Nuclear Spin-Lattice Relaxation in Superconducting Aluminum Alloys

YOSHIKA MASUDA*
International Business Machines, Watson Laboratory, Columbia University, New York, New York
(Received December 28, 1961)

The nuclear spin-lattice relaxation time, T_1, of superconducting aluminum alloys which contain up to 0.16% zinc or germanium has been measured in the range of 0.37°K to 1.2°K. A field cycling method was used. T_1 decreases slightly (less than 30%) with increasing-impurity concentration. The experimental data indicate that the anisotropy of the energy gap decreases with increasing reciprocal mean free path. The results are explained by means of the theory of dirty superconductors introduced by Anderson.

INTRODUCTION

THE measurement of the nuclear spin relaxation time, T_1, in superconducting metals is interesting because it provides a test of the gap model in the Bardeen, Cooper, and Schrieffer[1] (henceforth referred to as the BCS) theory. Hebel and Slichter first measured T_1 in superconducting aluminum.[2] They found that their results, when taken together with a result by Reif in superconducting mercury, would be impossible to explain on the basis of the conventional two-fluid model, but are explained by the BCS theory.[2,3] Further support for the BCS theory is found in the work of Redfield,[4] and of Masuda and Redfield,[5] who measured T_1 in superconducting aluminum with increased accuracy and over a wider temperature range (T_c/T $=0.9$ to 3.9, where $T_c=1.178$°K is the critical temperature of aluminum). Measurements of T_1 in superconductors recently were extended to cadmium,[6] for which the behavior is practically identical to that in aluminum.

These experiments on both superconducting aluminum and cadmium show that these metals have an energy gap at absolute zero of $2\epsilon_0(0)=3.2kT_c$, assuming that the BCS density of states function is smeared over a range of about 1/10 of $2\epsilon_0(0)$. The BCS theory applies to the homogeneous, pure, and isotropic electron gas with a simplified interaction term and pure plane-wave functions. If, instead of the constant electron-electron interaction, one were to use wave functions and an electron-electron interaction which are non-constant and anisotropic (as might be expected in actual metals), one would expect to find that the energy gap is a function of a momentum vector, as well as temperature. Thus, the energy gap of a single particle excitation depends upon the direction, as well as the magnitude of its momentum vector. But nuclear-spin relaxation has no momentum selection rule for the initial and final states of the transition, so the average density of states determines T_1, not the density of states in any particular k direction. Thus, as far as spin relaxation is concerned, the effect of anisotropy is to smear the BCS density of states by an amount equal to the anisotropy. Such a smearing was in fact introduced by Hebel and Slichter[2] to obtain order of magnitude agreement between their data and the BCS theory; without any such smearing the BCS theory predicts a very short relaxation time, which is a consequence of the singularities in the density of states function at the edge of the gap. The later data[5,6] could be explained quantitatively by assuming a smearing or anisotropy of the gap which is one tenth of the gap at all temperatures; in other words, as the temperature increases toward T_c the absolute value of the smearing decreases. Of course, the BCS density of states could be smeared by excitation lifetime or other effects, but the anisotropy interpretation seems the most natural,[5] and is also supported by the results reported in this article.[7]

In a dilute alloy, plane-wave states with fixed spin are no longer good one-electron functions. Anderson[8] developed a BCS type of theory for dirty superconductors, in which elastic scattering from physical and chemical impurities is large compared with the energy gap. He argued that a ground-state pair should be formed by pairing a one-electron state with its exact time reverse. This is a generalization of the k up, $-k$ down pairing of the BCS theory which is independent of impurity scattering. If the electronic mean free path is large compared to the coherence length, the impurities will mix plane-wave states weakly as the electron moves through a coherence length. But when the mean free path is small compared to the coherence length, the wave function can no longer be approximated by a single plane wave. Thus, the states are taken more or less randomly from all parts of the Fermi surface, thereby removing the source of anisotropy in the energy gap.

