Size Effect of Nuclear Spin Relaxation Time in Superconducting Aluminum

YOSHIKA MASUDA* AND A. G. REDFIELD
IBM Watson Laboratory, Columbia University, New York, New York
(Received 2 October 1963)

Particles of aluminum having diameters less than 2000 Å were produced by evaporation in an argon atmosphere. The nuclear spin relaxation time was measured for three such samples in the normal and superconducting states between 0.36° and 1.3°K, for applied fields up to 400 G. In the normal state, and near T_c, the relaxation time is nearly the same as for bulk aluminum. Well below T_c the zero-field relaxation time is shorter than that of bulk aluminum, being less than one-fifth the bulk value at 0.4°K for two of the samples studied. At low temperatures there is also a field dependence which is characteristic of the superconducting state; T_1 increases with increasing field. At all fields, and low temperatures, the slope of a plot of $\ln T_1$ versus T_c/T indicates a gap considerably smaller than the bulk value, but the limited temperature range covered makes such conclusions dubious.

INTRODUCTION

MEASUREMENTS of the Knight shift in superconductors must, of necessity, be made on samples small compared to the penetration depth in order that variations in the Knight shift will not be confused with the shift due to the Meissner effect. The Knight shift is found to persist in the superconducting state, contrary to expectations based on a simple energy-gap model.[1] In contrast to the Knight shift, measurements of the nuclear spin relaxation time T_1 are in good agreement with the BCS theory; these measurements have been made on "bulk" samples, that is, powders large compared to the coherence length.[2–5] In view of the disagreement of the Knight-shift measurements with the BCS theory we felt that it would be interesting to see if there is an anomaly in the relaxation time as well, when the particle size becomes small compared to the coherence length or the penetration depth.

An important size dependence of T_1 was found, but we have been unable to explain these results in a satisfactory way. Therefore, we are publishing our data now, despite its incompleteness, in the hope that further theoretical work will be stimulated.

EXPERIMENTAL DETAILS

The relaxation time was measured by the field-cycling method; the apparatus has been described previously.[3–6] Provision was made to measure T_1 at several magnetic field values.

Three samples were prepared by vaporizing aluminum in an atmosphere of argon at a pressure of a few torr. This vaporization is done in an ordinary evaporator, and the vapor particles, which appear as grey smoke issuing from the evaporator boat, deposit on the wall of the evaporator from which they can subsequently be brushed and collected.

The first sample used (sample I) was supplied by T. R. Carver and R. Berry, who also were the first to tell us about this technique of sample preparation and who gave us much useful information.

Samples II and III were prepared in this laboratory in a special evaporator whose bell jar was replaced by a horizontal 10-in.-diam glass tube closed at the end with a metal plate and O-ring seal. The evaporation boat could be translated horizontally within the glass tube, so that the wall of the tube could be coated uniformly with a monolayer of particles. Several such evaporations were made in order to produce a single 25-mg sample of aluminum. A brush which could be manipulated from outside the vacuum chamber was used to remove the particles from the surface between evaporations, without opening the vacuum chamber. No extraordinary precautions were taken to purify the argon in the bell jar, because trace impurities[4] do not seem to effect T_1, and because we hoped that formation of an oxide surface layer would retard coagulation of the particles. A number of test samples were made under various conditions to try to control the particle size, and electron micrographs were made of the collected powders and also of particles deposited on a collodion film which was exposed inside the vacuum chamber during a single evaporation. No very consistent results were obtained, mostly because evaporations had to be done rapidly and nonreproducibly in order to retard mechanical deterioration of the tantalum boat used to heat the aluminum. In general it seems that larger particles are produced at higher argon pressures.

Electron micrographs of the samples are shown in Fig. 1, and it will be seen that they are not uniform. Samples I and II are composed of particles up to about 1000 Å in diameter. Sample III contains many aggregates of small-diameter (≃200 Å) particles, but prob-

* Present address: Physics Department, Kobe University, Mikage, Kobe, Japan.

