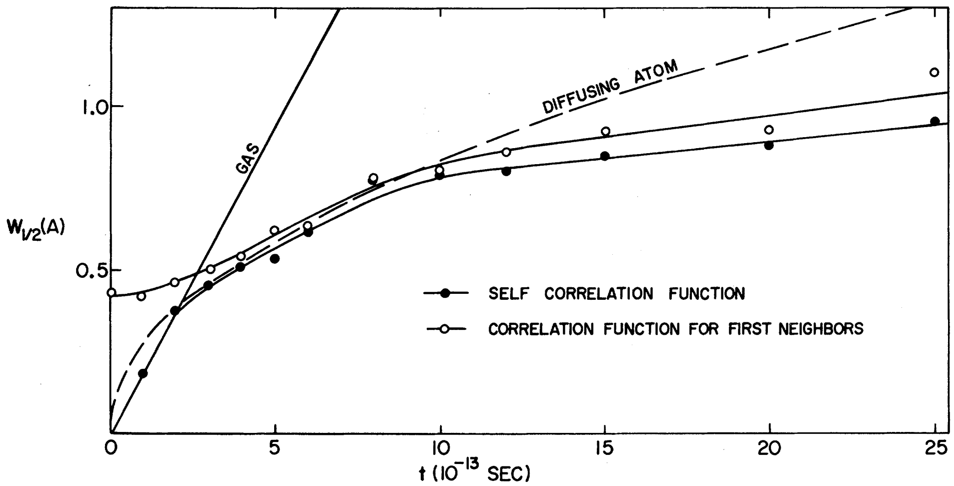

FIG. 3. The radius at half maximum of the self-correlation function (closed circles) and the half-width at half maximum of the correlation function for first neighbors (open circles) as functions of the time.

atoms in the first shell move in a somewhat complicated way. At times $t \gtrsim 8\times10^{-13}$ sec the atoms seem to be settling down into a diffusive type of motion, but the rate of diffusion appears to be less than the rate of self-diffusion measured by tracers. This suggests that, in addition to the small motions ("jitter") of the atoms, which show up as a continuous diffusive expansion of the correlation functions, there also occur significant numbers of comparatively large diffusion "jumps." Such behavior was previously postulated[2] to explain the results on water. The distribution of "jump sizes" could possibly be studied by means of the shapes of the correlation functions. The present results, however, are not sufficiently precise for this to be possible.

Details of the experiments and of the analysis will be published on conclusion of the work.

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KNIGHT SHIFT IN SUPERCONDUCTORS*

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The theory of Townes *et al.*[1] of the Knight shift in the frequency of nuclear resonance in a metal predicts a fractional change of

$$\frac{\Delta H}{H}=\frac{8\pi}{3}\frac{\langle|\psi_F(0)|^2\rangle_{\mathrm{Av}}}{n_a}\chi, \quad (1)$$

where χ is the magnetic spin susceptibility *per unit volume*, n_a is the atomic density, and the square of the wave function is evaluated at the nucleus and averaged over the Fermi surface.[2] The measurements of Reif[3] and of Androes and Knight[4] indicate shifts for superconducting mercury and tin almost as large as that for the metals in the normal state. This would seem to indicate according to Eq. (1) that the superconducting and normal susceptibilities are practically equal, even at zero temperature (which is the case to which we limit ourselves). This interpretation conflicts with the theory of Bardeen et al.,[5] which establishes a strict energy gap and a vanishing spin susceptibility for the superconducting ground state.[6] The exact pairing of electrons in momentum space has been relaxed by Heine and Pippard[7] to permit spin excitations and a susceptibility almost as large in the superconducting as in the normal state. It is not impossible that this modification of the BCS theory does indeed provide the correct explanation of the finite Knight shift for superconductors. But on the other hand, there is a danger that when the details of this modification are worked out, a discrepancy may arise with the specific heat. If the spin excitations which are allowed by Heine and Pippard prove to have appreciable statistical weight, they will yield a measurable contribution to the specific heat, in disagreement with experiment. Furthermore, evidence against the existence of the spin excitations is provided by the marked increase in the nuclear spin relaxation time in superconducting aluminum, as the temperature is decreased.[8]

The purpose of the present note is to propose an alternative explanation of the Knight shift in superconductors which is free of the above difficulties. We assume that low-lying excitations do not exist for a bulk superconductor, for which the susceptibility can indeed be taken to be zero. But we present some theoretical considerations which indicate that for a finite sample the susceptibility should rise when the geometrical dimensions are made smaller than the coherence length, to a value comparable to that in the normal state. This proposed size dependence is quite plausible, since it is generally accepted that the superconducting state depends in a very essential way on long-range correlations.

