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Millimeter-Microwave Studies of Energy-Gap Anisotropy in Superconductors*

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Measurements of the absorption of polarized microwaves have been made on superconducting single crystals of aluminum and zinc as a function of frequency in the region where the photon energy spans the superconducting energy gap. When plotted as isotherms of surface resistance ratio versus photon energy the results for aluminum show, in three different crystal faces (100, 110, and 111), two rapid changes in slope occurring at values of energy about 10% apart. The photon energies at these slope changes are interpreted as indicating the positions of two different superconducting energy gaps. We also find small differences in the energy-gap values ($\sim$3%) among the three different crystal faces. All the measured values of energy gaps at $T=0$ in aluminum lie between $3.04kT_c$ and $3.50kT_c$, where $T_c=1.175$°K. Preliminary results on a single crystal of zinc yield an energy gap at $T=0$ of $(3.00\pm0.15)\ kT_c$, where $T_c=0.838$°K.

I. INTRODUCTION

THE superconducting energy gap has been measured directly by two quite different techniques: (1) detection of a critical frequency above which the absorption of electromagnetic energy increases markedly,[1–4] and (2) determination of the potential difference at which there is a sharp rise in the current tunneling through the insulator in a superconductor-insulator-conductor sandwich.[5] In addition to these direct measurements, the energy gap has been inferred from the temperature dependence of a number of properties such as heat capacity, acoustic absorption, and nuclear spin relaxation rate,[6,7] which, at low temperatures, vary approximately as $\exp(-\Delta/kT)$, where Δ is half the energy gap, k is Boltzman's constant, and T is the absolute temperature.

The microscopic theory of superconductivity of Bardeen, Cooper, and Shrieffer[8] (BCS theory), which leads to the prediction of a gap in the one-electron energy states, has, with minor exceptions,[9] satisfactorily described electromagnetic absorption and penetration, electron tunneling, and thermal properties of ideal superconductors.[10] However, the BCS theory deals with idealized, isotropic superconductors and thus ignores the possibility of anisotropy in the superconducting properties introduced by the crystalline lattice of a real metal. In order to explain some of the small discrepancies between the predictions of the BCS theory and observed thermal properties, the concept of an anisotropy in the interaction and thus in the energy gap has been proposed (e.g., Bardeen and Schrieffer[10]), and Anderson has introduced an anisotropic energy gap in pure metals as a postulate in his theory of "dirty" superconductors.[11] In Anderson's theory, the anisotropy that exists in the pure metal is reduced by the introduction of small amounts of

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[1] R. E. Glover, III, and M. Tinkham, Phys. Rev. **108**, 243 (1957).
[2] M. A. Biondi and M. P. Garfunkel, Phys. Rev. **116**, 853 (1959).
[3] P. L. Richards and M. Tinkham, Phys. Rev. **119**, 575 (1960).
[4] D. M. Ginsberg and M. Tinkham, Phys. Rev. **118**, 990 (1960).
[5] I. Giaever and K. Megerle, Phys. Rev. **122**, 1101 (1961).
[6] M. A. Biondi, A. T. Forrester, M. P. Garfunkel, and C. B. Satterthwaite, Rev. Mod. Phys. **30**, 1109 (1958). This paper is a review of the experimental evidence for an energy gap in superconductors up to 1958.
[7] D. H. Douglas, Jr., and L. M. Falicov, in *Progress in Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, to be published), Vol. IV. This article provides a new comprehensive review of both theoretical and experimental aspects of the superconducting energy gap.
[8] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[9] The BCS theory has not, by itself, explained the existence of a Knight shift in superconductors at $T=0$. It has also failed to describe the large effect that a static magnetic field has on microwave absorption. Finally, it was not designed to account for anisotropy or other sources of multiple energy gaps which may be characteristic of real superconductors.
[10] See J. Bardeen and J. R. Schrieffer, *Progress in Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1961), Vol. III, p. 170 ff. for a comparison of the theoretical predictions of the BCS theory with experiments.
[11] P. W. Anderson, Phys. Chem. Solids **11**, 26 (1959).

impurity which reduce the electron mean free path to less than the superconducting coherence length ξ_0.

Experimentally, anisotropy of the energy gap has been inferred from the temperature dependence of the attenuation of ultrasound propagated along different crystalline directions in superconducting tin,[12] by the absorption of far-infrared radiation on single-crystal faces of superconducting tin,[13] from the anisotropy of the tunneling current from superconducting tin single crystals,[14] from microwave absorption experiments on superconducting tin at frequencies where $h\nu \ll 2\Delta$,[15] and from absorption of polarized microwaves by superconducting aluminum at frequencies where $h\nu \gtrsim 2\Delta$.[16]

It is the purpose of this paper to describe in detail an experiment[16] in which a small anisotropy in the energy gap in aluminum has been observed in measurements of the absorption of polarized microwave radiation by single crystals. In addition to the orientation dependence of the energy gap, we shall see that there is evidence for two substantially different energy gaps for each crystalline direction. A preliminary determination of the energy gap for a single crystal of zinc is also reported.

In order to observe anisotropy in the microwave absorption in a metal with cubic symmetry (aluminum), the conductivity and frequency must be such that we are in the regime of the anomalous skin effect, where only those electrons which move almost parallel to the surface of the sample contribute to the absorption.[17]

The condition for the anomalous skin effect in normal metals[17,18] is

$$\delta_{cl}/l \ll (1+\omega^2\tau^2)^{-3/4}, \tag{1}$$

where ω is the angular frequency of the electromagnetic wave, τ is the average time between collisions for the conduction electrons, l is the electron mean free path, and δ_{cl} is the classical skin depth, given by

$$\delta_{cl} \equiv c(2\pi\omega\sigma)^{-1/2},$$

where c is the velocity of light and σ is the conductivity of the metal. This condition reduces to

$$\omega\delta/v_F \ll 1, \tag{2}$$

when $\omega\tau > 1$ (i.e., the case of the work to be reported in this paper), where δ is the actual skin depth and v_F the Fermi velocity of the conduction electrons.

