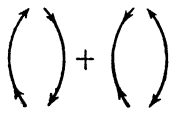

FIG. 1

In our case all quantities in (2) and (3) contain the interaction with the atoms of the impurities. In zeroth order in this interaction we must substitute the known expressions for the Green's functions of the pure superconductor in (3):

$$\mathcal{G}_{\alpha\beta}(x - y) = \delta_{\alpha\beta} T (2\pi)^{-3} \sum_\omega \int d^3\mathbf{p}\, \mathcal{G}(p) \exp\{i\mathbf{p}(\mathbf{x} - \mathbf{y}) - i\omega(\tau_x - \tau_y)\},$$

$$\mathfrak{F}^+_{\alpha\beta}(x - y) = -\mathfrak{F}_{\alpha\beta}(x - y) = \hat{g}_{\alpha\beta} T (2\pi)^{-3} \sum_\omega \int d^3\mathbf{p}\, \mathfrak{F}(p) \times \exp\{i\mathbf{p}(\mathbf{x} - \mathbf{y}) - i\omega(\tau_x - \tau_y)\}, \quad (4)$$

where

$$\mathcal{G}(p) = -\frac{i\omega + \xi}{\omega^2 + \xi^2 + \Delta^2}, \qquad \mathfrak{F}(p) = \frac{\Delta}{\omega^2 + \xi^2 + \Delta^2}, \quad (4')$$

g is the spin metric tensor ($g_{11} = g_{22} = 0$, $g_{12} = -g_{21} = 1$), Δ is the energy gap in the spectrum of the pure superconductor, and $\xi = v(p - p_0)$. The frequencies ω appearing in the Fourier series in τ take the values $\omega = (2n + 1)\pi T$ $(n = 0, \pm 1, \ldots)$, and $\sum_\omega \varphi(\omega)$ means $\sum_n \varphi(2n + 1)\pi T$.

Taking account of the interaction with the impurities changes expressions (4) and (4'). In Fig. 2 we show diagrams for expression (3) in which the crosses indicate the act of scattering of the electron with the separate atoms of the impurity. The scattering of the electron by an atom located at the point $\mathbf{r}_a$ gives rise to a factor $f_{\alpha\beta}(\mathbf{p}, \mathbf{p}') \times \exp\{i(\mathbf{p}' - \mathbf{p}) \cdot \mathbf{r}_a\}$ in the matrix element in the momentum representation.

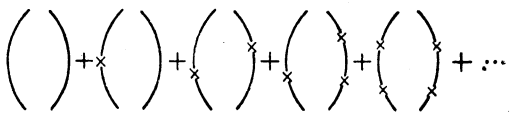

FIG. 2

*$([\mathbf{p}, \mathbf{p}']\, \hat{\sigma}) = [(\mathbf{p} \times \mathbf{p}') \cdot \hat{\sigma}]$

In the following we shall be interested in the values of all quantities, including (2), averaged over the positions of all atoms of the impurity. The relevant momenta in our problem are all of the order $p \sim p_0 \sim 1/a$, where a is the interatomic distance. Therefore the average of the factor $\exp\{i(\mathbf{p}'-\mathbf{p})\cdot\mathbf{r}_a\}$ over $\mathbf{r}_a$ is zero and so is every matrix element unless it contains yet another factor $\exp\{-i(\mathbf{p}'-\mathbf{p})\cdot\mathbf{r}\}$ corresponding to the scattering on the same atom of the impurity with the initial and final states interchanged. In taking the average we must therefore sum over pairs of scatterings on the same atom.

The whole averaging procedure can be illustrated by a special diagram technique which has been developed by the authors.[12] The pairwise averaging is represented by a dotted line in the diagram, which joins two identical crosses (scattering by the same atoms). In the matrix element the dotted line corresponds to the factor

$$n(2\pi)^{-3} f_{\alpha\beta}(\mathbf{p}, \mathbf{p}') f_{\gamma\delta}(\mathbf{p}', \mathbf{p})$$

where n is the number density of the atoms of the impurity. With an accuracy up to small terms of order a/l it is sufficient to consider only nonintersecting dotted lines.

