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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‡National Science Foundation predoctoral fellow.

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KNIGHT SHIFT IN SUPERCONDUCTORS

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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.

A nonvanishing value of $\chi_s(0)$ can be obtained by including a mean free path, l, in constructing the normal state wave functions. Let the single-particle wave functions in the normal state, including the effects of the scattering centers which give rise to the finite mean free path, be ψ_n having energies ϵ_n. The Hamiltonian describing the interaction of the magnetic field H, which is taken to be in the z direction, and the electron spins is

$$\mathcal{H}_{\text{mag}} = \mu_B \sum_{nn'} \int \psi_{n'}^*(\vec{r}) H(\vec{r}) \psi_n(\vec{r}) d^3r \times \{c_{n'\uparrow}^\dagger c_{n\uparrow} - c_{-n\downarrow}^\dagger c_{-n'\downarrow}\}, \qquad (1)$$

where $\psi_n = \psi_{-n}^*$ and the c's obey the usual Fermi anticommutation rules. If the BCS states are constructed in terms of the ψ_n's, the shift in energy to second order in H_{mag} when averaged over all positions of the scattering centers may be expressed as

$$\langle E^{(2)} \rangle_{\text{Av}} = -\mu_B^2 \langle \sum_{n,n'} \int \psi_{n'}^*(\vec{r}) H(\vec{r}) \psi_n(\vec{r}) \psi_n^*(\vec{r}\,') H(\vec{r}\,') \psi_{n'}(\vec{r}\,') d^3r\, d^3r'\, L(\epsilon_n, \epsilon_{n'}) \rangle_{\text{Av}}, \qquad (2)$$

where $L(\epsilon_n, \epsilon_{n'})$ is given by (5.16) of I. In order to perform the sums in (2), we require averages of the form

$$\langle \sum_{\epsilon_n, \epsilon_{n'} = \text{const}} \psi_{n'}^*(\vec{r}) \psi_{n'}(\vec{r}\,') \psi_n^*(\vec{r}\,') \psi_n(\vec{r}) \rangle_{\text{Av}} = \frac{\sin kR \sin k'R}{kk'R^2} e^{-R/l}, \qquad R = |\vec{r} - \vec{r}\,'|, \qquad (3)$$

where the average has been approximated by the product of the averages of the n and n' sums and we have used the results of Weiss and Abrahams[8] for the averages involved. The states ψ_n reduce to linear combinations of plane-wave states with wave number $|\vec{k}|$ in the limit $l \to \infty$.

The nonlocal susceptibility is given by

$$\chi(R) = \frac{-\delta^2 \langle E^{(2)} \rangle_{\text{Av}}}{\delta H(\vec{r}) \delta H(\vec{r}\,')} = \mu_B^2 \sum_{kk'} \frac{\sin kR \sin k'R}{kk'R^2} e^{-R/l} L(\epsilon_k, \epsilon_{k'}). \qquad (4)$$

Since $L(\epsilon_k, \epsilon_{k'})$ is nonzero only when $|\epsilon_k|, |\epsilon_{k'}| \lesssim \epsilon_0$, it is easily seen from (5.3) and (5.15) of I that $\chi(R)$ is related to the kernel $K(R)$ for orbital diamagnetism by

$$\chi(R) = \chi_n [\delta(R) - \lambda_L^2(0) K(R)], \qquad (5)$$

where $\chi_n = 2\mu_B^2 N(0)$ is the spin susceptibility in the normal state and $K(R)$ is given by

$$K(R) = \frac{J(R,T) e^{-R/l}}{4\pi \lambda_L^2(T) \xi_0}, \quad J(R,T) \simeq e^{-R/\xi_0}. \qquad (6)$$

Thus, for magnetic fields which vary slowly over distances of the order of ξ, we have

$$M(\vec{r}) = \int \chi(R) H(\vec{r}\,') d^3r' = \chi_n H(\vec{r}) \left\{ 1 - \frac{\xi}{\xi_0} \left[\frac{\lambda_L(0)}{\lambda_L(T)} \right]^2 \right\}, \qquad (7)$$

where

$$\frac{1}{\xi} = \frac{1}{\xi_0} + \frac{1}{l}.$$

For $l \to \infty$ this expression reduces to the result of Yosida; however, for finite l one obtains a nonvanishing magnetization at $T = 0$. To obtain agreement with the experiments of Reif and Androes and Knight one would have to choose l/ξ_0 to be 0.50 and 0.37, respectively. The coherence length, ξ_0, for tin is 2.5×10^{-5} cm,[4] so that $l \sim 10^{-5}$ cm for the latter experiment. This value is an order of magnitude larger than the mean dimension of Androes and Knight's plates, which suggests that a large amount of specular scattering occurs at the surface. The same situation exists for Reif's experiment.

