Nuclear Spin-Lattice Relaxation in Superconducting Aluminum

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The nuclear spin-lattice relaxation time of superconducting aluminum has been measured from 0.35°K to the critical temperature. The method used was that of Hebel and Slichter; low temperatures were attained through the use of a helium-three cryostat. The estimated energy gap is $3.2\ kT_c$, in agreement with microwave measurements. The data are in good agreement with the predictions of Hebel and Slichter based on the Bardeen, Cooper, and Schrieffer theory of superconductivity. The data indicate a smearing or width of the BCS energy levels which decreases with increasing temperature and is approximately 1/10 of the energy gap at all temperatures.

I. INTRODUCTION

THE nuclear spin relaxation time (T_1) in superconducting aluminum was first measured by Hebel and Slichter.[1] It was obvious that the nuclear T_1 would be worth knowing, but these measurements were even more interesting than had been anticipated, because taken together with a measurement by Reif of T_1 in mercury[1] they were in striking conflict with any two-fluid model of superconductivity, but could be easily explained using a simple energy-gap model.

Hebel and Slichter also calculated[1,2] the relaxation time predicted by the Bardeen, Cooper, and Schrieffer (BCS) theory of superconductivity,[3] and found that their experimental T_1 data were consistent with the BCS theory. In fact, the T_1 measurement together with acoustic absorption measurements[4] provide some confirmation of the choice of spin pairing of the BCS wave functions.[3] The agreement of the nuclear relaxation time with theory is in contrast with the behavior of Knight shift,[5] which remains finite in superconductors at absolute zero, a result which is difficult to explain in any simple way.[6]

In this paper we describe measurements of T_1 of greater accuracy, and over a wider temperature range, than those of Hebel and Slichter. We use the same method, that is, the sample is soaked in a large field (4000 gauss) for a time long compared to T_1, to polarize the nuclei; the field is then reduced to zero in a time short compared to T_1, and left at zero field for a variable time τ. The field is then turned on again (to 1000 gauss) and the nuclear resonance signal is observed in the normal state in a time short compared to T_1, to see how much the spins depolarized when the field was zero and the sample was superconducting. We refer the reader to the article of Hebel and Slichter for an excellent and clear analysis of this procedure, and also to an article by Anderson and one of us[7] for a further discussion of this type of measurement as applied to normal metals.

II. EXPERIMENTAL DETAILS

Much of the apparatus used in these measurements was the same as that described in reference 7, and we describe only these parts which were different. An earlier version of the apparatus using adiabatic demagnetization has been described elsewhere.[8]

To attain the low temperatures needed a He^3 cryostat was used, as shown in Fig. 1. The system used was

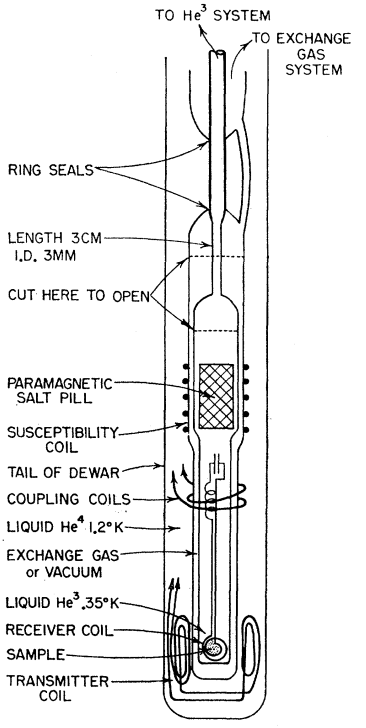

FIG. 1. Schematic drawing of the He^3 cryostat. The thermal link between the salt pill and the sample is discussed in the text.

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

[2] L. C. Hebel, Phys. Rev. **116**, 79 (1959).

[3] J. Bardeen, L. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[4] H. V. Bohm and R. Morse, Phys. Rev. **108**, 1094 (1957).

[5] F. Reif, Phys. Rev. **106**, 208 (1957); G. M. Androes and W. D. Knight, Phys. Rev. Letters **2**, 386 (1959).

[6] R. A. Ferrell, Phys. Rev. Letters **3**, 262 (1959); P. L. Martin and L. P. Kadanoff, *ibid.* **3**, 322 (1959); J. R. Schrieffer, *ibid.* **3**, 323 (1959); P. W. Anderson, *ibid.* **3**, 325 (1959).