Let us introduce the notation

$$\Pi^{(1)}_{\alpha\beta}(x-y, y-x') = \overline{\langle T(\psi_\alpha(x)\psi^+_\delta(y)\sigma_{\delta\lambda}\psi_\lambda(y)\psi^+_\beta(x'))\rangle}. \tag{5}$$

(The bar denotes the average over the positions of the atoms of the impurity). Let us write

$$\Pi^{(1)}_{\alpha\beta}(x-y, y-x') = T^2(2\pi)^{-6}\sum_{\omega_+\omega_-}\int\int d^3\mathbf{p}_+\, d^3\mathbf{p}_-\, \Pi^{(1)}_{\alpha\beta}(p_+, p_-)$$
$$\times \exp\{i\mathbf{p}_+(\mathbf{x}-\mathbf{y}) + i\mathbf{p}_-(\mathbf{y}-\mathbf{x}')$$
$$- i\omega_+(\tau_x-\tau_y) - i\omega_-(\tau_y-\tau_{x'})\}. \tag{5'}$$

The magnetic moment is given in terms of $\Pi^{(1)}_{\alpha\beta}$ by the relation

$$\mathbf{M} = -\mu_0^2\sigma_{\alpha\beta}T(2\pi)^{-3}\sum_\omega\int(\mathbf{H}\Pi^{(1)}_{\alpha\beta}(p, p))\, d^3\mathbf{p}. \tag{6}$$

Some lowest order diagrams in the perturbation expansion of (5) are shown schematically (without indicating the direction of the arrows) in Fig. 3. In accordance with the general recipe we leave out all diagrams with intersecting dotted lines, as well as diagrams in which the dotted line goes into a vertex with a large ($\sim p_0$) momentum transfer. In these diagrams part of the integration is over momenta far away from the Fermi surface, which reduces the contribution from these diagrams by a factor of order $1/p_0 l \sim a/l \ll 1$ as compared to diagrams of the "ladder" type. In the remaining

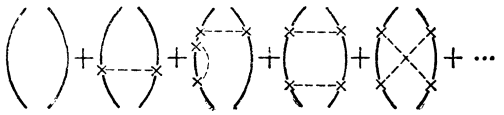

FIG. 3

diagrams the dotted line either joins two different electron lines or begins and ends on the same line (but without intersecting the "steps" of the ladder). In the latter case all such dotted lines evidently represent corrections from the interaction with the impurities to the Green's functions themselves. In order to derive an equation for $\Pi^{(1)}_{\alpha\beta}(p_+, p_-)$ it is therefore sufficient to consider only the "ladder" diagrams in which the dotted lines join different electron lines. The different sections of the electron lines in these diagrams represent the exact (averaged over the positions of the impurities) Green's functions $\mathfrak{G}$, $\mathfrak{F}$, and $\mathfrak{F}^+$ in the matrix element.

The equations for the Green's functions themselves in a superconductor with impurities coincide in this case exactly with the equations of [12]. Solving these equations, we find again that the averaged Green's functions for a superconductor with impurities can be obtained from (4) and (4') by the replacement

$$\{\omega, \Delta\} \to \{\omega\eta, \Delta\eta\}; \tag{7}$$
$$\eta = 1 + 1/2\tau\sqrt{\omega^2+\Delta^2}, \tag{8}$$
$$\frac{1}{\tau} = \frac{nmp_0}{4\pi^2}\int d\Omega\,(|a|^2 + |b|^2\sin^2\theta) = \frac{1}{\tau_0} + \frac{1}{\tau_1}. \tag{9}$$

Here we differ from [12] only in that $1/\tau$ now contains a contribution from the part of the scattering amplitude arising from the spin-orbit interaction:

$$\frac{1}{\tau_1} = \frac{nmp_0}{4\pi^2}\int |b|^2\sin^2\theta\, d\Omega. \tag{10}$$