* Present address: Physics Department, Kobe University, Mikage, Kobe, Japan. Q. W. Boese Fellow, Columbia University, 1959–1960.

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[2] L. C. Hebel and C. P. Slichter, Phys. Rev. **107**, 401 (1957); **113**, 1504 (1959).

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[4] A. G. Redfield, Phys. Rev. Letters **3**, 85 (1959).

[5] Y. Masuda and A. G. Redfield, Phys. Rev. **125**, 159 (1962).

[6] Y. Masuda, IBM J. Research Develop. **6**, 24 (1962).

[7] A preliminary report on the results given in this article appeared in *Proceedings of the Seventh International Conference on Low-Temperature Physics, Toronto, 1960* (University of Toronto Press, Toronto, 1961), p. 412.

[8] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959); also see P. W. Anderson, reference 7, p. 298. Dr. Anderson first pointed out to us the role of anisotropy in nuclear relaxation in superconductors.

Chanin, Lynton, and Serin[9] have measured the effect of the electron mean free path, l, on the superconducting-transition temperature T_c. Their results show that (i) for small impurity concentrations T_c decreases linearly with increasing reciprocal mean free path $1/l$, (ii) for large impurity concentration T_c shows different behavior according to the valence difference between solvent and solute. T_c has a sharp upward trend for the specimens which contain the electro-positive impurities; for those with the electronegative impurities T_c tends to flatten out, and then to saturate.

Recent measurements[10] of T_c for Al-Zn alloys revealed that a Zn-rich solid solution (21 at. % zinc) is superconducting at a temperature above T_c for pure aluminum. The addition of such a large amount of impurity sets up strain-induced electric field gradients which interact with the nuclear-quadrupole moments, thus affecting the relaxation process in a complicated way. Therefore our measurements of T_1 were limited to the samples which contained small concentrations of impurities.

In this paper, we shall describe measurements of T_1 in superconducting aluminum alloys containing small amounts of an electro-positive impurity (Zn) or an electro-negative impurity (Ge).

EXPERIMENTAL DETAILS AND RESULTS

The measurements were done in the temperature range between 0.37°K and 1.2°K using a He^3 cryostat. A field cycling method[2,5] was used to measure T_1. In this method the nuclear spins are first polarized by the application of a large field (about 4000 gauss) for a time long compared to T_1. Then the field is turned off, and the spins relax at zero field in the superconducting state. After a variable time τ, the field is turned on again to about 1000 gauss and immediately swept past 1045 gauss to observe the spin polarization in the normal state by nuclear resonance. From the variation of the resonance signal intensity with τ, which is proportional to the spin polarization at that time, the relaxation time can be determined.

Professor B. Serin of Rutgers University very kindly supplied ingots of the aluminum alloys for which he had measured the dependence of T_c on the electron mean free path.[9] In order to eliminate undesirable impurity contamination caused by filing, the ingots were drawn into wire of 0.0065 cm diameter, and then cut into pieces roughly 0.5 mm long. This material, along with some uncut pieces of wire was then annealed at 450°C for 20 hr in a vacuum of about 10^{-5} mm Hg and cooled slowly.

After the annealing, the residual resistance of the uncut pieces of wire was measured in order to obtain an index of the homogeneity of the alloy, and of the electron mean free path. From the measured resistance values R and $R_{4.2}$, at room temperature t and at 4.2°K respectively, we calculate for each specimen the residual resistance ratio[9]

$$\rho=R_{4.2}/(R-R_{4.2})(1-\alpha t), \quad (1)$$

where α is the temperature coefficient of resistance for pure aluminum at 0°C. From the linearity of the increase in ρ with composition, we are fairly sure that the alloys were reasonably homogeneous and in solid solution. Our measurements of ρ, which are shown in Table I, were in good agreement with Serin's, of course. Table I also includes the experimental data of the corrected change in critical temperature ΔT_c^* relative to ideally pure aluminum, as measured by Chanin, Lynton, and Serin.[9]

TABLE I. Properties of the samples used. ΔT_c^* is the corrected change in critical temperature relative to an ideally pure aluminum; ρ is the measured value of the residual resistance ratio and $1/l$ the reciprocal mean free path. The data on ΔT_c^* were taken from reference 9.