In the superconducting state, we can arrive at the conditions under which the anomalous skin effect is operative for photon energies of the order of the energy gap, $\hbar\omega \sim 2\Delta(0)$, by considering the conservation of energy and momentum for electrons absorbing a photon in the surface layer.[19] Under the influence of an electromagnetic field, the transition of an electron from a state with wave vector $\mathbf{k}$ to a state with wave vector $\mathbf{k}+\mathbf{q}$ is limited to those $\mathbf{q}$ values where there are appreciable amplitudes of the Fourier transform of the electromagnetic field in the skin depth. The direction of the $\mathbf{q}$ vectors is, of course, normal to the surface. A larger part of the absorption is associated with values of $q \equiv |\mathbf{q}| \sim 1/\lambda$, where λ is the superconducting penetration depth,[20] since it is for values of q in this range that the Fourier components of the field are appreciable. The energy change of an electron on absorption of a photon is $\hbar\omega(\sim 2\Delta(0))$. Using the BCS[8] expression for energy in terms of the wave vectors $\mathbf{k}$ and $\mathbf{q}$, the energy change is

$$E(\mathbf{k}+\mathbf{q})-E(\mathbf{k}) = \left\{\Delta^2+\left[\frac{h^2}{2m}(\mathbf{k}+\mathbf{q})^2-\epsilon_F\right]^2\right\}^{1/2} - \left\{\Delta^2+\left[\frac{h^2}{2m}\mathbf{k}^2-\epsilon_F\right]^2\right\}^{1/2}, \tag{3}$$

where ϵ_F is the Fermi energy. Noting that the only electrons that can contribute significantly to the absorption lie within $\hbar\omega(\sim 2\Delta(0))$ of the Fermi surface, we can show from Eq. (3) that $h^2\mathbf{k}\cdot\mathbf{q}/m \lesssim \Delta(0)$ or

$$(h^2/m)kq\cos\theta \lesssim \Delta(0) \sim \hbar\omega, \tag{4}$$

where θ is the angle between $\mathbf{k}$ and $\mathbf{q}$. Since the energy gap is related to the superconducting coherence length ξ_0 by

$$\Delta(0) = hv_F/\xi_0, \tag{5}$$

and since $hk = mv_F$, Eq. (4) reduces to

$$\cos\theta \lesssim 1/(q\xi_0) \simeq \lambda/\xi_0. \tag{6}$$

For conditions encountered in pure superconducting aluminum, i.e., $\lambda/\xi_0 \ll 1$, the angle $\theta \sim \pi/2$; thus the effective electrons must be moving almost parallel to the surface.

As the photon energies approach and exceed the energy-gap value, these relations must reduce to those appropriate for the normal state of the metal.

[12] R. W. Morse, T. Olsen, and J. D. Gavenda, Phys. Rev. Letters **3**, 15 (1959); P. A. Bezuglyi, A. A. Galkin, and A. P. Karolyuk, Zh. Eksperim. i Teor. Fiz. **36**, 1951 (1959) [English transl.: Soviet Phys.—JETP **9**, 1388 (1959)].

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

[14] N. V. Zavarithskii, Zh. Eksperim. i Teor. Fiz. **43**, 1123 (1962) [English transl.: Soviet Phys.—JETP **16**, 793 (1963)].

[15] J. R. Waldran, Advan. Phys. **13**, 1 (1964).

[16] A brief preliminary report of the work described in this paper was given at the International Conference on the Science of Superconductivity held at Colgate University, Hamilton, New York, in August 1963. This appears in Rev. Mod. Phys. **36**, 197 (1964); see Discussion **30**, under Garfunkel.

[17] See A. B. Pippard, in *Advances in Electron Physics*, edited by L. Marton (Academic Press Inc., New York, 1956), Vol. VI, p. 1, for a discussion of the ineffectiveness concept applied to normal metals.

[18] G. E. H. Reuter and E. H. Sondheimer, Proc. Roy. Soc. (London) **A195**, 336 (1948).

[19] We are indebted to T. Holstein for pointing out this simple way of looking at the ineffectiveness concept. The argument, of course, applies equally well to the normal and to the superconducting states.

[20] Actually, we should use δ_s, the penetration depth at the frequency in question, rather than λ which is the superconducting penetration depth at $\omega = 0$, but these two quantities are the same order of magnitude, as was shown in M. A. Biondi and M. P. Garfunkel, Phys. Rev. **116**, 862 (1959).

From Eq. (4), we obtain

$$v_F q \cos\theta \lesssim \omega. \tag{7}$$

At frequencies near the energy gap, one finds that $\lambda \to \delta$; thus, $q \sim 1/\delta$ and

$$\cos\theta \lesssim \omega\delta/v_F, \tag{8}$$

and the condition for the anomalous skin effect reduces to Eq. (2) above, showing that near the energy gap the criterion for the anomalous skin effect is the same in both the normal and in the superconducting states.

II. EXPERIMENTAL TECHNIQUES

A. Microwave Sources and Frequency Measurements

In the present studies the frequency range 15 Gc (wavelength 20 mm) to 100 Gc (wavelength 3.0 mm) is covered essentially continuously by the use of reflex klystrons capable of generating $\sim 10-100$ mW of continuous rf power. The absolute values of the microwave frequencies are determined within an accuracy of $\pm 0.2\%$ by means of absorption-cavity wave meters, while the relative frequency accuracy is expected to be somewhat better. In the energy-gap frequency region to be discussed later, each of two wave meters spans the interesting frequency range, permitting highly accurate relative-frequency determinations.

B. Apparatus

In order to carry out measurements over the temperature range 0.35–1.3°K, a double Dewar apparatus is used, consisting of an outer He^4 bath pumped to ~ 1.2°K acting as a heat shield for an inner He^3 section. The He^3 section is contained in an evacuated housing, and connections to the outer section are via poor thermal conductors, e.g., thin-walled stainless steel wave guide. Pumping on the liquid He^3 reservoir then reduces the temperature of the inner section to ~ 0.3°K. An electronic temperature regulator using a carbon resistance thermometer as sensing element maintains the He^3 reservoir temperature constant to $\pm 10^{-5}$°K.

As in the earlier studies of polycrystalline aluminum,[2] the absorption of microwave energy by the superconductor is determined calorimetrically. A highly schematic diagram of the evacuated calorimeter section of the apparatus is shown in Fig. 1. The superconductor sample takes the form of a single-crystal circular disk (1.2 in. in diameter and 0.060 in. thick), which is placed very close to but does not touch (gap <0.001 in.) the end of a copper wave guide section (internal cross section 0.170 in. $\times$ 0.420 in.).