As was shown in [12], formulas (4'), (7) to (9) imply that in the coordinate representation, the Green's function for a pure superconductor is to be multiplied by the factor

$$\exp\{-|r-r'|/2l\},$$

to account for the contamination by impurities, where $l = v\tau$ is the mean free path.* It follows from this that the introduction of impurities does not affect the thermodynamics of a superconductor, and, in particular, the transition temperature at which the system goes into the superconducting state remains unchanged. In the following all expressions will contain only the Green's functions for a superconductor with impurities, for which

*We note that $l_{s.o.} \approx v\tau_1$.

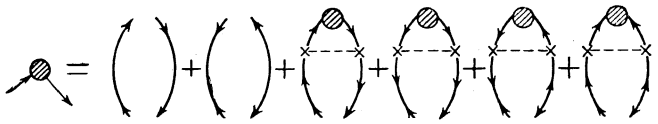

FIG. 4

we can, therefore, use the old symbols $\mathfrak{G}$, $\mathfrak{F}$, and $\mathfrak{F}^+$.

Figure 4 shows a graphical representation of the equation for $\Pi^{(1)}_{\alpha\beta}(p_+, p_-)$. We see that the determination of $\Pi^{(1)}_{\alpha\beta}(p_+, p_-)$ requires, in general, the knowledge of three new quantities which differ graphically from one another by the directions of the arrows. We define these quantities as Fourier transforms of the following expressions:

$$\Pi^{(2)}_{\alpha\beta}(x-y, y-x') = \overline{\langle T((\hat{g}\psi^+(x))_\alpha \psi^+_\delta(y)\sigma_{\delta\lambda}\psi_\lambda(y)\psi^+_\beta(x'))\rangle},$$

$$\Pi^{(3)}_{\alpha\beta}(x-y, y-x') = \overline{\langle T((\hat{g}\psi^+(x))_\alpha \psi^+_\delta(y)\sigma_{\delta\lambda}\psi_\lambda(y)(\psi(x')\hat{g})_\beta)\rangle},$$

$$\Pi^{(4)}_{\alpha\beta}(x-y, y-x') = \overline{\langle T(\psi_\alpha(x)\psi^+_\delta(y)\sigma_{\delta\lambda}\psi_\lambda(y)(\psi^+(x')\hat{g})_\beta)\rangle}.$$

Expression (6) involves only the component $\Pi^{(1)}_{\alpha\beta}(p, p)$. Therefore we shall not write down the general equations for $\Pi^{(i)}_{\alpha\beta}(p_+, p_-)$, but remark only that for $p_+ = p_- = p$ the equations imply

$$\Pi^{(3)}_{\alpha\beta}(p, p) = -\Pi^{(1)}_{\alpha\beta}(p, p), \qquad \Pi^{(4)}_{\alpha\beta}(p, p) = \Pi^{(2)}_{\alpha\beta}(p, p).$$

Using these results, we can obtain from the equation Fig. 4 the following expression for $\Pi^{(1)}_{\alpha\beta}(p, p)$:

$$\Pi^{(1)}_{\alpha\beta}(p, p) = [\mathfrak{G}^2(p) + \mathfrak{F}^2(p)](\sigma_{\alpha\beta} + \Lambda^{(1)}_{\alpha\beta}(p)) + 2\mathfrak{F}(p)\mathfrak{G}(p)\Lambda^{(2)}_{\alpha\beta}(p), \tag{11}$$

where we have introduced the notation

$$\Lambda^{(1)}_{\alpha\beta}(p) = \frac{n}{(2\pi)^3}\int \hat{f}_{\alpha\delta}(\mathbf{p}, \mathbf{p}')\Pi^{(1)}_{\delta\lambda}(p', p')\hat{f}_{\lambda\beta}(\mathbf{p}', \mathbf{p})\, d^3\mathbf{p}',$$

$$\Lambda^{(2)}_{\alpha\beta}(p) = \frac{n}{(2\pi)^3}\int \hat{f}_{\alpha\delta}(\mathbf{p}, \mathbf{p}')\Pi^{(2)}_{\delta\lambda}(p', p')\hat{f}_{\lambda\beta}(\mathbf{p}', \mathbf{p})\, d^3\mathbf{p}'. \tag{12}$$

