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Nuclear Spin Relaxation in Superconducting Cadmium

Abstract: The nuclear spin-lattice relaxation time, T_1, in superconducting cadmium has been measured in the range of 0.37°K to 0.6°K. A field-cycling method was used. The results are explained by the theory of Bardeen, Cooper, and Schrieffer, and give another confirmation of the theory. The temperature dependence of T_1 in cadmium is identical to that in aluminum, which is surprising in view of the different crystal symmetry and band structure of the two metals.

I. Introduction

The nuclear spin-lattice relaxation time T_1 is a measure of the rate of exchange of energy between a spin system and the rest of the lattice, and it is most generally defined as the ratio of the deviation of spin energy from its equilibrium value to the rate of change of spin energy. In a normal metal T_1 is usually determined by the interaction of nuclear spins and conduction electron spins. The Knight shift and the nuclear spin-lattice relaxation time T_1 are two important quantities which give much information on the properties of the conduction electrons. In particular, T_1 provides information on the density of states near the Fermi surface. The properties of the conduction electrons will be greatly modified when a metal makes the transition into the superconducting state. Accordingly, it is expected that both effects provide a test of any theory of superconductivity.

Hebel and Slichter[1] first measured the T_1 in superconducting aluminum. Redfield[2] and recently Redfield and myself[3] also measured the T_1 of superconducting aluminum with greater accuracy and over a wider temperature range. These results disagree with a simple two-fluid model, but are explained by the Bardeen, Cooper, and Schrieffer (henceforth referred to as BCS) theory of superconductivity,[4] assuming an energy gap at absolute zero of $2\varepsilon_0(0) = 3.2kT_c$ and a constant relative anisotropy of the energy gap. The anisotropy will be discussed further in Sec. III.

In this paper we describe measurements of T_1 in superconducting cadmium as another example of a superconducting metal which obeys the BCS theory. For cadmium, the critical field at absolute zero, $H_c(0)$, is 28.8 gauss. The critical temperature T_c is 0.560°K[5] and the energy gap at absolute zero is $2\varepsilon_0(0) = 3.3kT_c$.[6]

It is known that the nuclear magnetic resonance line of metallic cadmium in the normal state is asymmetric. This indicates an anisotropy of the Knight shift, which is due to the asymmetry in p-character of the conduction electrons.[7] It is therefore anticipated that cadmium has a much larger anisotropy of the energy gap than aluminum.

II. Experiment

We used the same method as that used by Hebel and Slichter, which is a field-cycling method. This method is discussed in greater detail by Hebel and Slichter,[1] Anderson and Redfield,[8] and Redfield and Masuda.[3] In this method the nuclear spins are polarized through the application of a large field of about 4000 gauss for a time long compared to T_1; then the field is turned off, and the spins begin to relax at zero field in the superconducting state with a relaxation time characteristic of the superconducting state. After a variable time τ the field is turned on again to about 1200 gauss and the spin polarization is measured in the normal state by nuclear resonance at 1160 kc. The resonance signal intensity is proportional to the spin polarization, and from its variation with τ the relaxation time can be determined. The apparatus and field timing sequence are described in more detail in References 3 and 8.

In order to work at the critical temperature and below in cadmium ($T_c = 0.560$°K) a He^3 cryostat was used. The lowest temperature attained was 0.37°K, which corresponds to $T_c/T = 1.5$; it was not low enough to study the detailed behavior of T_1 in supercon-

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ducting cadmium. No attempt was made to get temperatures lower than those described in Reference 3.