Impurity	Concentration (at. %)	ΔT_c^* (°K)	ρ	$1/l$ (10^6 cm^{-1})
Zinc	0.036	−0.0123	0.0060	0.0038
	0.055	−0.0170	0.0088	0.0055
Germanium	0.012	−0.0073	0.0070	0.0044
	0.039	−0.0100	0.0195	0.0121
	0.160	−0.0019	0.0552	0.0342

We measured the T_1 of aluminum alloys containing 0.036 and 0.055 at. % zinc and 0.012, 0.039, and 0.16 at. % germanium. The results for T_1 in the superconducting state are shown in Figs. 1 and 2, as a function of T_c/T.

DISCUSSION

In the superconducting state the T_1 experimental data for pure metals are in semiquantitative agreement with the predictions of the BCS theory, assuming that the quasi-particle levels are not perfectly sharp.[2] This avoids the singularity in the BCS density of states at the edge of the energy gap and thus it will give a theoretical T_1 of the same order of magnitude as experiment. The source of this level broadening was uncertain. The present work suggests that the broadening arises from anisotropy of energy gap.

The theoretical equation for the relaxation rates, R_s and R_n, in superconducting and normal state is given by[2]

$$R_s/R_n=2\int_0^\infty \rho_s^2(E,T)[1+\epsilon_0^2(T)/E^2]f(E,T) \times[1-f(E,T)]dE, \quad (2)$$

where $\rho_s(E,T)$ is the normalized density of states in the superconductor, which from BCS theory has a temperature-dependent gap of half-width $\epsilon_0(T)$ centered

[9] G. Chanin, E. A. Lynton, and B. Serin, Phys. Rev. 114, 719 (1959).
[10] D. P. Seraphim, C. Chiou, and D. J. Quinn, Acta Met. (to be published).

about the Fermi energy E_F, and $f(E,T)$ is a Fermi function. The zero of the energy E is taken to be E_F. Hebel and Slichter obtained the density of states ρ_s by weighting the BCS density of states, ρ_{BCS}, with a function which characterizes the breadth of the energy levels. If an energy level breadth function is assumed to be a rectangle of width 2Δ and height $1/2\Delta$, then

$$\rho_s(E,T)=(2\Delta)^{-1}\int_{E-\Delta}^{E+\Delta}\rho_{BCS}(E',T)dE'. \qquad (3)$$

Using Eq. (2), we can calculate the temperature dependence of T_1 for various values of $r=\epsilon_0(0)/\Delta$. The parameter Δ might be temperature dependent as described elsewhere in detail.[5] The prediction corresponding to the assumption of $\Delta(T)$ proportional to $\epsilon_0(T)$ gave theoretical results which fit the data very well, in the case of pure metal. Thus, we regard the data on pure metal as evidence for the existence of an anisotropy in energy gap which, at any temperature, is of the order of 10% of the gap itself.

The experimental data on Al-Zn alloys are shown in Fig. 1. The data on the 0.036 at. % Zn alloy agree well with theory, assuming $r=40\epsilon_0(0)/\epsilon_0(T)$ and using the same energy gap $2\epsilon_0(0)=3.2kT_c$ as that used in pure bulk aluminum (solid line). Data on the 0.055 at. % Zn alloy show that r increases to 60 but the energy gap remains the same. Roughly speaking, the increase of r is proportional to the inverse mean free path $1/l$.