The sample is mechanically aligned with respect to the copper by means of a coupler which serves the dual function of thermally isolating the sample from the other parts of the apparatus and of absorbing microwave energy leaking out of the small gap between the sample and the wave guide. (The absorbers will be discussed in more detail shortly.) Leakage energy absorbed by the coupler is thermally "grounded" to the He^3 reservoir by means of a heavy copper rod.

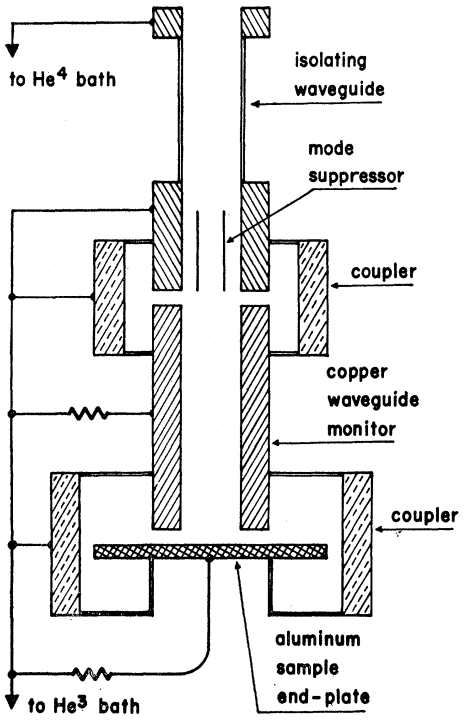

FIG. 1. Schematic diagram of calorimeter section of the apparatus. See the text for a discussion of the function of the various components.

The wave guide carrying the microwave energy is capable of supporting more than one mode of propagation at the shorter wavelengths; therefore, to eliminate TM modes and to assure polarization of the TE modes perpendicular to the long dimension of the guide, copper vanes are inserted parallel to this dimension in the isolating feed wave guide. The microwave energy incident on the sample is monitored by the copper wave guide, which is also thermally isolated from other parts of the apparatus by couplers. Appropriate response times for the copper wave guide and sample are obtained by adjusting the values of the heat leaks (indicated by the resistor symbols) from these sections to the He^3 reservoir.

In the present study, establishing single, known orientations of the microwave field with respect to crystalline axes dictated the use of a sample in the form of a single-crystal end plate, with the result that only $\sim 1:10^4$ of the incident power is absorbed by the sample in the normal state just above T_c. (This is to be contrasted with $1:10^2$ in the experiment described in Ref. 2.) Thus, an elaborate coupler design is required to reduce absorption of the leakage energy at sensitive locations to acceptable levels ($<1:10^6$ of the incident energy) for the absolute absorption determinations.

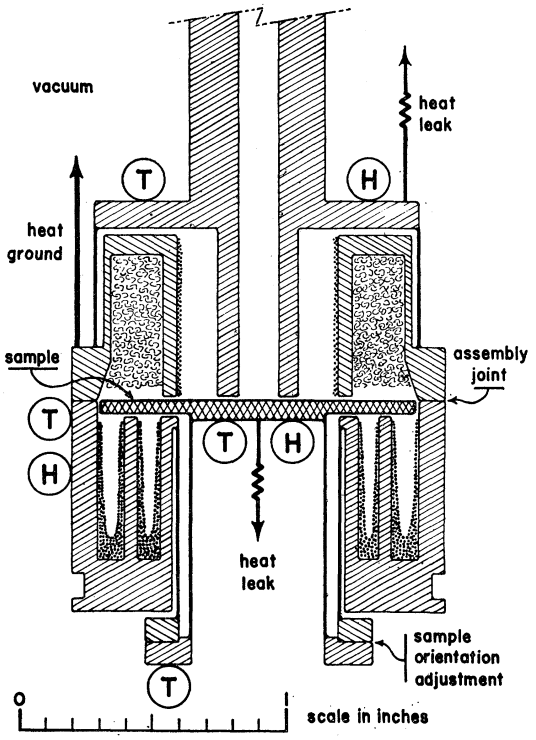

FIG. 2. Detail drawing of the sample, its mounting, the copper monitor section, and the coupler. The letters T and H refer to carbon resistance thermometers and heaters, respectively. See the text for a discussion of the various features shown.

The design of the section containing the sample, coupler, and copper monitor is shown in more detail in the cross section drawing of Fig. 2. It is necessary to cover the outside of mechanical joints between sections, such as the assembly joint in the coupler, with colloidal silver conducting paint to reduce leakage of microwave energy to the outer surfaces of the apparatus to sufficiently small levels. Microwave energy from the source passes vertically downward through the copper monitor section, a portion of which is shown at the top of the figure. The sample (double cross hatching) is mounted very close to, but not touching, the copper monitor.

Thermal isolation of the sample and the monitor is provided by the coupler, which consists of thin-walled stainless tubing from the copper monitor to the main body of the coupler and from the sample to the coupler body. The body of the coupler is of copper and contains cavities lined with absorbing material (either painted layers of colloidal graphite in lacquer or glass wool coated with the graphite bearing lacquer).

Microwave energy leaking into the gap between the copper waveguide and the sample first encounters a cavity consisting of an outer polished surface of the copper monitor and a surface of the coupler body which is thickly ($\sim$0.010 in.) coated with graphited lacquer. Some of the energy propagates past the small gap between the coupler body and the sample and enters a cavity in the coupler which is very loosely packed with glass wool covered with graphited lacquer. Any remaining energy which propagates past the end of the aluminum disk into the lower coupler section must pass two cavities lined with graphited lacquer absorber before reaching either the thin-walled stainless-steel isolating section between coupler body and sample or the cemented joint between the stainless steel and the sample. In order to monitor whether any microwave power has been able to proceed this far without absorption, a thermometer (bottom of figure) is attached to the copper ring at the midpoint of the stainless-steel isolator section. The copper ring is in two parts to permit rotation of the sample with respect to the wave guide.

Since the sample is chemically polished on all surfaces (see description in the following subsection), it is assumed that the absorptivity of the surfaces outside the desired region (roughly, the projected wave-guide cross section on the front face, where the microwave polarization is in the desired direction) is approximately the same as for the front face. Thus, absorption of the small leakage energy by the sample is negligible and does not interfere with determinations of the absorptivity as a function of orientation of the microwave field with respect to given crystalline directions.