The cadmium sample was made in the form of a powder by filing from a 99.999% purity ingot obtained from American Smelting and Refining Company. The filings were sieved through a 325 mesh sieve. The average particle size was about 10 microns. The only impurity detected by chemical analysis of the samples was copper, present in one part per million. These analyses do not include impurities in the sample which were introduced in the process of filing. It is anticipated that impurities and dislocations introduced in the preparation of the sample might affect T_1 in the superconducting state. These possible impurity effects will be discussed in detail later.[9]

In a magnetic field greater than the critical field, the metal is normal and therefore it is always necessary to make sure that the residual field was negligible during the time interval τ. This is especially important for measurements close to the critical temperature, particularly for such a case of low critical field as cadmium. In these experiments the residual field was less than 1/2 gauss.

III. Results and discussion

The data for the relaxation time in the superconducting state are shown in Fig. 1, as a function of T_c/T (assuming $T_c = 0.560°K$). The data were obtained for Cd^{113} of natural abundance. The signal-to-noise ratio was very poor because natural cadmium only contains, as the magnetic isotopes, Cd^{111} of abundance ratio 12.86 percent and Cd^{113} of abundance ratio 12.34 percent. Both cadmium nuclei have spin $I = 1/2$ and hence zero quadrupole moment, so that quadrupole effects are excluded. The fact that T_1 varies as $\exp[\varepsilon_0(0)/kT]$ for $T \ll T_c$ is a rather general consequence of any gap model. But the temperature range over which T_1 was measured is not wide enough to determine the slope of the curve, from which we would determine the energy gap width, $\varepsilon_0(0)$. The theoretical lines shown in Fig. 1 were derived from the BCS theory assuming a gap of $2\varepsilon_0(0) = 3.5kT_c$, and following the procedure given by Hebel.[10] Eliminating the singularity in the BCS density of states at the edge of the energy gap, Hebel and Slichter assumed that the BCS density of states was smeared by an amount $2\varepsilon_0(0)/r$. This means that they used a rectangular energy level breadth function of width $2\varepsilon_0(0)/r$ and height $[2\varepsilon_0(0)/r]^{-1}$. The dashed line in Fig. 1 was calculated for $r = 10$ and $2\varepsilon_0(0) = 3.5kT_c$.

A possible source of the smearing of the BCS density of states is anisotropy of the energy gap. There is no momentum selection rule for the initial and final states in nuclear spin relaxation, so the average density of states determine T_1, not the density of states in any particular k direction. Thus we will have a density of states smeared by an amount equal to the anisotropy of the gap. As the temperature T approaches T_c, the gap $2\varepsilon_0(T)$ decreases, according to the BCS theory, so it

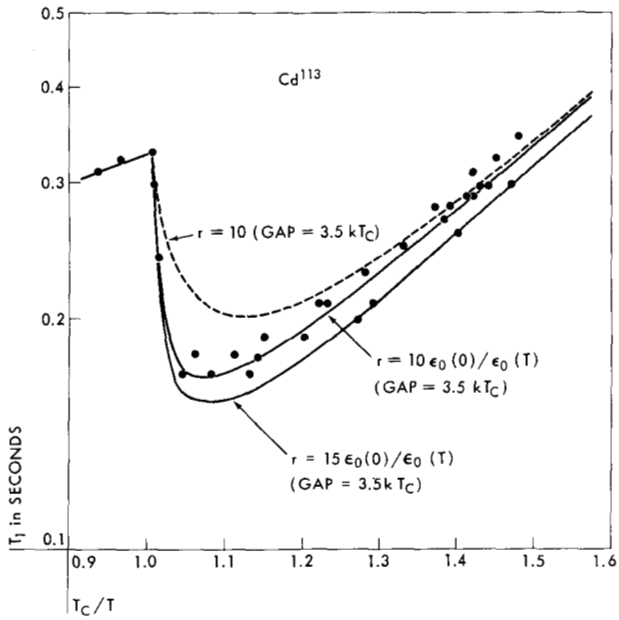

Figure 1 **Measured values of T_1 in the powdered cadmium sample.** *T_c was taken to be* 0.56°K. *Theoretical curves were derived assuming a gap of $2\varepsilon_0(0) = 3.5kT_c$ and various values for the parameter r.*

