accuracy of the T_1 measurements still leaves room for a possible 10% increase in relaxation rate in the superconductor just below the transition. Furthermore, the relaxation may be affected by impurities, and, since the relaxation measurements were taken some time after the samples were made we are less certain of the significance of the measurements. A smearing of the energy gap might account for the results.

ACKNOWLEDGMENTS

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Nuclear Magnetic Resonance and Relaxation in Superconducting Aluminum

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I. INTRODUCTION

There have been a number of theories[1–8] concerning the change in the Knight shift in a superconductor. In particular, they are concerned with attempting to understand why it is that, in the reported measurements to date,[9–11] the shift does not decrease to zero at $T = 0°K$, as has been predicted by the BCS theory.[1] A feature of two of these theories[4,5] is the strength of the spin-orbit coupling. Aluminum is the superconducting metal with the smallest atomic weight, and thus, it is expected to have a smaller spin-orbit coupling than other superconductors. A feature of another theory[3] is the size of the sample. Aluminum is a convenient metal in this regard because of its strong NMR signal and because of its large coherent length it is possible to study the NMR in a wide range of film thickness. Finally aluminum has no d electrons, and we can assume that the paramagnetic susceptibility is entirely due to conduction electrons.

We have recently started some measurements of the Knight shift, nuclear spin–lattice relaxation rate, and resistivity in thin films of aluminum. The preliminary results on one sample are presented here.

II. RESULTS

In Fig. 1 is shown the change of the Knight shift of aluminum in the transition, plotted as the ratio of the NMR shift in normal and superconducting states. These measurements were made at a magnetic field of 3.8 kG. The critical temperature for this field is apparently 0.82°K as judged from the change in Knight shift, and also as judged by the temperature for which the resistance of one film is reduced by $\frac{1}{2}$. The dashed curve is the theoretical result of Yosida[1] based on the BCS theory. Shown also are the apparent values of the Knight shift in other metals at $T = 0°K$. Our result is that the amount of the Knight shift for aluminum at $T = 0°K$ is about 75%, as compared to 100% for vanadium,[11] 75% for tin,[10] and 65% for mercury.[9]

An important consideration is: are the results characteristic of a thin film in the superconducting state, or, is part of the sample actually normal. The rest of the paper is concerned with this question.

III. MEASUREMENTS

Sample

The sample was made by the evaporation of one layer of aluminum onto large sheets of Mylar. The estimated thickness of the aluminum was 200 Å. The calculated and measured critical field of 7 kG at

[1] K. Yosida, Phys. Rev. **110**, 769 (1958).
[2] P. C. Martin and L. P. Kadanoff, Phys. Rev. Letters **3**, 322 (1959).
[3] J. R. Schrieffer, Phys. Rev. Letters **3**, 323 (1959).
[4] P. W. Anderson, Phys. Rev. Letters **3**, 325 (1959).
[5] R. D. Ferrell, Phys. Rev. Letters **3**, 262 (1959).
[6] A. B. Pippard and V. Heine, Phil. Mag. **3**, 1046 (1958).
[7] L. N. Cooper, Phys. Rev. Letters **8**, 367 (1961).
[8] J. C. Fisher, Australian J. Phys. **13**, 446 (1960).
[9] F. Reif, Phys. Rev. **106**, 208 (1957).
[10] C. M. Androes and W. D. Knight, Phys. Rev. **121**, 779 (1961).
[11] R. J. Noer and W. D. Knight, Bull. Am. Phys. Soc. **2**, 122 (1961).

$T = 0$°K agreed with this, as did the integrated NMR intensity. The sheets of Mylar were cut up and stacked, attempting to keep the sheets as parallel as possible. Copper foil was inserted at intervals, extending past the ends of the aluminum sample in order that thermal contact could be made with other interleaved copper foils that were, in turn, soldered to the liquid He^3 container. He^3 gas helped maintain thermal equilibrium between the layers of the sample. The copper served another important function: Since the difference in NMR frequencies between aluminum and copper is only approximately 74 kc/sec at the field used (3.8 kG), it was possible

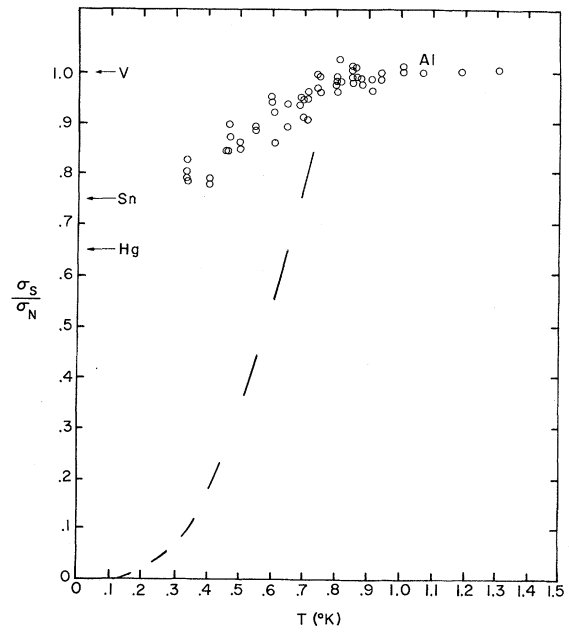

FIG. 1. Ratio of NMR shift in normal and superconducting states versus temperature. Aluminum 200 Å film data taken at 3.8 kG. The results of other measurements at 0°K are indicated by the arrows. The dashed curve is a theoretical result of Yosida, assuming the NMR shift is proportional to spin susceptibility.

to measure the aluminum NMR with respect to the copper by sweeping the spectrometer through both lines. The only requirement on the stability of the magnetic field is that it does not change during this sweep. This was monitored by an external proton resonance. Furthermore, any problem of the diamagnetic shielding of the aluminum sample from the magnetic field due to large superconducting regions is removed since the copper NMR is measured in the same field. Incidentally, the copper resonance did not change below the aluminum transition.