The analogous expression for $\Pi^{(2)}_{\alpha\beta}$ is

$$\Pi^{(2)}_{\alpha\beta}(p, p) = -[\mathfrak{G}(p)\mathfrak{F}(p) - \mathfrak{F}(p)\mathfrak{G}(-p)](\sigma_{\alpha\beta} + \Lambda^{(1)}_{\alpha\beta}(p)) - (\mathfrak{F}^2(p) - \mathfrak{G}(p)\mathfrak{G}(-p))\Lambda^{(2)}_{\alpha\beta}(p). \tag{13}$$

The vector $\Lambda^{(i)}$ can be directed either along σ or $\mathbf{p}$. Accordingly it is convenient to write $\Lambda^{(i)}$ as the sum of two parts:

$$\Lambda^{(i)}_{\alpha\beta}(p) = \sigma_{\alpha\beta}\Lambda^{(i)}_\sigma(p) + (\sigma\mathbf{p})_{\alpha\beta}\mathbf{p}p_0^{-2}\Lambda^{(i)}_p(p). \tag{14}$$

Substituting (11) and (13) in (12), we obtain a system of four equations for the quantities $\Lambda^{(1,2)}_\sigma(p)$ and $\Lambda^{(1,2)}_p(p)$. Using the expressions (4′) and (7) for the Green's functions, we can easily show that all the quantities $\Lambda^{(1,2)}_{(\sigma,p)}(p)$ depend only on the fourth component of p, i.e., on the frequency ω. Owing to this circumstance the system of equations (11) to (14) can be reduced to algebraic form:

$$\left[(\omega^2+\Delta^2)^{3/2}\eta - \frac{\Delta^2}{2\tau_0}\right](1+\Lambda^{(1)}_\sigma) + \frac{i\Delta\omega}{2\tau_0} = (\omega^2+\Delta^2)^{3/2}\eta + \frac{1}{2\tau_0'}(\Delta^2\Lambda^{(1)}_p - i\Delta\omega\Lambda^{(2)}_p),$$

$$\left[(\omega^2+\Delta^2)^{3/2}\eta - \frac{\omega^2}{2\tau_0}\right]\Lambda^{(2)}_\sigma - \frac{i\Delta\omega}{2\tau_0}(1+\Lambda^{(1)}_\sigma) = \frac{1}{2\tau_0'}(i\Delta\omega\Lambda^{(1)}_p + \omega^2\Lambda^{(2)}_p),$$

$$\left[(\omega^2+\Delta^2)^{3/2}\eta - \frac{\Delta^2}{2\tau_0''}\right]\Lambda^{(1)}_p + \frac{i\Delta\omega}{2\tau_0''}\Lambda^{(2)}_p = -\frac{\Delta^2}{2\tau_1}(1+\Lambda^{(1)}_\sigma) + \frac{i\Delta\omega}{2\tau_1}\Lambda^{(2)}_\sigma,$$

$$\left[(\omega^2+\Delta^2)^{3/2}\eta - \frac{\omega^2}{2\tau_0''}\right]\Lambda^{(2)}_p - \frac{i\Delta\omega}{2\tau_0''}\Lambda^{(1)}_p = -\frac{i\Delta\omega}{2\tau_1}(1+\Lambda^{(1)}_\sigma) - \frac{\omega^2}{2\tau_1}\Lambda^{(2)}_\sigma. \tag{15}$$

Here

$$\frac{1}{\tau_0''} = \frac{1}{\tau_0} - \frac{3}{\tau_0'}; \qquad \frac{1}{\tau_0'} = \frac{nmp_0}{8\pi^2}\int |a|^2 \sin^2\theta\, d\Omega.$$