Temperature rises of the sample, copper power monitor, coupler body and isolator midpoint are detected by carbon resistance thermometers (T) [1200 Ω Speer Type AR7404 carbon resistors] mounted on the outside of each section. In all but the case of the sample isolator midpoint, the temperature rise caused by the absorption of microwave power on a particular section is reproduced by dc power fed to the resistance wire heater (H) attached to that section. When the dc power levels are set to reproduce the temperature rises produced by the microwave absorption, the thermometer on the isolator midpoint often reproduces the resistance value obtained with the microwave heating, suggesting that the microwave leakage energy reaching that point is acceptably small. (Since the isolator midpoint has no direct heat leak to "thermal ground," its sensitivity to power absorption is rather high, as evidenced by its long response time to temperature changes of the sample or of the coupler.)

C. Sample Preparation

The single-crystal samples of high-purity aluminum were obtained by melting zone-refined ($<1:10^6$ impurity) aluminum obtained from Cominco Products, Inc.,[21] in a graphite crucible designed to cause self-seeding single-crystal growth on cooling in a temperature gradient. One end of the ingot so obtained was cut off by spark cutting to permit x-ray orientation. Following this, a rough disk whose normal lay in a desired

[21] Address: Cominco Products, Inc., Spokane, Washington.

crystalline direction was spark cut from the ingot. The final shape of an aluminum sample, that of a disk with a small aligning boss centered on its back surface, was obtained by spark machining.

In preliminary studies of zinc, a single crystal was grown from high-purity zinc supplied by Cominco Products, Inc. ($<1:10^5$ impurity) in a mold approximating the desired shape and then lightly machined to final sample shape.

The front faces of all samples were mechanically polished to flatness using fine abrasives, and the whole sample was chemically polished (with a solution of 94% phosphoric acid, 6% nitric acid at 95°C, in the case of aluminum, and with a solution of 88% phosphoric acid, 12% nitric acid at 25°C, in the case of zinc) to remove remelted or mechanically worked material. The sample was then annealed near its melting point, following which a final chemical polish was carried out. The resulting surfaces show a slight filming and small pock marks, neither of which is expected to lead to appreciable residual absorption of microwave energy. The sample was then cemented to its stainless-steel isolating holder with a varnish (General Electric Type 7031).

The purity of the samples was determined by a residual resistance measurement carried out on the sample itself. The disk-shaped sample was placed in a solenoid and the decay time of eddy currents induced in the sample determined. The decay time is proportional to the resistivity of the sample. The inferred ratio of resistivity at room temperature to that at low temperatures is a measure of the purity of the sample. The values of the ratios for the different samples are given in Sec. III.

III. RESULTS

The measurements, taken as a function of temperature at constant frequency and with the magnetic field cancelled to $<10^{-2}$ G, involve recording the readings of the thermometers on the sample, copper monitor, coupler, and isolator midpoint with the microwave power on. Then, with the microwaves turned off, the powers absorbed in the sample and in the copper section are obtained by measurements of the current needed in the heaters on the sample and copper monitor to reproduce the temperature rises that had resulted from the microwave-energy absorption. In order to discount power-level drifts of the incident microwaves, the power absorbed in the sample is divided by the power absorbed in the copper. These ratios are then normalized to the value of the same ratio measured just above the superconducting transition temperature T_c, and thus yield the ratio of the absorptivity in the superconducting state to that in the normal state. For the high conductivity of pure metals, this absorptivity ratio is indistinguishable from the surface resistance ratio $r\equiv R/R_n$, where R and R_n are the real parts of the surface impedance in the superconducting and normal states, respectively. The surface impedance is defined as $Z\equiv 4\pi E(0)/H(0)$, where $E(0)$ and $H(0)$ are the electric and magnetic fields, respectively, at the surface of the sample.

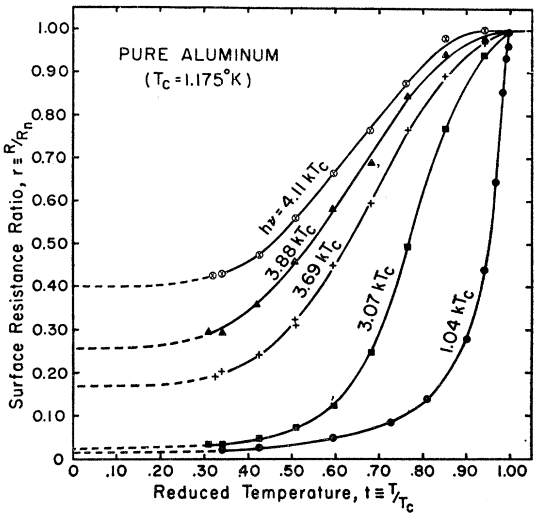

FIG. 3. Surface resistance ratio versus reduced temperature at five microwave frequencies for a (100) plane of aluminum. The dashed portions of the curves are extrapolations to $T=0$ by the method described in the text.

A. Aluminum

Figure 3 is a plot of typical curves, at several frequencies, of the surface resistance ratio r of a (100) crystal face of aluminum, as a function of the reduced temperature $t\equiv T/T_c$. The superconducting transition temperature has been determined for each of the single-crystal samples from the lowest frequency curve ($h\nu/kT_c\sim 1$). It is $T_c=(1.175\pm 0.001)$°K[22] for all three of the aluminum samples, in agreement with the value obtained in the precise critical field measurements of Chanin and Caplan.[23] The surface-resistance ratio curves have the same form as those reported by Biondi and Garfunkel[2] for the polycrystalline samples. These curves have been extrapolated to $t=0$, as shown in Fig. 3 by the dashed sections, by assuming that r is proportional to the function $f(t)=t^4(1-t)^2/(1+t^4)^2$, as proposed by Pippard,[24] and previously used by Biondi and Garfunkel.[2] There are two characteristics to note in these curves; (1) as frequency is increased, there is a change from a sharp drop below $t=1$ to a more gradual one with the opposite curvature; this comes about when the photon energy exceeds $2\Delta(t\sim 1)$, the superconducting energy gap, at temperatures near T_c; and (2) at

[22] $T_{62}He^3$ temperature scale. See R. H. Sherman, S. G. Sydoriak, and T. R. Roberts, Report No. LAMS-2701, Los Alamos Scientific Laboratory (unpublished).

