NUCLEAR MAGNETIC RESONANCE IN SUPERCONDUCTING TIN*

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The difficulties of interpretation that plagued previous nuclear magnetic resonance experiments in superconducting metals[1,2] arose mainly because the samples contained widely varying particle sizes. Thus, a significant fraction of the sample remained in the normal state at temperatures $< T_c$ in the fields employed. Since the two different types of particles contributed resonance lines which overlapped, it was difficult to separate the part arising from the absorption in the superconducting material. In order to avoid this difficulty, a sample has been built up by evaporating, alternately, layers of tin and a dielectric (Nylon). The metal in the sample (approximately one gram) has the β tin structure, and is uniformly divided into small platelets with diameters, in the plane of the evaporated layers, of ~140 A, and thickness ~40 A. The critical temperature is found to be 3.712 ± 0.010°K, and the critical field at $T=0$ is 25 ± 3 kilogauss. Experiments have been performed with the sample in the superconducting state in fields up to 8.8 kilogauss.

The resonance has an almost Gaussian shape, a width which varies linearly with the magnetic field, and, aside from the usual T^{-1} variation of intensity, no observable temperature dependence. That is, to the accuracy of measurement (signal to noise ratio of $\lesssim 10$ at 4.2°K), the line shape and width are the same above, in, and below the superconducting transition. Work on other tin samples containing somewhat larger particles indicates that the line width is also inversely proportional to particle size, and in the final sample it is ~4.5 times the width for "bulk" tin (taken as $\nu_{\parallel} - \nu_{\perp}$)[3] in the same field. These characteristics may be explained by considering, in conjunction with the theory of Bloembergen and Rowland,[3] that the conduction electrons near the surface of a piece of metal do not see the regular tin lattice symmetry. In the platelets in the sample, half or more of the atoms are within 10 A of the surface. The variety of the surface positions in relation to the crystal axes, and the effects of some sort of random particle-size distribution account for the shape of the line.

The nuclear magnetic resonance shift in the evaporated metal at 4.2°K was found to be the same as the isotropic shift in "bulk" tin. But comparison with several diamagnetic salts[4] yields values of the shift in normal metal ranging from 0.63 to 0.81%, depending on the salt. Therefore, a quantity $D = (\nu_{sc} - \nu_n)/\nu_n$ will be used to describe the behavior of the resonant frequency, ν_{sc}, in the superconducting state. Here ν_n is the resonant frequency in the normal metal at 4.2°K. Figure 1 is a plot of D vs the reduced temperature, $t(H) = T/T_c(H)$, for an applied field of 1.2 kilogauss. The curve extrapolates to $D_0 \sim 0.2\%$ at $T=0$. Whether or not this extrapolation is valid, it is clear that the curve has not reached an asymptotic value at $t(H) = 0.4$.

Similar curves of D vs $t(H)$ are obtained in fields up to 8.8 kilogauss. At $t(H) = \frac{1}{2}$ they fall within a range of 0.02% above the 1.2 kilogauss value in Fig. 1. The effects of the magnetic field are thus small. Details will be reported later.

We conclude that the nuclear magnetic resonance shift in superconducting tin does not approach zero as T goes to zero. If $SnCl_2$ is used as the reference salt, $(\Delta H/H)_{T=0} \approx 0.55\%$, which

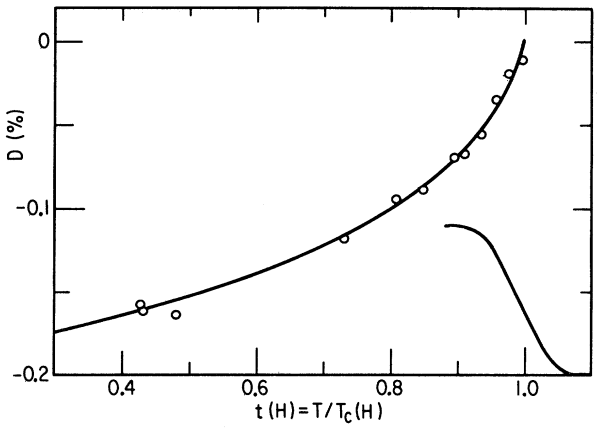

FIG. 1. Deviation of the resonant frequency in superconducting tin. $D = (\nu_{sc} - \nu_n)/\nu_n$, where ν_{sc} is the resonant frequency in the superconducting state, and ν_n is the resonant frequency in the normal state at 4.2°K. The experimental points are for $H = 1.2$ kilogauss; $T_c(H)$ is 3.68°K for this field. The solid line is a plot of the equation $t(H) \sim \cosh[a(D-d)]$, a and d being constants. The lower curve is a plot of the change in frequency of the experimental oscillator (arbitrary units) as the temperature was lowered through the transition. Any correction in D for the demagnetization factor of the sample is less than 0.01%.

is approximately 73% of its value in normal tin. This is consistent with the results of Reif[1] for mercury.

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EFFECTS OF SPIN-ORBIT COUPLING IN RARE EARTH METALS, AND IN SOLUTIONS OF RARE EARTH METALS

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There are three phenomena of the same general character that occur in rare earth metals or solution thereof:

(1) The reduction of superconducting transition temperature in dilute solutions of the rare earths in lanthanum,[1] or of rare earth compounds in $CeRu_2$[2] or $OsRu_2$.[3]

(2) An extra resistance of the pure metals (and presumably of the alloys[4]) due to spin disorder scattering.

(3) An indirect exchange coupling among the ion spins in analogy with the Ruderman-Kittel mechanism of nuclear spin-spin interaction in metals.[5] This indirect exchange is thought to be responsible for the observed ferromagnetism and/or antiferromagnetism at temperatures of the order of 100°K.[6]

All three effects are supposed to arise from the exchange interaction $A\vec{S}_{ion}\cdot\vec{S}_{cond}$ of the f-shell spins with the spins of the conduction electrons. The purpose of this note is to point out the bearing which spin-orbit coupling has on the interaction in the above three cases. Except in the case of europium, discussed separately, we assume the multiplet splitting to be much greater than crystal field splitting. We consider the above three effects in turn.

(1) In a previous note by Herring[7] and in a detailed paper by Suhl and Matthias,[8] it was shown that on the basis of the Bardeen, Cooper, Schrieffer theory of superconductivity,[9] one expects the exchange interaction to lower the transition temperature of the superconducting state. This depression results from the fact that, partly because of the energy gap, and partly because of the spin-coherence properties of the BCS wave function, the exchange scattering lowers the free energy of the normal state more than that of the superconducting state. It was shown in reference 8 that if spin-orbit coupling is neglected, the reduction is proportional to $\vec{S}^2 = S(S+1)$, while when it is included, the reduction is very nearly proportional to the square of the projection of $\vec{S}$ on the $\vec{J}$ appropriate to the ground state. The only exception is europium ($J=0$) for which this projection vanishes. In almost all other cases, the agreement with the observed depression of T_C was substantially improved by using $\vec{J}(\vec{S}\cdot\vec{J})/J^2$ rather than $\vec{S}$. The reason is as follows: The calculation of the depression of free energy is a matter of second order perturbation theory. The operator $\vec{S}_{ion}\cdot\vec{S}_{cond}$ connects the ground state to states with one conduction electron excited and with J either unchanged or changed by 1. Since in the ground state J has its maximum or minimum permissible value,[10] only the $J\to J-1$ or the $J\to J+1$ transition need be considered. For definiteness we shall from now on consider only the case $J\to J-1$. Now the state $\psi(J-1)$ is removed from the ground state energy by Δ, the multiplet