servation 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

S_z is

$$S_z = \tfrac{1}{2}\hbar \sum_{n,n'} S_{nn'}(c_n{}^* c_{n'} - c_{-n'}{}^* c_{-n}), \tag{2}$$

where in terms of $\vec{k}, \sigma$ states it was

$$S_z = \tfrac{1}{2}\hbar \sum_{\vec{k}} (c_{\vec{k}\uparrow}{}^* c_{\vec{k}\uparrow} - c_{-\vec{k}\downarrow}{}^* c_{-\vec{k}\downarrow}).$$

The energy spectrum of the coefficient $S_{nn'}$ is in principle easily determined from a measurement of the absorptive component of the susceptibility in the normal state:

$$\chi''(\omega) \propto \sum_{n,n'} \delta(\epsilon_n - \epsilon_{n'} - \omega) |S_{nn'}|^2 = f(\omega\tau), \tag{3}$$

defining the relaxation function f and the spin relaxation time τ. f might be taken proportional to $(1+\omega^2\tau^2)^{-1}$, for instance.

We actually use (3) in such a way that the average over n is taken only over functions with the same energy. This is no limitation; there is no reason to expect relaxation times to vary over $\sim 1°K$ from the Fermi surface. It is this observation that one can use an observed relaxation function to get the energy dependence of the matrix elements that makes the technique work. A similar trick should give accurate results for the electrodynamics of dirty superconductors.

The susceptibility is to be calculated from

$$\chi = (\beta^2/\hbar^2) \sum_m (0|S_z|m)(m|S_z|0)(E_m - E_0)^{-1}. \tag{4}$$

If we assume a Bogolyubov[5] ground state defined by the "quasi-particle operators"

$$\alpha_n = u_n c_n{}^* - v_n c_{-n},$$

$$\alpha_{-n} = u_n c_{-n}{}^* + v_n c_n, \tag{5}$$

(u_n and v_n are the usual functions of energy ϵ_n), only the part of S_z proportional to $\alpha_n{}^\dagger \alpha_{n'}{}^\dagger$ has matrix elements with the ground state; inserting (5) into (2) we get

$$S_z = \tfrac{1}{2}\hbar \sum_{n,n'} (u_n v_{n'} - u_{n'} v_n) \alpha_n{}^\dagger \alpha_{-n'}{}^\dagger S_{nn'} + \text{c.c.} + \alpha^\dagger\alpha \text{ terms}, \tag{6}$$

and χ from (4) becomes

$$\chi = 4\beta^2 \sum_{n,n'} |S_{nn'}|^2 (u_n v_{n'} - u_{n'} v_n)^2 (E_n + E_{n'})^{-1}. \tag{7}$$

Here $E_n = (\epsilon_n{}^2 + \epsilon_0{}^2)^{1/2}$. Clearly this is zero if $\epsilon_n = \epsilon_{n'}$, but otherwise not.

Since u, v, and ϵ are only functions of ϵ_n, we may use (3) to obtain the final answer in terms of the energy gap and relaxation function:

$$\frac{\chi_s}{\chi_n} = \frac{\int d\epsilon \int d\epsilon' f[(\epsilon - \epsilon')\tau\hbar^{-1}][u(\epsilon)v(\epsilon') - u(\epsilon')v(\epsilon)]^2 (E + E')^{-1}}{\lim_{\epsilon_0 \to 0} \int d\epsilon \int d\epsilon' \cdots} \tag{8}$$

The quadrature could be done numerically; rough approximate results are

$$\chi_s/\chi_n \simeq 1 - (2\epsilon_0\tau/\hbar), \quad \epsilon_0 \ll h/\tau \tag{9}$$

$$\chi_s/\chi_n \simeq \tfrac{1}{6}\langle(\epsilon - \epsilon')^2\rangle/\epsilon_0{}^2, \quad \epsilon_0 \gg h/\tau$$

$$\simeq \tfrac{1}{6}\hbar/\epsilon_0\tau. \tag{10}$$

In the case of Knight and Androes' measurements on Sn, (9) gives $2\epsilon_0\tau/\hbar \simeq \frac{1}{5}$, and using the usual energy gap[6] this means $\tau \simeq 1.2\times10^{-13}$, corresponding to spin reversal once every 10-20 collisions with the surface: slightly less often than Ferrell found.

It is interesting that a finite Knight shift will be observed for almost any size of sample. Once the sample is large enough that the above effect does not work, the nonlocal nature of the electron susceptibility[7] will begin to be felt, so that a positive Knight shift will be seen in the surface layer, a negative one in the inaccessible interior. This will greatly complicate the size dependence.

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