[23] G. Chanin and S. Caplan, Bull. Am. Phys. Soc. **9**, 30 (1964)

[24] A. B. Pippard, Proc. Roy. Soc. (London) **A203**, 98 (1950)

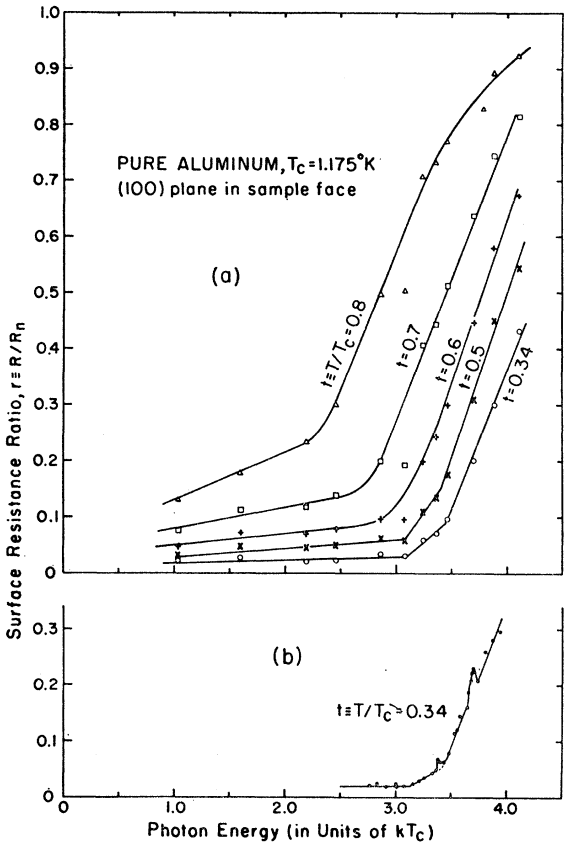

FIG. 4. (a) Isotherms of surface resistance ratio versus photon energy in a (100) plane of aluminum. (b) A repeat of the $t=0.34$ isotherm of (a) under improved rf shielding conditions. Note that, although there are less scatter and slightly different values of the surface resistance ratio, the discontinuities in slope occur at the same photon energies. In these measurements the electric field is polarized along a [100] direction; however, for this plane no polarization dependence is expected.

$t=0$, r goes to zero[25] for all photon energies less than $2\Delta(0)$ (the energy gap at $t=0$) then r increases from zero as the photon energy exceeds $2\Delta(0)$. These features are better illustrated by isothermal plots of surface resistance as a function of photon energy (frequency) as in Figs. 4, 5, and 6, which show the results for three different crystal faces of aluminum: a (100) face obtained from the smoothed curves of Fig. 3, a (111) face, and a (110) face, respectively.

To provide a meaningful discussion of the features of these curves, it is first necessary to discuss the accuracy of the measurements and other possible sources of error. The sensitivity and noise level of the thermometers and the accuracy of measurements of heater power make possible, at the usual microwave power level used, an uncertainty in the measurements used to determine the surface resistance of less than 0.2% of the normal-state value over the whole temperature range (at the lowest temperatures the uncertainty is considerably less than this). These sources of random error, then, only matter at a certain few frequencies (mostly in the frequency region near 60 Gc/sec) where the available microwave power is very small. Of far greater significance are the following four sources of systematic error: (1) Rapid drifts in the microwave power level which cannot be normalized properly because the sample and the copper absorber have different thermal time constants. This difficulty has the virtue of being apparent to the experimenter. (2) Pickup of stray rf on the thermometer leads which is then dissipated in the thermometers, bringing them to a different temperature. This can appear either as a random or a systematic variation in the data, since changes in the stray rf in the laboratory are not correlated with this experiment. (3) Leakage of microwaves around the edge of the sample (see Fig. 2) to the support, which then appears as absorption in the sample. (4) Drifts in the frequency of the microwaves which can cause unknown variations in the normalization, since the ratio of power absorbed on the sample to that absorbed on the copper surfaces can be extremely frequency-dependent through the resonant properties of the two couplers (see Figs. 1 and 2), and also can effect the errors mentioned in (3) above.

Probably the best way to estimate (1) and (2) is through the reproducibility of experiments conducted on different days. From this we estimate a probable

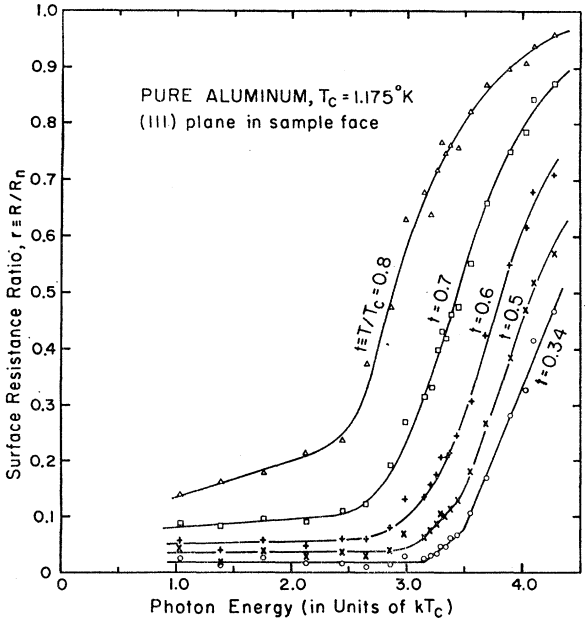

FIG. 5. Isotherms of surface resistance ratio versus photon energy in a (111) plane of aluminum. In these measurements the electric field is polarized along a [110] direction. For the (111) plane no polarization dependence is expected.

[25] Actually $r(0)$ is rarely zero but is typically (at the lower frequencies) several tenths of a percent. This nonzero value is thought to be instrumental and we, therefore, assume it to be zero in the text. (See discussion of the accuracy of the measurements for possible sources of this "residual absorptivity.") This assumption might overlook significant results regarding evidence for states in the energy gap, but since the absorption we have observed is small and does not seem reproducible, we are probably correct in neglecting it.