It is possible that in small superconducting samples the low-lying continuum of magnetic states which gives rise to the Knight shift can be described by a continuous change of pairing with magnetization. For example, one could start with the magnetized state in the normal metal and begin pairing states on the spin-up Fermi surface with those on the spin-down Fermi surface in such a manner that a maximum number of pair states are connected by the two-body interaction, consistent with the conservation laws of the problem. If these states being paired were strictly plane waves, then momentum conservation would forbid the states interacting with each other, since in general the pairs would have different total momentum. However, the experiments mentioned above have been performed on samples whose dimensions were such that the spread in momentum of the single-particle states due to finite sample size was large compared to the momentum difference Δk due to the change in pairing caused by the magnetic field. Indeed, $\Delta k\, \xi_0 \ll 1$ for the magnetic fields employed in these experiments, where ξ_0 is the coherence length. It would appear that pairing exactly time-reversed states as one does for the ground state, or pairing states which differ slightly from these, should not alter the interaction energy strongly and it is possible that one would obtain a finite Knight shift in this manner. If this description were valid, then the magnetic continuum would be analogous to the continuum of current carrying states found by pairing single-particle plane-wave states $(\vec{k}+\vec{q}\uparrow, -\vec{k}+\vec{q}\downarrow)$. The vanishing of the nuclear spin relaxation[9] rate as $T \to 0$ indicates that the density of these magnetic states would be small just as in the case of the current-carrying states and that an energy gap would continue to exist for single-particle-like excitations.

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KNIGHT SHIFT IN SUPERCONDUCTORS

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Ferrell[1] has recently explained the observation by Reif[2] and by Androes and Knight[3] of finite Knight shifts in tin and mercury in terms of spin-reversing scattering (a spin-orbit effect) at the surfaces of the fine particles used. This theory might be questioned because it uses concepts—coherence length and plane wave states—which are well defined only for bulk samples of pure superconductors, while the experiments are done on fine particles. This Letter demonstrates that the spin susceptibility and Knight shift may be calculated using the theory of very imperfect ("dirty") superconductors proposed by the author,[4] with no further assumptions. The result confirms Ferrell's physical reasoning.

In a very imperfect metal, plane-wave states with fixed spin are no longer good one-electron functions, so the theory of reference 4 introduces hypothetical exact one-electron functions,

$$\psi_n = \sum_{\vec{k},\sigma} (n|\vec{k}\sigma)\psi_{\vec{k}\sigma}; \quad \text{energy } \epsilon_n. \tag{1}$$

It is observed that in the absence of magnetic centers the Kramers time-reversal degeneracy must be present, so that the distinct state

$$\psi_{-n} = \sum_{\vec{k},\sigma} (n|\vec{k}\sigma)^* \psi_{-\vec{k}\,-\sigma},$$

is also an eigenstate of energy ϵ_n. Then it is shown that the pairing $(n, -n)$ leads to a BCS state with essentially the average energy gap of the bulk superconductor, explaining the fact that such samples as those of Androes and Knight have nearly the bulk T_c.

In the presence of spin-orbit scattering, the state ψ_n must not be an eigenstate of the spin; in fact it will normally have no average spin component in any direction. Thus the spin operator $\vec{S}$ has now only off-diagonal components, causing transitions from states n to n'. If ϵ_n and $\epsilon_{n'}$ usually differ by more than the gap, clearly the resulting spin susceptibility is not much affected by superconductivity; our theory merely expresses this physical fact.

Using time-reversal symmetry and Hermiticity, it may be shown that in terms of scattered function fermion operators c_n, the spin operator