[7] A. G. Anderson and A. G. Redfield, Phys. Rev. **116**, 583 (1959).

[8] A. G. Redfield, Proceedings of the IXth International Congress of Refrigeration (Delft, 1958), Supplement au Bulletin de l'Institute International du Froid, 1958.

similar to that described by Keesom and Seidel.[9] The concentric glass tubes at the top of Fig. 1 were connected at room temperature to suitable valves and vacuum connections by means of concentric O-ring joints. The exchange gas space was connected to a small diffusion pump and He^4 exchange gas system. Exchange gas pressures of a few microns were used. The He^3 pumping tube was connected to a movable He^3 handling and pumping system which consisted of a Welch 1400 pump (capacity 21 liters/min) immersed in oil, and a number of valves and Bourdon gauges. The shaft seal on the pump was changed to a graphite seal which was supplied by the manufacturer. No diffusion pump was used and the lowest temperature attained was 0.35°K. The system contained 400 cc of gaseous He^3; this was sufficient for over one hour of running time.

The cryostat in Fig. 1 was made of glass to permit the rf field to penetrate from the He^4 to the He^3 space, so that the transmitter coil could be located in the He^4 bath. In this way the heat dissipation in the He^3 could be reduced considerably. The sample was changed by cutting the glass at the two points indicated, and later resealing; this procedure was more satisfactory than the ground glass seals and special stopcock grease which we used on an earlier apparatus.[8] The ring seal system was needed to insure that the He^3 tube was not above the temperature of the He^4 bath close to the He^3 space. A third concentric stainless steel tube (not shown) 3 mm in diameter was inserted inside the He^3 pumping line and extended from the top of the cryostat down to almost the top of the ring seal system. It was connected via a valve to an oil manometer, to measure the vapor pressure of the He^3 liquid. This tube, plus some other rudimentary shields, served to reduce thermal radiation coming down the He^3 pumping tube. Radiation from outside the He^3 cryostat was reduced by covering it with glass tape and painting the glass tape black with colloidal graphite paint, except where the rf field had to penetrate the glass. The He^4 Dewar also contained some radiation baffles. It was found advantageous to have the inner tube of the He^3 cryostat somewhat askew, so that it touched the outer wall at the bottom, reducing vibration and thus reducing microphonics and vibrational heating. The thermal conduction across such a "thermal short" is negligible between 0.35 and 1.2°K.

In this experiment the sample must be immersed in He^3; otherwise there is a possibility that it will heat due to the magnetocaloric effect[10] when the field is turned off. If the sample is in liquid He^3 its large surface to volume ratio, and the high specific heat of He^3, will assure that the sample temperature rises negligibly. The sample coil thus had to be at the very bottom of the cryostat, and it was estimated that less than 0.2 cc of liquid He^3 would suffice to cover it. The amount of He^3 remaining in the cryostat could be deduced by reading the pressure gauges in the gas handling system, and it was always kept at more than 0.2 cc.

Temperatures above 0.8°K were deduced from vapor pressure measurements of the He^4 and He^3, using the He^3 temperature scale of Sydoriak and Roberts.[11] Below 0.8°K the susceptibiltly of a salt pill was measured, using a crude susceptibility bridge similar to that of Nicol.[12] The salt pill was a solid single crystal of iron ammonium alum grown from a supersaturated solution around a number of gold wires. These wires extended a few cm below the pill, and were close to a copper strap, to which they theoretically made thermal contact via He^3 gas convection. The copper strap was soldered to a number of insulated silver wires which extended into the He^3 bath next to the sample. The wires, sample, and He^3 bath were thus supposedly at a uniform temperature because of horizontal conduction (via convection) in the He^3 bath, and vertical conduction down the wires. The salt pill was of the form of a cylinder 1.2 cm in diameter and 5 cm long, somewhat irregular at the edges owing to the ravages of several years' use. It was calibrated during every run above 0.8°K, and was assumed to obey Curie's law down to 0.35°K. At the lowest temperatures a small demagnetizing correction was made, using a demagnetizing factor[13] appropriate to a 4:1 ellipsoid. The temperature could also be checked to within about 2% by observing the size of the nuclear signal. Although the technique used to infer the temperature below 0.8°K is not the most elegant possible, we feel that any errors thus introduced are negligible considering the scatter in the nuclear relaxation time data.