The last two equations are convenient for expressing $\Lambda^{(1)}_p$ and $\Lambda^{(2)}_p$ in terms of $\Lambda^{(1)}_\sigma$ and $\Lambda^{(2)}_\sigma$:

$$\Lambda^{(1)}_p = -\frac{1}{3}\frac{\tau_0'}{\tau_1}\frac{\Delta^2(1+\Lambda^{(1)}_\sigma) - i\Delta\omega\Lambda^{(2)}_\sigma}{\omega^2+\Delta^2},$$

$$\Lambda^{(2)}_p = -\frac{1}{3}\frac{\tau_0'}{\tau_1}\frac{\omega^2(1+\Lambda^{(1)}_\sigma) + i\Delta\omega\Lambda^{(2)}_\sigma}{\omega^2+\Delta^2}. \tag{16}$$

Since $\tau_0'/\tau_1 \ll 1$, we have, in the derivation of the equations above, neglected interference terms and terms quadratic in the amplitude of the spin-orbit interaction in all expressions containing $\Lambda^{(1)}_p$ and $\Lambda^{(2)}_p$. The last-mentioned terms appear as a result of the multiplication of two scattering amplitudes (1) in the definition of the quantities $\Lambda^{(i)}$ [formula (12)].

With the help of (16) we find from the first two equations (15)

$$1+\Lambda^{(1)}_\sigma = \frac{(\omega^2+\Delta^2)^{3/2}\eta - \omega^2(1/\tau_0 - 1/3\tau_1)/2}{(\omega^2+\Delta^2)[(\omega^2+\Delta^2)^{1/2}\eta - 1/2\tau_0 + 1/6\tau_1]},$$

$$\Lambda^{(2)}_\sigma = \frac{i\Delta\omega}{2}\frac{1/\tau_0 - 1/3\tau_1}{(\omega^2+\Delta^2)[(\omega^2+\Delta^2)^{1/2}\eta - 1/2\tau_0 + 1/6\tau_1]}. \tag{17}$$

We now have to calculate the susceptibility χ_s according to (6). Substituting (17) in (11), we obtain

after integration finally

$$\frac{\chi_s}{\chi_n} = 1 - \Delta^2 \pi T \sum_{\omega=-\infty}^{\infty} \frac{1}{(\omega^2+\Delta^2)\left[\sqrt{\omega^2+\Delta^2}+2/3\tau_1\right]}. \quad (18)$$

The contributions from $\Lambda_p^{(1)}$ and $\Lambda_p^{(2)}$ to χ can be neglected, since, according to (16), they are of the order $l/l_{s.o.}$, whereas the contributions from $\Lambda_\sigma^{(1)}$ and $\Lambda_\sigma^{(2)}$ are of the order ξ_0/l.*

In conclusion we write down the final formulas. If the spin-orbit interaction is very small ($l_{s.o.}$ large in comparison with ξ_0), then

$$\frac{\chi_s}{\chi_n} = \frac{N_n(T)}{N} - \frac{\pi\Delta}{6\tau_1}\frac{d}{d\Delta}\left(\frac{1}{\Delta}\,\mathrm{th}\,\frac{\Delta}{2T}\right). \quad (19)\dagger$$

The first term represents the ratio of the number of "normal" electrons over the total number of electrons and agrees with the results of Yosida and the earlier work of the authors.[1,4] For $T = 0$ we have, of course, $N_n(0) = 0$.

In the opposite limiting case of small mean free paths $l_{s.o.}$, we find that $\chi_s/\chi_n \to 1$:

$$\chi_s/\chi_n = 1 - \tfrac{3}{4}\pi\tau_1\Delta\,\mathrm{th}\,(\Delta/2T). \quad (20)$$

The symbol Δ in formulas (18) to (20) denotes the equilibrium gap in the spectrum of the superconductor at the given temperature.