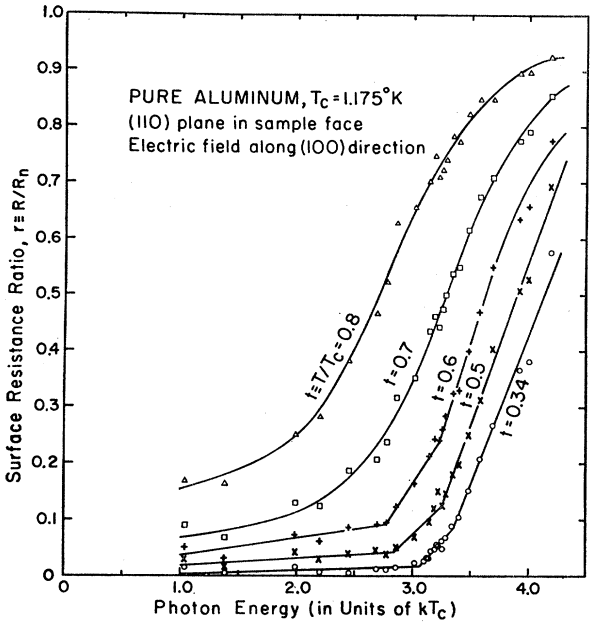

FIG. 6. Isotherms of surface resistance ratio versus photon energy in a (110) plane of aluminum. The electric field is polarized along a [100] direction.

error of less than 1% of the normal-state value but with occasional experiments possibly having as much as 3 or 4% error (if all of the variation were from this source alone). The normalization error, (4) above, can be estimated by checking normalization at the beginning and end of each experiment. This error is usually found to be just a few percent, with occasional apparent errors in normalization as high as 5%. Since the error from this source is proportional to the absorptivity, it is not significant at low values of the absorptivity. Finally, the leakage of microwaves around the edge of the sample is apt to be a serious source of error in the surface-resistance determinations. In this case, it is probably most significant at the lowest temperatures (as a result of the way the measurements are normalized), and it undoubtedly varies substantially with frequency, as a result of the many low-Q resonances of the coupler. The best estimate for this error comes from the observed absorption, extrapolated to $t=0$, at frequencies well below the energy gap. If one assumes that in this range $r(t=0)$ should be zero,[25] then we again conclude that the error from microwave leakage is generally about 1% or less of the normal-state value, except at occasional frequencies where it may be as high as 2–3%. One last point is that the samples themselves may have strained, filmed, or otherwise imperfect areas of the surface causing some residual, frequency-dependent absorption. However, we have no reason to believe this is of any significance in the present experiment.

As the experiment has progressed, some of the sources of error have been reduced or eliminated. Thus, in the earliest work (on zinc) the scatter of the data was so large that we do not discuss the details but only give the more significant features. We also have a single experiment [a repeat of the lowest temperature curve of Fig. 4(a), shown as Fig. 4(b)], where the pickup of stray rf has been reduced by a sufficiently large factor to reduce the scatter of the results to less than $\frac{1}{2}$%.

If we now return to Figs. 4(a), 5, and 6, we note that the scatter of the points from the smooth curves has an rms value of about 1% of the normal-state value, with a few points well off the curves. The particular shapes of curves that we have put through the points in these three figures are not uniquely determined by the data. Nevertheless, it does seem that the emphasis we put on the straight-line segments, notably at the lowest temperatures, is justified. This is especially true in the case of the $t=0.34$ isotherm of Fig. 6, which could be fitted with a smooth curve about the energy gap only by an assumption of systematic errors near the two knees in the curve. In the case of Fig. 4(b), where the scatter has been reduced (by recent improvements in rf shielding), we find that in addition to the two knees, which are quite well established, there appear two small resonances, one at $3.38kT_c$ and the other at $3.70kT_c$. These are too well traced out to ascribe to scatter. Whether they are from some instrumental effect that we do not at this time understand, or whether they are real properties of aluminum must await more experiments. Thus, although less scattered data are desirable and perhaps even necessary to assure our interpretation, it seems that, with the data we present here, the straight-line segments are an essential feature of the curves. The curves at the higher temperatures are, unfortunately, more difficult to draw, in part because the slope discontinuities at these temperatures occur at frequencies where the data are sparse. Thus, two gaps are not generally observable in our data at the higher temperatures.

From Figs. 4, 5, and 6 we see that each of the three crystal faces, (100) with fourfold symmetry, (111) with threefold symmetry, and (110) with twofold symmetry, exhibit the same features. That is, they all start off at low frequencies with a small slope (zero for $t=0$) up to some critical frequency where the slope has its first discontinuous change, then at a somewhat higher frequency (about 10% higher) there is a second discontinuous change in slope and then a continuous increase in value toward the normal-state value. In the earlier work on aluminum at these frequencies,[2] the sample was polycrystalline and the data near the slope discontinuities (knees) were sparse, so that the presently observed double knees could not have been observed. Furthermore, the uncertainty in the position in energy of the knee in the earlier work was comparable to the spacing between the two knees observed in the present work. Thus, the present results are compatible with the earlier work.

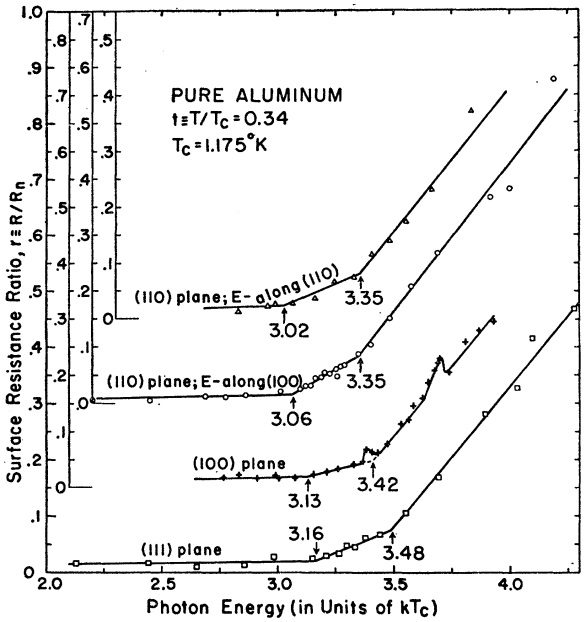

FIG. 7. Comparison of the $t=0.34$ isotherms of surface resistance ratio versus photon energy for the (111), (100), and two polarizations in the (110) plane for pure aluminum. The arrows indicate the energies at which there are discontinuities in the slopes of these curves and thus are to be associated with values for the superconducting energy gap.