The results on Al-Ge alloy are shown in Fig. 2. The

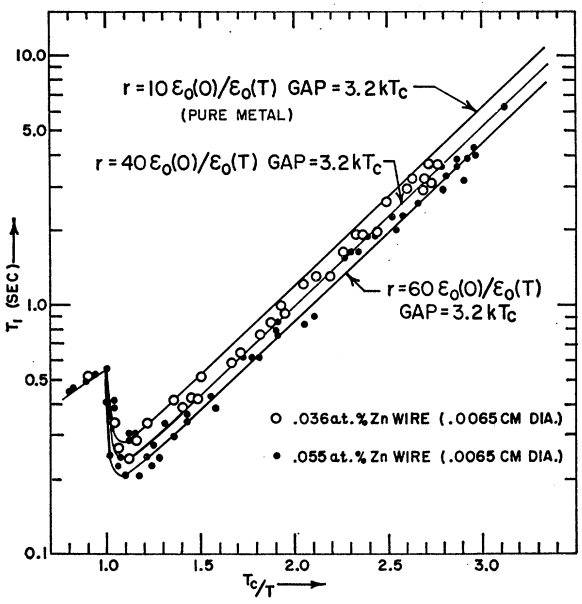

FIG. 1. Measured values of T_1 in Al-Zn alloys. T_c was taken to be 1.178°K. The solid lines are calculated using the BCS density of states smeared over a range of 1/10, 1/40, and 1/60 of the energy gap at $T=0$, assuming a smearing proportional to the energy gap. Data taken on a pure sample (not shown; see reference 5) are in good agreement with the curve for $r=10\epsilon_0(0)/\epsilon_0(T)$.

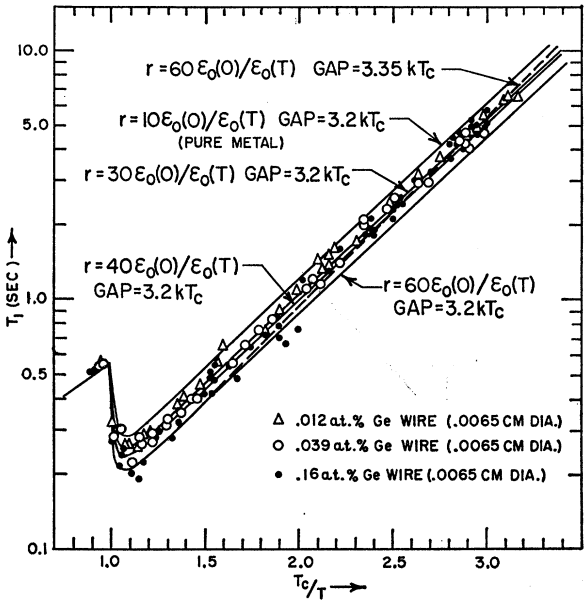

FIG. 2. Measured values of T_1 in Al-Ge alloys assuming $T_c=1.178$°K. The theoretical curves are calculated as in Fig. 1. The dashed line is calculated using an energy gap of $3.35kT_c$.

data for 0.012 at. % Ge alloy show that $r=30\epsilon_0(0)/\epsilon_0(T)$ and $2\epsilon_0(0)=3.2kT_c$. The data for 0.039 at. % and 0.16 at. % Ge alloys, are both quite close to the line $r=40\epsilon_0(0)/\epsilon_0(T)$ and $2\epsilon_0(0)=3.2kT_c$, but in the high-temperature region there is a tendency to follow the line of $r=60\epsilon_0(0)/\epsilon_0(T)$ and $2\epsilon_0(0)=3.35kT_c$ (dashed line). If this is so, then the experimental data are close to the value of $3.5kT_c$ as predicted by BCS for the case of constant interaction. As can be seen from these figures, the parameter r can be estimated to an accuracy of $\pm 20\%$ or better.