In the general case, when the mean free path $l_{s.o.}$ is comparable with the correlation length ξ_0, closed expressions can be written down for χ_s in the cases $T = 0$ and $|T_c - T| \ll T_c$. For $T = 0$ we have ($\rho_0 = \frac{2}{3}\tau_1\Delta_0$):

$$\frac{\chi_s}{\chi_n} = \begin{cases} 1 - \dfrac{1}{\rho_0}\left[\dfrac{\pi}{2} - \dfrac{\mathrm{arch}\,\rho_0}{\sqrt{\rho_0^2-1}}\right], & \rho_0 > 1 \\ 1 - \dfrac{1}{\rho_0}\left[\dfrac{\pi}{2} - \dfrac{\arccos\rho_0}{\sqrt{1-\rho_0^2}}\right], & \rho_0 < 1 \end{cases} \quad (21)\ddagger$$

This function is shown in Fig. 5.

For $|T - T_c| \ll T_c$ ($\Delta \to 0$) we find

$$\frac{\chi_s}{\chi_n} = 1 - \frac{2\Delta^2}{(\pi T)^2\rho_c}\left\{\frac{\pi^2}{8} + \frac{1}{2\rho_c}\left[\psi\left(\frac{1}{2}\right) - \psi\left(\frac{1}{2}+\frac{\rho_c}{2}\right)\right]\right\}. \quad (22)$$

Here $\rho_c = \frac{2}{3}\tau_1\pi T_c = \rho_0/\gamma$, where γ is the Euler constant, $\gamma = 1.78$; $\psi(x)$ is the logarithmic derivative of the Γ function.

In the following section we shall compare our formulas with the experimental data.

3. DISCUSSION OF THE EXPERIMENTAL DATA

It has already been noted in [4] that such a comparison cannot be based on data which have been obtained with too large specimens and too strong fields. This limitation is due not only to the circumstance that the field is inhomogeneous in specimens with dimensions larger than the penetration depth. Another factor is important, too. It is known that if the dimensions of the specimen are smaller than the penetration depth the phase transition in the magnetic field is a second order transition and is connected with a gradual vanishing of the quantity Δ, the gap in the electron spectrum. The vanishing of the gap is, at the given temperature, accompanied by an increase in the number of "unpaired" electrons, i.e., an increase in the Knight shift. This last effect shows up, in particular, in the experiments of Androes and Knight (see Figs. 3 and 5 in [8]). In order to make this effect unimportant, the field must be weaker than the critical field of a specimen with the given dimensions d. Since $H_c \propto d^{-1}$, the effect of the change in the energy gap due to the external field is the smaller, the smaller the dimensions of the specimen.

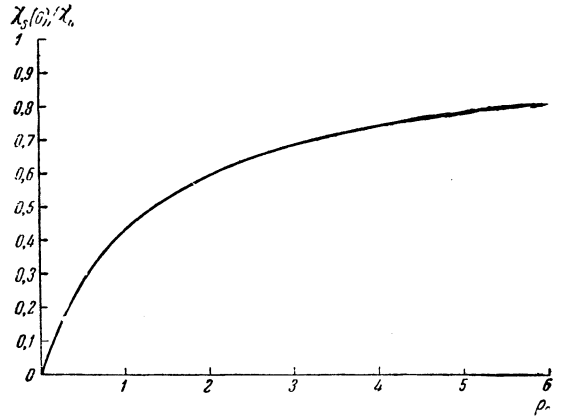

FIG. 5

For these reasons it is difficult to interpret the data of Reif[9] for colloidal mercury, for which the uncertainty in the size of the particles is large. This applies also to a considerable degree to the results of Androes and Knight[8] obtained with fields above 4 kilooersted. The critical field for the specimens used in [8] was 25 kilooersted at $T = 0$, and a field of 4 kilooersted could give a noticeable effect, in any case at temperatures which are close to the critical temperature. The attempt in [8] to interpret these data by taking account of the effect of the field through a change in the temperature scale does not seem convincing to us. A theory describing the effect of the field on the Knight shift does not exist as yet, and there are no indications whatever that a change in the temperature scale, and in particular, the one proposed in [8], has anything to do with the

*In the cases of interest to us the specimens have dimensions of the order 10^{-6} cm, i.e., $l \approx 10^{-6}$, so that $l \ll \xi_0 \approx 10^{-4}$ to 10^{-5} cm.