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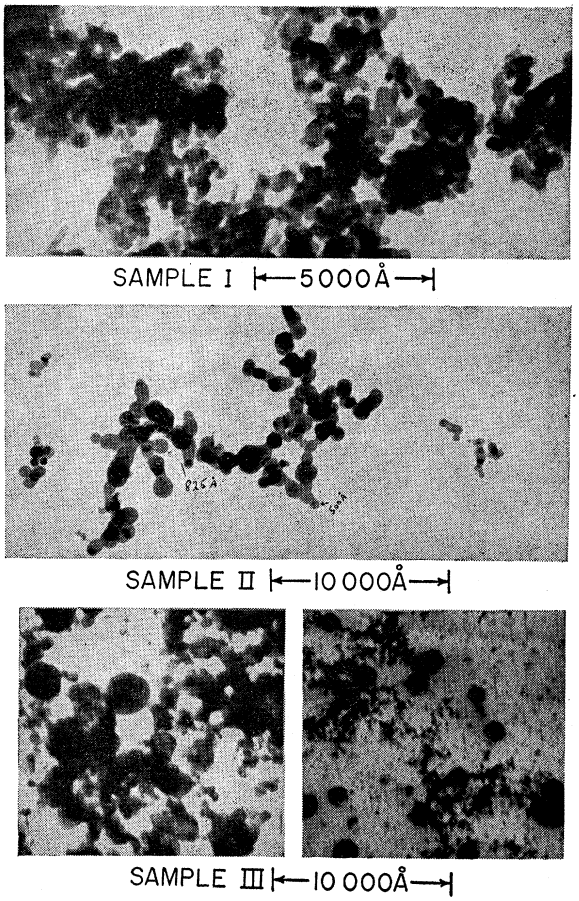

FIG. 1. Electron microscope pictures of samples used. All pictures are of powder obtained by brushing the sample from the walls of the evaporator except the right-hand picture of sample III, which was obtained by deposition, during a single evaporation, of particles on a colodion film suspended inside the evaporator.

ably most of the nuclear resonance signal comes from the few large (≃2000 Å) particles.

It is not *a priori* obvious that samples produced in this way will be metallic; it is conceivable that they immediately oxidize on exposure to air. Evidence that our samples are metallic is entirely internal: In the normal state T_1 and the linewidth are nearly the same as in bulk aluminum. Also, a marked change is observed in T_1 at a temperature within 2% of the bulk superconducting transition temperature.

EXPERIMENTAL DATA AND DISCUSSION

Data taken on the three samples are shown in Figs. 2 and 3. The field dependence of T_1 in sample II was studied extensively, and a few measurements of the field dependence for sample III were also made.

The relatively small change in T_1 in the normal state, compared to the bulk samples, may be the result of imperfection-induced quadrupole interaction. However, such a change was not observed when small amounts of impurities were added to bulk samples,[4,7] so the change may be a true size effect. Kubo[8] has discussed the specific heat and spin susceptibility of small particles, but probably his conclusions do not apply to particles as large as those we used. It is interesting to note that the electronic-level spacing in our particles is large compared to $\hbar/T_1$, in violation of the condition for the validity of time-dependent perturbation theory. This difficulty can probably be removed if it is realized that the electronic levels are broadened by interaction with lattice vibrations, and that the system, electrons plus lattice, has a much higher density of states than the electrons alone.

Turning to the superconducting state, the zero-field measurements on samples I and II can be fitted to a theoretical curve which is derived from Hebel's[9] calculation of T_1 based on the BCS theory. By a suitable change in temperature scale the theory can be adapted to an energy gap different from the BCS value of $3.5kT_c$, and in order to obtain agreement with experiment it is also necessary to smear the BCS density of states by an amount r^{-1} times the energy gap, where r is about 10. These procedures are discussed elsewhere,[4,7] and r^{-1} is generally assumed to be of the order of magnitude of the fractional gap anisotropy. For comparison we have shown the theoretical curve which best agrees with our previously published data on "bulk" aluminum[3] (10^{-3} cm), corresponding to a gap of $3.2kT_c$ and $r=10$ well below the critical temperature.

As in the bulk metal the data for samples I and II approach a straight line when plotted semilogarithmically in Figs. 2 and 3. The slope of the line is expected

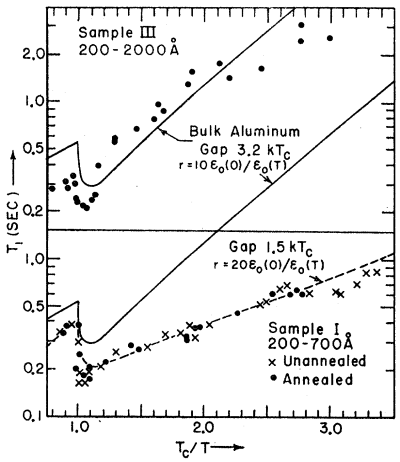

FIG. 2. Measured relaxiation times for samples I and III, together with theoretical relaxation-time curves appropriate to various energy-gap anisotropy parameters. The solid curve is in good agreement with measurements on bulk aluminum (Ref. 3). In sample III, nonexponential decays were observed, and the data plotted are the longest observed time constants.