The lower knee is to be interpreted as the first occurrence of excitation across the energy gap and thus is the smallest energy gap for electrons traveling parallel to the surface of the sample.[26] For the moment, let us consider the second knee as being identified with a second, larger energy gap occurring either in some other crystallographic direction (but still for electrons traveling parallel to the surface of the sample) or in the same direction. We examine this hypothesis in more detail below in the discussion. From this viewpoint, then, each of the microwave polarizations in each of the measured crystal faces reveals two distinguishable energy gaps (equal to the photon energies at each of the knees).

Next, we compare the absorption for different crystal orientations. In Fig. 7, we display surface resistance ratio versus photon energy for the $t=0.34$ curves for a (100) face, a (111) face, and two different polarizations in a (110) crystal face. There are clearly differences among the various orientations, indicating anisotropy in the absorption and therefore anisotropy in the energy gaps. However, this anisotropy is too small to measure accurately. The anisotropy appears to be about 3%, but with our uncertainty of about 1% in each of the gap determinations, it is difficult to obtain a quantitative measure of the differences. The values extrapolated to $t=0$ of these data are tabulated, along with the residual resistivity ratios for the three aluminum samples, in Table I.

TABLE I. Measured energy gaps for single-crystal aluminum, corrected to $t=0$.

Sample	d.c. resistivity ratio ($R_{300}/R_{4.2}$)	Crystal face	Electric field direction	Smaller energy gap (in units of kT_c)	Larger energy gap (in units of kT_c)
Al-24	2.6×10^3	100	100[a]	3.15±0.03	3.44±0.03
Al-20	1.8×10^3	111	110[a]	3.18±0.04	3.50±0.04
Al-18	2.2×10^3	110	100	3.08±0.04	3.37±0.04
			110	3.04±0.05	3.37±0.05

[a] Absorption is independent of electric-field polarization for this crystal face.

Finally, we show in Fig. 8 the temperature dependence of the lower energy gap inferred from the position of the lower knee for the (111) crystal face. This follows, within the experimental uncertainty, the form of the curve given in the BCS theory.

B. Zinc

The results for a single crystal of zinc were obtained before some of the sources of error were reduced to satisfactory levels. Consequently, there is a great deal of scatter in the data, enabling us to make only a crude estimate of the energy gap in a plane containing the c axis. The results for two polarizations at $t\equiv T/T_c=0.467$ ($T_c=0.838\pm0.002$°K [22]) are shown in Fig. 9. Let us ignore the violent oscillations in the data for $h\nu/kT_c<2.7$, since it is not clear whether these originate from real effects associated with the energy gap in zinc, or, as is more likely, from leakage of energy at resonant frequencies of the couplers used in the earlier work. Extrapolations to $r=0$ of the smoothly rising portions of the curves at $h\nu/kT_c\geq2.8$ indicate that the

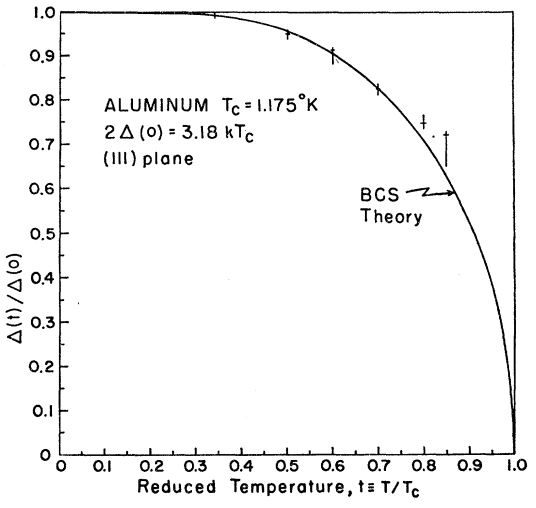

FIG. 8. The temperature dependence of the smallest energy gap in the (111) plane of aluminum. The ratio of the energy gap at reduced temperature t to that at absolute zero is plotted as a function of reduced temperature and compared with the form predicted by the BCS theory (Ref. 8).

[26] For the samples of aluminum $\omega\delta/v_F\simeq\lambda/\xi_0\simeq3\times10^{-2}$ at these frequencies. Thus, the effective electrons make an angle of at most a few degrees with the surface.

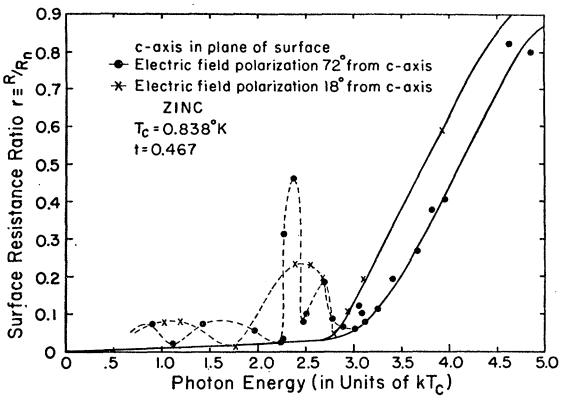

FIG. 9. Isotherms of surface resistance ratio versus photon energy for two electric-field polarizations in a single crystal of zinc. The violent fluctuations shown by the dashed lines may be of instrumental origin in these preliminary data.

energy gap in this plane is $(2.90\pm0.15)kT_c$ at $t=0.467$ for the average of the two polarizations. There is some evidence for anisotropy, but a quantitative estimate cannot properly be obtained from these preliminary data. Following Bardeen and Schrieffer,[10] we use the predicted variation of gap with temperature to extrapolate to $t=0$ and obtain the value $2\Delta(0)/kT_c=3.00\pm0.15$.

IV. DISCUSSION AND CONCLUSION

The interpretation of the results in the absence of more data and an adequate theory of anisotropic energy gaps is rather speculative. Instead of finding a broad knee in the curves of surface resistance versus photon energy as a result of a continuous variation of energy gap with crystalline direction, there appear to be only two rapid changes in slope (it is, of course, possible that there are additional changes in slope at higher frequencies which were not observed in our experiment). It seems reasonable to interpret these discontinuities in terms of two different energy gaps. Although two gaps are observed for a single electric-field polarization in a crystal face, it is possible that each is for a different crystal direction, since even in the regime of the anomalous skin effect we have averaging over those electrons traveling parallel to the surface of the sample. This averaging is weighted by $\cos^2\alpha$, where α is the angle between the electric-field polarization and the electron wave vector $\mathbf{k}$. Thus, because of the high symmetry in the cases of the (100) face and the (111) face, any differences in absorption by electrons with different wave vectors average in such a manner that the absorption is independent of polarization. However, in the (110) face, in spite of the averaging, it is possible to see some polarization anisotropy effects such as are expected to arise from energy-gap anisotropy. Indeed, we observe a small anisotropy for the two orthogonal polarizations in the (110) face, but the effect is not sufficiently large to exceed appreciably the experimental uncertainty in the data. Thus, the data taken as a whole suggest two distinct values of the energy gap; however, if they are associated with different crystalline directions, the data do not give enough information to assign gap values in particular directions.