would be reasonable to assume a constant anisotropy by setting $r(T) = 10\varepsilon_0(0)/\varepsilon_0(T)$. The calculated line corresponding to such an assumption is also shown in Fig. 1 by a solid line. The experimental data agree well with this theoretical prediction, which is equivalent to the assumption that the smearing function width or anisotropy have the same temperature dependence as the energy gap. The data show the existence of an anisotropy in the energy gap of the order of 10 per cent of the gap itself. Contrary to our expectations, the anisotropy is the same as that for aluminum, which should be more isotropic than cadmium. The crystal structure of cadmium is hexagonal-close-packed, with a c/a ratio of 1.886; this is a large deviation from the ideal value of 1.633. Naturally it has an axial symmetry about the c-axis but not a spherical symmetry, and it also is a divalent metal. If the symmetry of the environment of a nuclear spin is lower than cubic, the tensor describing the electron-nuclear spin coupling is not isotropic and the Knight shift will depend on the direction of the applied field with respect to the crystalline axes. Therefore, besides the isotropic part of the Knight shift, which is attributable to the hyperfine interaction between the nuclear spin and the conduction electron spin in the s-state, there is an anisotropic part which arises from the non-s-character (p, d, etc.) of the electron orbitals and is associated with an anomalous broadening and asymmetry of the resonance line. From the fact that the isotropic Knight shift in cadmium is 0.43 percent, the s-content of the wave function was estimated to be

about 20 percent. The asymmetry in p-character of the conduction electrons has also been estimated.[7] Harrison[11] has proposed an approximate band structure in cadmium, and Galt, Merritt, and Schmidt[12] have made cyclotron resonance measurements. Both of these give a complicated band structure. From these experimental facts, it was anticipated that cadmium would have a much larger anisotropy of the energy gap than would aluminum.

Nuclear spin relaxation time measurements are not sensitive to excitations from selected portions of the Fermi surface. Therefore, we cannot get more direct evidence of an anisotropy of the gap from the T_1 measurements.

Morse, Olsen, and Gavenda[13] used ultrasonics to investigate an anisotropy of the energy gap. They measured the attenuation of longitudinal waves in tin, and concluded that the energy gap varied between $3.2kT_c$ and $3.8kT_c$. Their results are in good agreement with the analogous measurements in tin using shear waves.[14] Recently, Morse[15] has extended the same measurements to aluminum, using also shear waves. The energy gap varied between $2.7kT_c$ and $3.2kT_c$. According to these experimental results, we would be led to believe that tin and aluminum have roughly the same anisotropy.

As we pointed out previously, there is a possibility that impurities affect T_1 in the superconducting state. That is, as we add impurities, the individual momentum states are scattered around the Fermi surface and therefore the angular dependence of the energy gap is removed from the individual excitation energy gap. An anisotropy of the energy gap may be washed out by the impurity scattering; therefore it is expected that r will increase as the impurity concentration increases. By the detailed measurements on aluminum wire samples of well-known impurity content, it was shown that for impurity concentrations as small as 10^{-4}, the observed T_1 in the superconducting state is measurably different from that of the "pure" metal.[16] There is also a possibility that dislocations affect T_1 in the superconducting state. It is expected that the changes in T_1 can be correlated with changes in the mean free path similar to the effect observed in superconducting aluminum alloys. However, it is highly improbable that the sample of cadmium used here contained sufficient impurities and dislocations to affect T_1.

Preliminary measurements of T_1 in gallium by Hammond and Knight[17] indicate that in that metal the temperature dependence of T_1 is similar to that in cadmium and aluminum. As in cadmium, this is rather surprising in view of the probable large anisotropy of the energy gap in gallium.

Of course, it is quite possible that the density of states function is smeared by something other than anisotropy, such as by an excitation lifetime effect. Resolution of this question must await a better understanding of the role of the band structure in superconductivity and further experimental work.

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