The nuclear resonance signal in this experiment is very much smaller than that observed above superconducting transition temperature because, as discussed by Hebel and Slichter, the nuclei are partially irreversably demagnetized by the sudden change of magnetic field to which they are subjected when the transition takes place between the normal and superconducting states. For the sample used in most of our measurements, the signal was reduced to less than 5% of the value it would have in a similar nonsuperconductor after the same sequence of field cycling. Therefore, considerable effort was spent in optimizing the signal-to-noise ratio. The resonance was detected with a crossed-coil bridge. The silver receiver coil was cast in araldite and the powdered sample was placed directly inside the coil without any container, to have a good filling factor. The transmitter coil was also cast in araldite, and was supported from above in the He^4 bath separately from the He^3 cryostat, so that the He^3 cryostat assembly could be rotated about a vertical axis relative to the transmitter coil for an optimum rf balance. Despite the lack of rigidity which resulted from this feature, it seemed to be advantageous for reducing

[9] P. H. Keesom and G. Seidel, Rev. Sci. Instr. **29**, 606 (1959).
[10] D. Shoenberg, *Superconductivity* (Cambridge University Press, New York, 1952).
[11] S. G. Sydoriak and T. R. Roberts, Phys. Rev. **106**, 175 (1957).
[12] J. Nicol, Rev. Sci. Instr. **31**, 211 (1960).
[13] J. A. Osborn, Phys. Rev. **67**, 351 (1945).

microphonics, and it also minimized the power dissipated in the receiver coil. The receiver coil was connected in a closed circuit tuned to the operating frequency (1160 kc/sec) and critically coupled by a coupling coil to another coil in the He^4 bath which was also resonated at 1160 kc/sec and connected to the input grid of a tuned radio frequency amplifier. In theory this coupling arrangement reduces the signal-to-noise ratio, but in fact there was little reduction because much of the noise was microphonic noise generated in the crossed coil, which was attenuated by the coupling as much as was the signal. The tuned radio-frequency receiver was connected to a phase-sensitive rf detector, whose phase reference was derived from the transmitter output through a variable phase shifter. The phase was adjusted to observe the dispersion mode, and the observed signal was a nonadiabatic rapid passage as discussed in reference 7. The rf field was about one gauss, and to avoid excessive heating it was turned on only as long as needed, about $\frac{1}{2}$ sec per observation.

The signal was also increased through the use of a more powerful magnet than that used in reference 7 which could operate stably up to fields of 4000 gauss. It was a small oil-cooled cylindrical magnet with an iron shell. Two different power supplies were used, one for polarization and the other for resonance. The polarization supply was a simple poorly filtered supply which was manually regulated. The resonance supply was less powerful, producing 1000 gauss, and was a transistorized supply made by the Kepko Manufacturing Company and altered by us, on advice from the manufacturer, to be current regulating. Some derivative feedback was needed to get the transient response needed for this experiment. A small biasing current was applied to the magnet to insure that the residual field was less than $\frac{1}{2}$ gauss when these power supplies were turned off; this precaution is important for measurements close to the critical temperature.

The timing, modulation, and sweep circuits were similar to those described in reference 7, with one exception. We used two trapezoidal sweep circuits (see Fig. 1, reference 7) in parallel to drive the sweep coil. The first of these provided the nuclear resonance linear sweep, as described in reference 7. The second was normally turned on, to give a steady field of about 100 gauss aiding the field of the main magnet. During a relaxation measurement, the main magnet was first turned off, but because this second sweep circuit was conducting the sample remained normal. After about 0.1 sec the switching transient of the main electromagnet had disappeared, and the second sweep was turned off, giving a controlled, reproducible decrease of the field to zero and thus an optimum rate of transition between normal and superconducting states. After a time τ this sweep was again turned on, raising the field to 100 gauss, and after the sweep was finished (typically in 0.2 sec) the main magnet was turned on, and later the first sweep was started to observe the resonance. A controlled rate of transition is necessary to reduce the irreversibility of the nuclear demagnetization; as we have already emphasized, this irreversibility reduces the strength of the available signal for this measurement.[1,7]