We can only speculate about possible sources of the two energy gaps observed. Since aluminum has its Fermi surface in two different Brillouin zones,[27] it is conceivable that each gap is associated with that part of the Fermi surface that is in a given zone; or possibly, one gap comes from those parts of the Fermi surface that are away from the zone boundaries, while in the region of the zone boundaries there is a distortion of the Fermi surface and of the energy gap[28] which is dominated by a single value of the gap. In either of these cases it appears that the existence of the double gap is to be associated with the anisotropy of the Fermi surface. Thus, it should be interesting to study materials with different distortions of the Fermi surface.

The small anisotropy that is observed among the different crystal faces is just large enough to be significant in view of our experimental accuracy. It is far too small to account for the shift in superconducting transition temperature observed in aluminum by Chanin, Lynton, and Serin[29] by use of the Anderson theory of dirty superconductors.[11] In this theory, the effect of impurities is to wash out anisotropy of the energy gap by having the different gaps approach a single average value, the smallest gaps increasing while the largest gaps decrease, causing T_c to decrease. The magnitude of the effect observed by Chanin *et al.*[29] requires that the largest gap change by 5 to 10%, too large an effect to be consistent with our observed anisotropy. Therefore, we conclude that, if Anderson's mechanism is to account for the results of Chanin *et al.*, either there is an anisotropic energy gap larger than any given in Table I, having more anisotropy than we observe, or the upper gap of each pair in Table I decreases by several percent with the addition of impurities.

There have been several studies of other materials, using a variety of techniques, in which multiple energy gaps, usually attributed to anisotropy,[12–15] have been inferred from the data. These studies are enumerated in the Introduction and are not discussed further here.

The previous work on polycrystalline aluminum by Biondi and Garfunkel[2] found the energy gap to be $3.25\pm0.10kT_c$. This compares with the energy gaps found in the present work of $3.04kT_c$ to $3.50kT_c$. The single gap inferred by Biondi and Garfunkel from the absorption threshold curves would correspond to

[27] B. Segall, Phys. Rev. **131**, 121 (1963); **124**, 1797 (1961).

[28] This latter possibility was suggested to us by Walter Harrison (private communication). He rejects the idea that there can be a different energy gap for undistorted parts of the Fermi surface in different zones, since in any zone the electrons appear nearly free except near the zone boundary.

[29] G. Chanin, E. A. Lynton, and B. Serin, Phys. Rev. **114**, 719 (1959).

some average over all the energy gaps of aluminum, and it is therefore in essential agreement with the present results.

There have been several determinations of the energy gap of aluminum by tunneling experiments.[5,30–32] The experiments by Giaever and Megerle[5] and by Shapiro *et al.*[30] seem to disagree with the present results, while those of Douglass and Meservey[31] and of Zavaritskii[32] seem to be in agreement. However, since all of the tunneling experiments have been conducted on aluminum films which have been deposited on an insulating substrate, they probably refer to strained material (as evidenced by the shifted superconducting transition temperatures) and should not be directly compared with our results.

David and Poulis[33] have estimated the energy gap in single-crystal aluminum from the temperature dependence of the ultrasonic attenuation for both the (100) and (110) directions of propagation. They find the gap to be $(3.7\pm0.3)kT_c$ in both of the above directions. With such a large estimated error it is not surprising that they found no anisotropy of the order we observe. Furthermore, their technique does not permit observation of multiple gaps in a single direction of propagation, making it impossible for a detailed comparison with our results.

Masuda and Redfield,[34] in their investigation of the temperature dependence of the nuclear spin relaxation rate in superconducting aluminum, found that they could explain their results with an energy gap of average value $3.2kT_c$ but required also a broadening (a range of values) of about $0.3kT_c$. They suggested anisotropy as the source of this broadening. Our results appear to confirm the validity of their model.

The only work with which we can compare our preliminary result on zinc is that of Zemon and Boorse,[35] who measured the microwave absorption in the frequency range 50 to 75 Gc/sec. They were able to determine $r(t)$ for $t>0$, and, by using the temperature dependence of $r(t)$ given by Pippard,[24] extrapolate their results to obtain $r(0)$. The frequency dependence of $r(0)$ leads to the value $2\Delta(0)=3.0kT_c$ in remarkable agreement with our value. This is not quite so good an agreement as it appears, since we determined the superconducting transition temperature of zinc to be $T_c=0.838°\mathrm{K}$, compared to the value of 0.825°K of Zemon and Boorse, but it is still well within the experimental error of either experiment.

To sum up, the present results indicate that there are two distinct energy gaps in superconducting aluminum ($T_c=1.175°\mathrm{K}$) observed in each of the crystal faces (100), (110), and (111), differing from each other by about 10%. In addition, there is a small anisotropy observed in the values of each gap measured with radiation incident on different crystal faces, the observed anisotropy amounting to about 3% or just outside the experimental error. At present, we cannot relate these results to the known crystal structure or Fermi surface structure of aluminum; however, they are in agreement with other evidence for multiple energy gaps in aluminum.

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[30] S. Shapiro, P. H. Smith, J. Nicol, J. L. Miles, and P. F. Strong, IBM J. Res. Develop. **6**, 34 (1962).

[31] D. H. Douglass, Jr., and R. Merservey, *Proceedings of the Eighth International Conference on Low Temperature Physics* (Butterworths Scientific Publications, Ltd., London, 1963), p. 180.

[32] N. V. Zavaritskii, Zh. Eksperim. i Teor. Fiz. **41**, 657 (1961) [English transl.: Soviet Phys.—JETP **14**, 470 (1962)].

[33] R. David and N. J. Poulis, *Proceedings of the Eighth International Conference on Low Temperature Physics* (Butterworths Scientific Publications., Ltd, London, 1963), p. 193.

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

[35] S. Zemon and H. A. Boorse, Bull. Am. Phys. Soc. **9**, 268 (1964).