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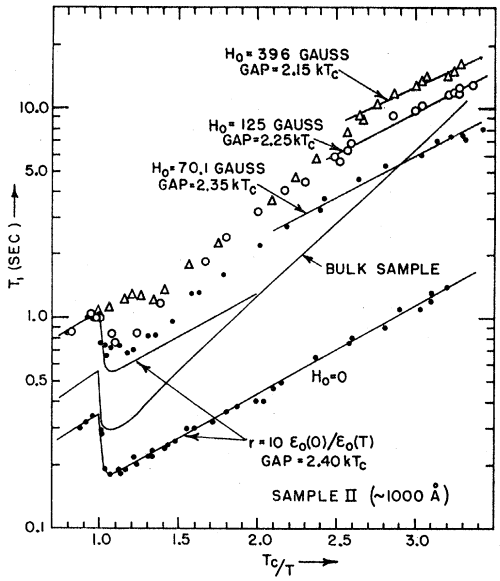

FIG. 3. Measurements on sample II for various applied dc fields, together with theoretical curves which best fit the data, and the curve which fits the bulk data of Ref. 3.

to be proportional to the energy gap, more or less independent of the theoretical model used, provided that a well-defined gap exists. Our data indicate a gap of the order of one-half the BCS value for samples I and II. Obviously, such a conclusion should be accepted cautiously since only a limited temperature range was covered, and experiments on thin films indicate no such strong size dependence of the gap. The small apparent gap in our samples is consistent with thin-film measurements only if it is assumed that three-dimensional smallness affects superconductivity more strongly than one-dimensional smallness.

The field dependence of T_1 in sample II was studied extensively. In order to interpret these data, the reader must realize that there occurs a field dependence in T_1 for the normal state in the region below about 50 G, where the external field nuclear Zeeman interaction becomes comparable to the magnetic field interaction between neighboring nuclear spins or to quadrupole interactions with lattice imperfections.[2,6] It will be seen from Fig. 3 that in the normal state above 70 G, T_1 is field-independent and is about three times its value at zero field.

At the lowest temperature attained, the entire sample is presumably superconducting, even at 400 G, and there is an additional field dependence above 70 G, which may be caused by some perturbation of the superconducting state by the field.

The temperature dependence of T_1 for sample III (Fig. 2) appears anomalous; there is a region around $T_c/T=1.5$ where T_1 is actually longer than in bulk samples. This behavior may be associated with the larger size of sample III, but we believe that it may be a result of flux trapped either by imperfections or coagulated closed chains of small particles which can be seen in Fig. 1. This hypothesis is supported by the fact that in this temperature region the decay of the signal with time (in zero field) is not exponential, as if the applied field (and thus T_1) were not homogenous. In Fig. 2 we have plotted the longest time constant of the decay, which would be characteristic of the highest field regions of the sample. Sample III may be more susceptible to flux trapping than the other two samples studied because of the existence in it of filamentary aggregates, and because it was used much sooner (one day) after being made than the other two samples.

To further test this flux-trapping hypothesis, we studied the field dependence of T_1 at three temperatures (Fig. 4). The field dependence of the longest time constant between 0 and 20 G is much stronger in the normal state than at 0.73°K. In this field range the field dependence is expected to be the same for both normal and superconducting states since it is determined by the internal magnetic and electric fields seen by the nuclei. Thus it appears that at 0.73°K the field applied to the nuclei is not zero when the external field is zero, consistent with these ideas and with the measurements on sample II if it is assumed that the flux-trapping rings can maintain only a certain critical current such that the field in the sample is about 50 G greater than the applied field.

CONCLUSION

Because of the limited number of samples studied and the range of sizes present it is not advisable to draw detailed conclusions from these data. However, it seems nearly certain that the size dependence and field dependence well below T_c are real effects. It is much less certain whether one is justified in using the BCS theory to interpret these results.