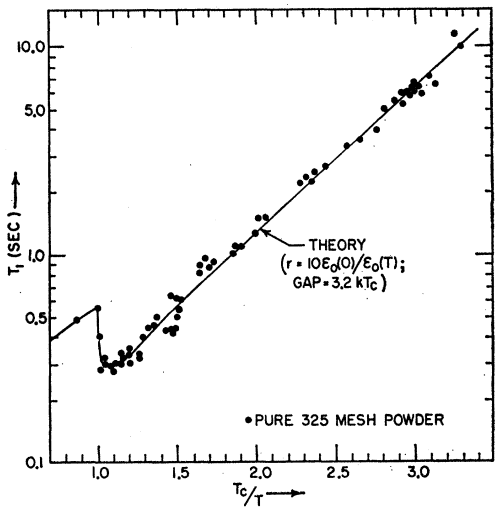

FIG. 2. Measured values of T_1 in the powdered sample. No points were rejected, so that the scatter gives a fairly good idea of the accuracy. T_c was taken to be 1.178°K. The theoretical curve is the same as the solid line of Fig. 5.

To measure a single point of T_1, about thirty observations of the nuclear signal were made using different values of τ, the time during which the field is zero. Usually the signal was a miserable pip superimposed on a somewhat reproducible, but not flat, baseline. The baseline shifts may have been caused by Hall effect. Some discretion was needed in reducing the data. In every case reported here the signal decayed exponentially with τ within experimental error. The accuracy is best judged from the scatter of data, which was much larger than any possible systematic error that we can think of.

III. EXPERIMENTAL RESULTS

The experimental values of T_1 are shown in Figs. 2 and 3. These values are in reasonable agreement with the measurements of Hebel and Slichter.[1] The values reported here[14] are somewhat higher than those quoted in a previous publication.[15]

The sample on which most of the data were taken was filed from a zone-refined ingot of aluminum thought to contain about one part per million impurities. This ingot was very kindly supplied by Dr. J. H. Wernick of Bell Telephone Laboratories. The filings were passed

[14] The present measurements were also reported in the *Proceedings of the Seventh International Conference on Low-Temperature Physics*, Toronto, 1960, edited by G. M. Graham and A. C. Hollis Hallet (University of Toronto Press, Toronto, 1960), p. 412.

[15] A. Redfield, Phys. Rev. Letters **3**, 85 (1959). These measurements were somewhat in error because of a spurious nuclear resonance signal originating in the copper receiver coil then used.

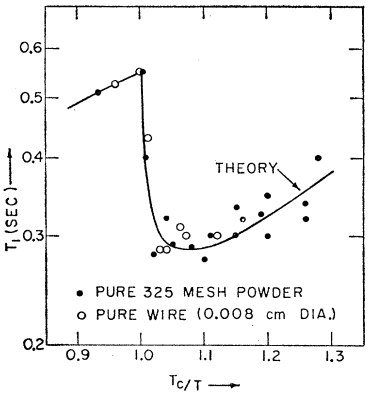

FIG. 3. Measured values of T_1 near T_c, assuming T_c 1.178°K. The theoretical curve is the same as in Fig. 5.

through a 325-mesh sieve and etched for 30 sec in 50% nitric acid, then annealed for several hours at 400°C in a vacuum of about 10^{-5} mm Hg and cooled slowly. This is the same sample on which measurements have been made previously in the normal state, reported elsewhere.[7] Some measurements were also made on a wire sample 0.008 cm in diameter drawn from a bar of Johnson-Mathey aluminum, cut into little pieces, and vacuum annealed. This sample had a resistance ratio between room and helium temperature of 855 after annealing.

It seemed quite possible to us that impurities and dislocations introduced in the preparation of the sample might affect our measurements somewhat. Therefore, we have made some measurements on wire samples of fairly well-known impurity content. These measurements will be reported elsewhere,[16] but they indicate that the observed relaxation time does not depend strongly on impurities, and that, within our experimental scatter, the data reported here are representative of a pure superconductor. Impurity concentrations of greater than 100 parts per million are required to produce measurable changes in T_1.