In order to establish that the superconducting Knight shift should be expected to possess a size dependence, it is convenient to avoid calculating the susceptibility directly, and instead to consider an alternative way of computing the shift. The effect results from an interference of two perturbing terms H' and H'' in the Hamiltonian for the electron system. The first represents the interaction between the electron spins and the laboratory magnetic field, and the second that between the electron spins and the nuclear magnetic moment. The part of the perturbed ground-state energy which depends in second order upon the interference of the two perturbations is given by

$$\Delta E = \sum_{n\neq 0} \frac{H_{0n}'H_{n0}''+H_{0n}''H_{n0}'}{E_0-E_n}, \qquad (2)$$

where the matrix elements are taken with respect to the unperturbed stationary states of energy E_n. This equation can be interpreted in two ways. One can imagine that H' produces a change ψ' in the wave function and that the energy of the perturbation H'' is then computed as an expectation value with respect to this perturbed wave function. This corresponds to Eq. (1), where the laboratory field first polarizes the electron gas, which then acts upon the nucleus. Alternatively, one can think of H'' as producing a different change ψ'', and can then use this wave function for computing the expectation value of H'. In other words, one can first "turn on" the nuclear magnetic moment, which then becomes "dressed" with a polarization cloud which changes its g factor and consequently its resonance frequency in the laboratory field. The latter picture has some merit conceptually, since in actual fact it is never possible to turn off the nuclear moment; the laboratory field is, of course, at one's disposal. We are therefore motivated to calculate the total magnetic moment induced in the electron gas by the nuclear magnetic dipole.

For our argument it is essential to establish the spatial distribution of the magnetization. We give the result of a calculation using the simple free-electron model, where the wave functions are plane waves. The nucleus is considered to be only a magnetic dipole; its Coulomb field is ignored. By applying Born's approximation we obtain a magnetization density[9] of

$$M(r) = (4\mu\chi/3r^2)j_1(2k_0r), \qquad (3)$$

where the spherical Bessel's function is

$$j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x}. \qquad (4)$$

μ is the nuclear magnetic dipole moment, k_0 the wave number at the top of the Fermi sea, and r the radial distance from the nucleus. This magnetization density can be integrated to give a total induced magnetic dipole moment in the vicinity of the nucleus whose ratio to the inducing nuclear moment is equal to

$$\frac{\Delta\mu}{\mu} = \frac{4\pi}{\mu}\int_0^\infty M(r)r^2dr = \frac{8\pi}{3}\chi. \qquad (5)$$

In the present model the square of the wave function equals the atomic density, so that the Knight shift predicted by Eqs. (1) and (5) is identical. This agreement was to be expected because of the equivalence of the two different ways of computing the energy change given by Eq. (2). But this second way of computing the Knight shift has the advantage of providing an intuitive picture for the effect. The magnetization density times $4\pi r^2$ is plotted in Fig. 1, which shows that most of the effect comes from close distances (high-energy virtual excitations). The arrow in Fig. 1 indicates approximately one-half of the average interelectron separation, and it is very natural to assume that the magnetization density at distances from the nucleus of this order of magnitude is completely unaffected by the superconducting transition.

The transition to the superconducting state can be expected to have an effect on the polarization cloud only over distances of the order of the coherence length, which is hundreds or thousands of times greater than the mean radius of the cloud shown in Fig. 1. To illustrate this, a very crude energy-gap model suffices. Let us modify the free-electron model by leaving all the matrix elements unchanged but by replacing all excitation energies less than $\hbar k_0\kappa/m$, by this quantity itself. The reciprocal of the parameter κ, which specifies the gap energy, is a rough measure of the coherence length. With this change, an additional contribution to the magnetization density appears of the form

$$M'(r) = -\frac{4\mu\chi}{3\pi r^2}\,\frac{1-\cos\kappa r}{\kappa r^2}. \qquad (6)$$

(Here we have omitted a fluctuating term proportional to $\cos 2k_0 r$ which gives no net magnetization.) Integrating over this, we find an additional induced moment corresponding to a fractional change in the nuclear g factor of

$$\frac{\Delta\mu'}{\mu} = -\frac{8\pi}{3}\chi. \qquad (7)$$

Adding this contribution to that found in Eq. (5) above, we obtain a vanishing net Knight shift, as expected for a strict energy-gap model which can possess no bulk susceptibility. But it is essential to note that the density of the compensating cloud described by Eq. (6) is extremely low compared to that of Eq. (2) at distances from the nucleus of the order of interatomic dimensions. It is only by integrating out to radii of the order of the coherence length that we produce a cancellation of the close-in cloud responsible for the normal Knight shift.