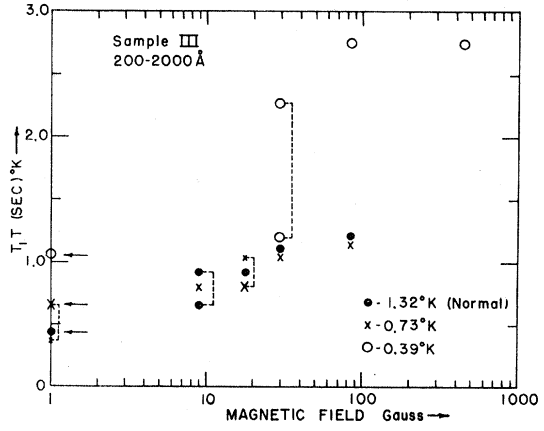

Fig. 4. Field dependence of T_1T in sample III. Nonexponential decays are denoted by two points connected by dashed lines; the two points give the limits of experimentally resolved time constants, and the dominant time constant, if any, is the larger of the two points. The arrows indicate points also plotted in Fig. 2.

We believe that this size effect is not due merely to a limiting of the electron mean free path by imperfections or the surface. One of us[4] has shown experimentally that T_1 is relatively insensitive to quantities of impurities sufficient to shorten the mean free path to a value comparable to particle diameters used in the present experiment. These experiments on impure superconductors also tend to rule out the possibility that we are observing a spin diffusion limited flow of energy to nuclei having a large quadrupolar specific heat as a result of lattice imperfections.[9]

It would obviously be interesting to study other properties of these small particles.

ACKNOWLEDGMENTS

We wish to thank R. Berry and T. R. Carver for providing sample I, E. Powell and W. Fite for making samples II and III, R. Gazinelli and W. Kiselewski for help in the experiment, and C. F. Aliotta and D. Camron for making electron microscope pictures of the samples. Several conversations with C. P. Slichter were helpful.

PHYSICAL REVIEW VOLUME 133, NUMBER 4A 17 FEBRUARY 1964

Inelastic Electron-Atom Collisions under Near-Resonance Conditions: Analysis of Transitions Involving Strong Coupling*

NEAL F. LANE† AND CHUN C. LIN‡
Department of Physics, University of Oklahoma, Norman, Oklahoma
(Received 3 September 1963)

A method has been devised to calculate the cross sections of inelastic electron-atom collisions under near-resonance conditions. This method (referred to as the method of resonance distortion) consists of solving the limiting exact-resonance problem as the zeroth-order approximation and using this solution to obtain the first-order solution by an iteration procedure, and is particularly suitable for treating optically allowed transitions produced by electron impact where the coupling between the initial and final states is strong and of long-range type. Application of this method has been made to a schematic model with an isotropic inverse-square interaction potential and to the problem of electron-atom collisions with $ns \rightarrow np$ transition. The general results indicate that (i) for weak coupling the collision strengths calculated by the resonance-distortion scheme reduce to those calculated by the method of distorted waves, (ii) the resonance-distortion method and Seaton's B'II method give nearly equal partial cross sections for large l, and (iii) at very low l, the B'II partial cross sections are substantially larger than those determined from the resonance-distortion method. The total cross sections for the $3s \rightarrow 3p$ transition in Na have been calculated by the resonance-distortion method for various incident electron energies, and the results show better agreement with experiment than do those of the Born approximation and of Seaton's version of the modified Born approximation.

I. INTRODUCTION

In the treatment of the inelastic collisions between electrons and atoms, the Born approximation, which consists of using the wave function of a free particle to obtain the first-order solution of the Schrödinger equation, is quite extensively employed.[1,2] However, when there exists a strong coupling between the initial and the final states of the atomic system, the Born approximation generally yields poor results.[3–7] The reasons for the failure of the usual Born approximation have been discussed by Seaton and modifications of the approximate method have been proposed.[4–7] The problem of the calculation of inelastic collision cross sections becomes more complicated when the change of energy in the atom is rather small (near resonance), because in such cases the expansion of the total cross section in terms of the phase shifts of the partial waves do not always converge rapidly and accurate calculations of more partial-wave cross sections are needed. In this paper we shall present a method for the calculation of cross sections for inelastic collisions under near-resonance conditions. In essence this is an iteration procedure in which we use the solution of the exact resonance problem as the zeroth-order approximation.

Consider an electron with linear momentum $\hbar\mathbf{k}_0$ colliding with an atom which was initially in the state characterized by ψ_0 and E_0. We shall denote the coordinates of the colliding electron by $\mathbf{r}$, those of the atomic electrons by $\mathbf{r}'$ and the potential energy between the electron and the atom by $V(\mathbf{r},\mathbf{r}')$. If the wave func-

* Supported by the U. S. Air Force Office of Scientific Research.
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