NMR Line

The aluminum NMR line in the normal state showed some first-order quadrupole broadening, probably due to strains at the film surface. The line shape did not change in the superconducting transition, that is, the width measured between the peaks of the derivative did not change more than 5%. The amplitude of the derivative peaks were equal at all times to 5%. These observations are good evidence that the whole sample was superconducting with the same change in the Knight shift throughout the sample.

Relaxation Time

Previous measurements of the nuclear spin-lattice relaxation time T_1 in aluminum,[12] gallium,[13] and cadmium[14] showed an enhancement in the rate $(1/T_1)$ just below T_c, followed by a rapid decrease at lower temperatures. In order to demonstrate that our sample was indeed superconducting we attempted to measure T_1 in our sample. The first indication that $1/T_1$ does increase below T_c came from comparing the heights of the aluminum and copper resonance

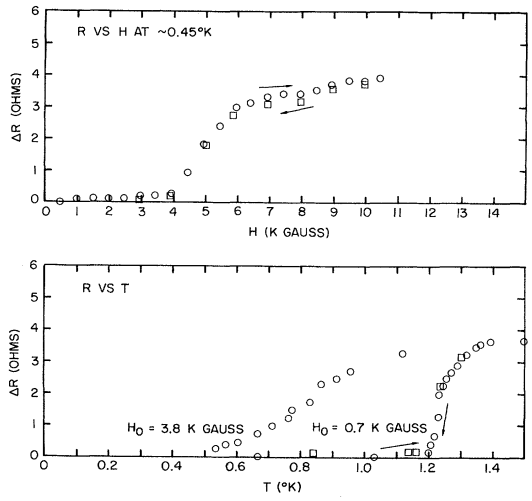

FIG. 2. Resistance measurements of one film in center of sample. Critical temperature at $H_0 = 0$ was ~1.3°K, and $H_c(0) \sim 7$ kG.

obtained in the measurements of the Knight shift. Because the spectrometer power was sufficient to slightly saturate the aluminum resonance (and, to a less extent, the copper), a plot of the amplitude ratio versus temperature compares the values of T_1 at each

[12] Y. Masuda and A. G. Redfield, Phys. Rev. **125**, 159 (1962).
[13] R. H. Hammond and W. D. Knight, Phys. Rev. **120**, 769 (1960).
[14] Y. Masuda, IBM J. Res. Develop. **6**, 24 (1962).

temperature. This plot showed that the aluminum relaxation rate did increase suddenly below T_c, followed by a decrease at lower temperatures. In order to substantiate this quantitatively measurements of the relaxation rate were made, first using continuous wave saturation methods, and recently using a coherent pulsed nuclear induction spectrometer. These measurements have not yet been very successful in terms of the quality of the data, but we can say that there is an enhancement of the rate of about 30% just below T_c. This is less than the 100% enhancement found for pure bulk aluminum[12] and the 80% found for gallium.[13] Our result could be explained by quasi-particle level broadening or by an energy gap anisotropy. Thus a 14% broadening or anisotropy reduces the enhancement to 20%. Another possibility is that the energy gap itself is considerably reduced in these samples. Tunneling measurements would help answer this.

Resistance Measurements

One of the films was picked at random and put in the center of the stack with leads so that the resistance could be measured. The measuring current was low, and no effect on the measurements were seen with changes in the current. Figure 2 shows these results. The gradual change in R at large magnetic fields is perhaps the effect of fluxoids due to a perpendicular component of the field, as discussed by Tinkham.[15]

IV. DISCUSSION

The resistivity measurements indicate that the sample possibly was in some sort of mixed state, perhaps with fluxoids and a spatial varying energy gap. The NMR line shape did not change below T_c, and thus the distance in which the electron paramagnetic susceptibility changes must be less than the mean free path. If a mixed state is present in quantity then the domain size must be less than the mean free path, which is of the order of the coherence length and the film thickness.

In conclusion, the change in Knight shift observed is believed to be that for all the sample, but the influence of a mixed state with a spatially varying energy gap may be important.

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[15] M. Tinkham, Phys. Rev. 129, 2413 (1963).

HIGH FREQUENCY ABSORPTION

CHAIRMAN: *A. B. Pippard*

Surface Impedance of Superconductors

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1. INTRODUCTION

This paper is not concerned with the most recent measurements of the surface impedance of superconductors, but with the type of experiment fashionable ten years ago, measurements at a few kMc/sec or less on superconductors near the weak coupling limit, such as tin. There is a great range of such measurements, and at frequencies well below the gap frequency ($\omega \ll \epsilon_0/\hbar$) they are well described by the microscopic theory of surface impedance developed by Mattis and Bardeen (1958) and by Abrikosov *et al.* (1958). Our purpose is to look back at the small discrepancies between theory and experiment which exist and to try to discover their significance. In doing so, we shall use a number of the special limits of the theory, which are often more easily understood and applied than the general formulation. We give