Impurities do affect our observations in one sense, however. The loss of intensity of the signal observed after switching the field off (for a time short compared to T_1) depends markedly on the sample used. The intensity was somewhat greater for alloys than for the pure powder sample, and for the pure wire sample described above the signal was unobservable below 1.1°K. These variations in intensity are probably due to the supercooling effect discussed in Sec. VII of Hebel and Slichter,[1] but they may also be due to the existence of quadrupole interactions in increasing amounts with increasing impurity concentration. The quadrupole interaction would act to increase the local field of the spins, and thus give more nearly reversible behavior for a given rate of transition between normal and superconducting states. There is considerable, but ambiguous, evidence[7] that such quadrupole interactions exist, even in carefully prepared samples as used here. Such interactions are likely to affect the relaxation time, but it is hoped that they will affect T_1 equally in the normal and superconducting state. It must be emphasized, however, that quadrupole interactions provide a possible source of ambiguity in the interpretation of the temperature and impurity dependence of T_1.

Hebel and Slichter suggest that trapped flux may be a source of error in this type of measurement. We have not found any evidence for trapped flux, but we cannot rule it out as a possible source of error.

IV. DISCUSSION

The values of T_1 in the superconducting state predicted directly by the BCS theory, as calculated by Hebel and Slichter, are much shorter than those observed, and much shorter than T_1 in the normal state, near T_c. The BCS theory gives a short relaxation time because of the singularity in the BCS density of states at the edge of the energy gap. In order to get a theoretical T_1 of the same order of magnitude as experiment, Hebel and Slichter found it necessary to assume that the true density of states was the BCS density of states function smeared over a range of about $\frac{1}{10}$ of the energy gap at absolute zero. Specifically, they used the BCS density of states folded with a function of rectangular shape and width 2Δ. The temperature dependence of T_1 calculated in this way by Hebel[2,17] is shown in Fig. 4 for $r=10$ and $r=60$, where $r=\epsilon_0(0)/\Delta$ and $2\epsilon_0(T)$ is the energy gap at temperature T. It is found that T_1 is

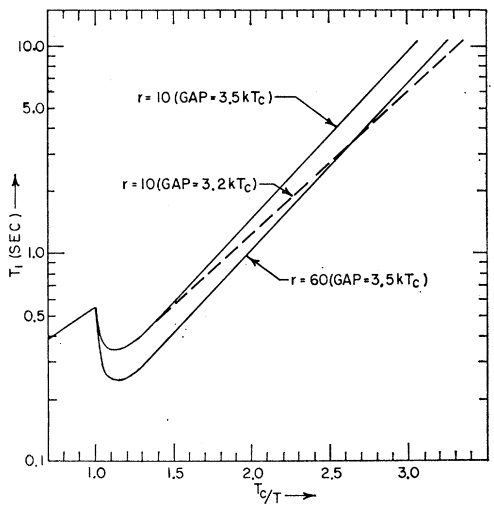

FIG. 4. Theoretical behavior of T_1 versus temperature predicted by the BCS theory, as calculated by Hebel. The solid lines are calculated using the BCS density of states smeared over a range of 1/10 and 1/60 of the energy gap at $T=0$. The dashed curve is calculated using the energy gap inferred from microwave absorption measurements of Biondi and Garfunkel (reference 18).

[16] Y. Masuda (to be published in IBM Journal Research Develop.); see Y. Masuda, Bull. Am. Phys. Soc. **6**, 122 (1961).

[17] For $r=10$ Eq. (7) of reference 2 is not a sufficiently good approximation, and we used Eq. (6) of that reference to calculate T_1 for $r=10$.

proportional to $\ln r$ for $T \ll T_c$. The fact that T_1 is predicted to vary as $\exp[\epsilon_0(0)/kT]$ for $T \ll T_c$ is, of course, a rather general consequence of any gap model. At very low temperatures, however, deviations from this exponential behavior should again occur, when kT becomes comparable to the energy range of any structure at the edge of the gap. These deviations would be expected when $kT \simeq \Delta$.

Microwave measurements[18,19] indicate that the energy gap at absolute zero is 3.2 kT_c, rather than the BCS value of 3.5 kT_c. From the slope of our data at low temperatures we also get a gap of 3.2 kT_c, though perhaps less accurately than the microwave measurements. Therefore, it seems reasonable to correct the theoretical T_1 for this smaller gap. This correction is made[2] simply by changing the temperature scale by a constant factor, which is evidently equivalent to assuming that the BCS wave functions are correct but that their energy is not correctly estimated by the BCS theory. The prediction obtained in this way for a gap of 3.2 kT_c and $r=10$ is also shown in Figs. 4 and 5 (dashed curve).