†th = tanh.

‡arch = $\cosh^{-1}$

problem. In particular, Androes and Knight[8] assume that near T_c one has $H_c \approx 2H(0)(1-T/T_c)$, whereas it is known that for films $H_c \sim H_{cm}\delta/d$, where $H_{cm} \sim 1-T/T_c$ is the field for a bulky specimen and $\delta \sim 1/\sqrt{1-T/T_c}$ is the penetration depth, i.e., $H_c \sim \sqrt{1-T/T_c}$.

Therefore, we have compared our results only with the data obtained in [8] with a field of 1.2 kilooersted (Fig. 6). The theoretical curves correspond to different values of ρ_0. The lower dashed curve refers to the case $\rho_0 = 0$, i.e., shows the dependence of the paramagnetic susceptibility of a superconductor in the absence of spin-orbit coupling.[1]

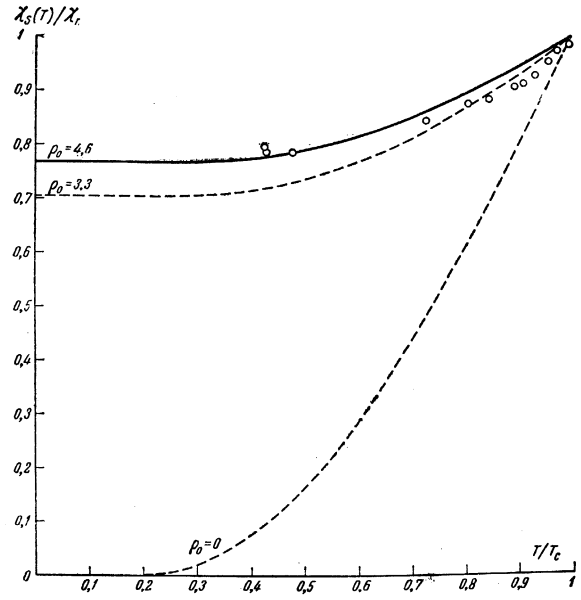

FIG. 6

It is seen from Fig. 6 that the theory is in satisfactory agreement with experiment. The small discrepancies for temperatures near T_c may be due to the effect of the field. The value $\rho_0 = 4.6$ was obtained with the help of formula (18) from experimental data in the low temperature region.

For $T = 0$ we have $\chi_s(0)/\chi_n = 0.77$. Assuming that $\rho_0 = 2\pi\xi_0/3l_{s.o.} = 4.6$ and using the fact that $\xi_0 = 2 \times 10^{-5}$ for tin,[7] we obtain $l_{s.o.} = 1.0 \times 10^{-5}$ cm. Assuming further that the mean free path l is of the order of the dimensions of the specimen, i.e., $l \sim 10^{-6}$, we find that $l \sim 0.1\, l_{s.o.}$, which implies that the spin-orbit interaction is somewhat weaker than usual.

In conclusion we make one further remark. Androes and Knight[8] have expressed doubt that the Knight shift can be explained with the help of the spin-orbit interaction, since they did not observe any appreciable dependence on the dimensions of the specimen in their experiments. Measurements on specimens with dimensions of ~ 1000 Å gave the same order of magnitude for the Knight shift as films with a thickness of 40 Å. In our opinion, these results are not sufficient to make the above-mentioned conclusion convincing. If the critical field for specimens with dimensions of 40 Å was 25 kilooersted, then specimens with dimensions of 1000 Å have a critical field of 1 kilooersted, and for this reason alone the Knight shift may have a magnitude of order unity.

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179