Fig. 3 shows the relation between r and ΔT_c^*, where ΔT_c^* is the corrected change in the critical temperature relative to ideally pure aluminum, which was measured by Chanin, Lynton, and Serin.[9] Except for the 0.16 at. % Ge alloy, we can see that the change in r is roughly proportional to the ΔT_c^*.

As we add impurities, the individual momentum states are scattered around the Fermi surface. Therefore, the angular dependence of the energy gap is removed from the individual excitation energy gap. If Δ represents an anisotropy of the energy gap present in pure aluminum, Δ decreases (or r increases) as the impurity concentration increases. For sufficiently small concentrations of impurities, the experimental data indicate that r increases linearly with increasing reciprocal mean free path. This apparent linear increase of r with l^{-1} may be fortuitous, since the accuracy of our determination of r is poor. One expects r^{-1}, not r, to be the significant quantity, since r^{-1} is presumably a measure of the anisotropy.

The data on 0.16 at. % Ge alloy indicate that the

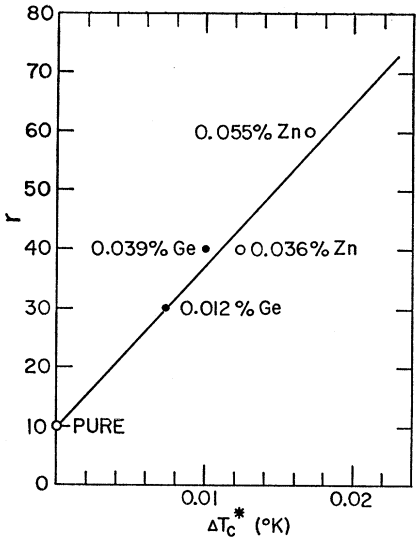

FIG. 3. Relation between r and ΔT_c^*, where ΔT_c^* is the corrected change in the critical temperature relative to ideally pure aluminum, which was taken from reference 9.

energy gap width will be close to the value predicted by the BCS theory in the case of constant interaction. Once the mixing is complete, the effect on superconductivity should saturate. If we could measure T_1 in very impure samples without quadrupolar effects, the saturation value of r might be observed. But, as T_1 is proportional to $\log r$ for $T \ll T_c$, it should be hard to determine r correctly.

It is perhaps interesting to note that there is a correlation between our values of r^{-1} and the ΔT_c^* observed by Chanin, Lynton and Serin.[9,11] Within the rather large experimental error the following empirical expression holds:

$$\Delta T_c^*/T_c = \pm 0.002\xi/l + 0.12r^{-1} - 0.012. \quad (4)$$

Here ξ is the coherence length. The minus sign applies to electropositive impurities and the plus sign to electronegative impurities. The second term of (4) might be regarded as the contribution of anisotropy to T_c, although this interpretation is questionable in view of the high-concentration data of reference 10, where the anisotropy may become unimportant.

Recently, Yaqub[12] measured the electronic specific heat in the superconducting state of pure tin and tin-indium alloys of 1 and 2% concentrations. His data did not give any direct confirmation on the existence of anisotropy of the energy gap, but they showed that the exponential law derived by BCS should be obeyed by alloys more exactly than by pure metals, according to the same reason which was stated above in our case. Infrared evidence supporting our interpretation of these data has recently been reported by Richards.[13]

We believe that our experiments on T_1 in aluminum alloys, together with T_c, specific heat, and infrared measurements on impure superconductors provide experimental confirmation of the theory of dirty superconductors.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Professor B. Serin who supplied ingots of the aluminum alloys. He also wishes to thank Dr. A. G. Redfield for the use of his equipment and for many stimulating discussions. He has had useful discussions with Dr. P. W. Anderson and Dr. C. P. Slichter. Finally, he would like to thank many members of the IBM Watson Laboratory for their kind help and hospitality.

[11] See also B. Serin, reference 7, p. 194.

[12] M. Yaqub, Cryogenics **1**, 166 (1961).

[13] P. L. Richards, Phys. Rev. Letters **7**, 412 (1961).