Because of the boundary effects, it is difficult to give a rigorous treatment of the compensating cloud set up in a small sample. For simplicity, imagine that the nucleus is at the center of a sphere of diameter L much less than $\xi_0 \approx \kappa^{-1}$, the coherence length. As a first approximation we can take the magnetization density at any distance less than $L/2$ to be the same as that which would exist around the nucleus in a bulk sample. Then it follows from the preceding paragraph that the superconducting fractional decrease in the Knight shift is of the order of $L/\xi_0 \ll 1$. But this is much too crude a treatment, as can be seen from the following transport picture:[10] The magnetization cloud in a bulk sample is established by electrons which interact with the nucleus and then carry the effect of the perturbation radially outward. In a small sample, these electrons will be reflected back at the surface and will build up a magnetization larger by the factor f, the number of times that they can be scattered before the spin-orbit force flips their spin.[11] Thus we obtain, to within a multiplicative numerical constant, the following rough equality for the normal-superconducting difference:

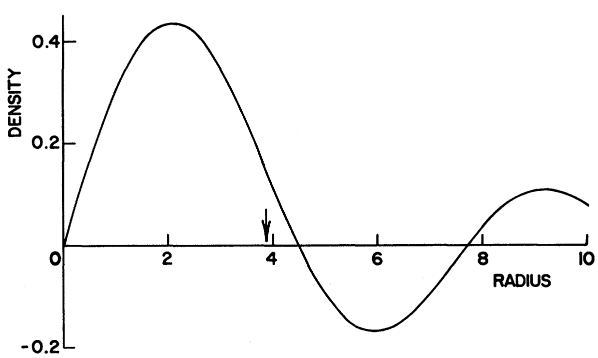

FIG. 1. Radial magnetization density vs radius r, measured in units of $(2k_0)^{-1}$ [or $(4\pi)^{-1}$ times the deBroglie wavelength at the Fermi surface]. The ordinate is proportional to $(dr)^{-1}$ times the magnetization contained between spheres of radius r and $r+dr$. The curve represents the polarization cloud surrounding a point magnetic dipole (nucleus) in a free-electron gas and is given by $j_1(2k_0r)$. The arrow indicates a radius roughly equal to one-half of the average interelectron separation, within which most of the polarization cloud is contained. The superconducting transition cannot affect this cloud, which changes the total magnetic moment of the "dressed" nucleus and consequently yields the Knight shift, because it arises from virtual excitation to states very far above the energy gap.

$$(\Delta H_n - \Delta H_s)/\Delta H_n \approx f L/\xi_0. \tag{8}$$

(This equation applies only when L is less than ξ_0/f. For larger values of L, $\Delta H_s/\Delta H_n$ approaches zero.) Substituting from reference 4 the values $(\Delta H_n - \Delta H_s)/\Delta H_n = 0.27$ and $L \approx 100$ A (a weighted geometrical mean value of the diameter and thickness of the platelets), and $\xi_0 = 2500$ A from reference 5, we obtain $f \approx 6$, a reasonable value.

Summarizing, we have seen that the Knight shift results from a normal magnetization cloud, which is closely bound to the nucleus and is the same in both the normal and superconducting states, and a diffuse compensating cloud which appears only in the superconducting state and is of very great linear dimensions. Since only a fraction of this cloud is contained in a small sample, the superconducting shift is expected to be smaller than but comparable to the normal shift. The actual magnitude of the decrease has been interpreted in Eq. (8) as being dependent on the spin-orbit coupling. It should be emphasized that the spin-orbit force is quite essential, since it is only by means of it that the total electron spin ceases to be a good quantum number. It then becomes possible for the magnetic field to mix in virtual excitations from above the gap, yielding a nonvanishing susceptibility. Since the spin-orbit coupling is very strongly dependent on atomic number, f may be expected to be very large for a light element, which should consequently show a Knight shift very much reduced in the superconducting state, in definite contrast to the nearly full shift exhibited by the heavy elements. It would be highly desirable to test experimentally this aspect of Eq. (8), as well as the linear dependence on L.

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MAGNETIC EFFECTS ON SHEAR WAVE ATTENUATION IN SINGLE CRYSTAL COPPER

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Recently there has been much interest in the effects of a magnetic field on ultrasonic attenuation at low temperatures, and much experimental work has been directed toward the study of longitudinal[1] waves. To our knowledge, resonances in the attenuation of shear waves in single crystals have not been previously reported in detail. These are of interest because recently published theories[2,3] predict the existence of oscillations in the attenuation *versus* magnetic field data only for certain orientations of field, polarization, and propagation directions. In particular no oscillations should be observed when the magnetic field is parallel to the polarization direction, although the attenuation should decrease with increasing magnetic field. Our preliminary observations show that oscillations occur in shear wave attenuation when the field is either