The most natural source of the smearing of the BCS density of states which one can postulate is an anisotropy of the gap.[2,20] There is no momentum selection rule for the initial and final states in nuclear relaxation, so the average density of states determines T_1, not the density of states in any particular $\mathbf{k}$ direction. Thus, a gap anisotropy will smear the density of states by an amount equal to the anisotropy. The theory described here should give the correct value of T_1 if the parameter Δ is chosen to be approximately equal to the anisotropy.

The curves shown in Fig. 2 were obtained under the assumption that Δ (and thus r) is independent of temperature. Actually, of course, Δ might be temperature dependent. Now, as T approaches T_c the gap $2\epsilon_0(T)$ decreases, and it would be natural to assume that the anisotropy decreases and is perhaps proportional to the gap. In that case we would have $\Delta(T)$ proportional to $\epsilon_0(T)$. The prediction corresponding to such an assumption is shown in Fig. 5 (solid line) and Figs. 2 and 3. It is obtained from Hebel's calculations by changing the temperature scale to correspond to a gap of 3.2 kT_c, and by setting $\Delta(T)=\epsilon_0(T)/10$, or

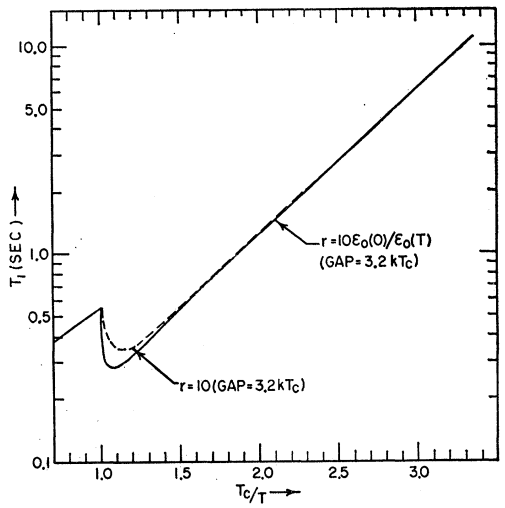

FIG. 5. Comparison of theory using the BCS density of states smeared over a fixed energy range as in Fig. 4 (dashed curve) with that using a smearing proportional to the energy gap (solid curve).

$r(T)=10\epsilon_0(0)/\epsilon_0(T)$. As can be seen from Figs. 2 to 5, the parameters $\Delta(T)$ or r can be estimated to an accuracy of $\pm 30\%$ or better, and the theoretical curve which fits the data considerably better than any of the other curves is that corresponding to the assumption that $\Delta(T)$ is proportional to $\epsilon_0(T)$.

We regard these data as evidence for the existence of an anisotropy in the energy gap which, at any temperature, is of the order of 10% of the gap itself. No theoretical estimate of the anisotropy has been made. An anisotropy of 10% is close to the upper limit which might be inferred from the microwave data.[18] However, we wish to emphasize that these data give only an upper limit to the anisotropy of the gap. The quantity $\Delta(T)$ could be interpreted in some other way, such as an inverse lifetime for scattering by imperfections or electrons. We have emphasized anisotropy in this paper simply because the temperature dependence of Δ or r is most naturally explained in terms of anisotropy.

ACKNOWLEDGMENTS

We wish to thank Mr. R. Gazinelli for assisting us in this experiment. We thank the many members of this laboratory who helped us, especially Mr. W. Kiselewski and Dr. A. G. Anderson who built much of the apparatus. We have had useful discussions with Dr. P. W. Anderson, Dr. L. C. Hebel, and Dr. C. P. Slichter, and we wish especially to thank Dr. Hebel and Slichter for keeping us informed of their work before publication.

[18] M. A. Biondi and M. P. Garfunkel, Phys. Rev. **116**, 853 (1959).

[19] However, recent measurements of the energy gap by means of the tunnel technique indicate a somewhat smaller gap, corresponding to $\epsilon_0(0) \cong 2.7\ kT_c$. See J. Nicol, S. Shapiro, and P. H. Smith, Phys. Rev. Letters **5**, 461 (1960).

[20] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959). We are indebted to Dr. Anderson for first pointing out to us that anisotropy of the energy gap would lead to a smearing of states as introduced by Hebel and Slichter.