Millimeter Wave Absorption in Superconducting Aluminum. I. Temperature Dependence of the Energy Gap

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Measurements of the temperature dependence of the microwave absorption in superconducting aluminum have been made in the wavelength region 20 mm to 3 mm. The results, when plotted as isotherms of surface resistance ratio *vs* photon energy, show that, at a well-defined energy for each temperature, there is a rapid rise in absorption with increasing energy. This has been interpreted as the onset of absorption resulting from direct excitation of electrons across a forbidden energy gap. The isotherms then permit the determination of the temperature dependence of this energy gap. At absolute zero the gap value is found to be $\mathcal{E}_g(0)=(3.2\pm0.1)kT_c$ (where $T_c=1.178$°K is the superconducting transition temperature), in reasonable agreement with the theoretical value of $3.52kT_c$ obtained by Bardeen, Cooper, and Schrieffer. Furthermore, the temperature variation of the gap exhibits the same shape as that given by the theory. Finally, reasonable agreement is obtained between theory and experiment concerning the detailed shapes of the surface resistance *vs* temperature curves over the measured wavelength range, provided that the experimental value $\mathcal{E}_g(0)$ is used in the theory.

I. INTRODUCTION

THE existence of a gap in the electronic energy spectrum of superconductors has become evident both from experimental and theoretical points of view. Experimentally an energy gap has been inferred from two basically different observations: (a) the existence of a threshold frequency in the electromagnetic absorption spectrum,[1–3] and (b) the exponential temperature variation of properties which depend on the number of electrons thermally excited across the energy gap.[3–6] Recent theories of superconductivity[7,8] have an energy gap in the electronic spectrum which is a universal function of the superconducting transition temperature, T_c. Furthermore the gap width is a function of temperature, decreasing monotonically to zero at T_c. Recently, Tinkham and Ferrell,[9] and Ferrell[10] have shown that, independent of a detailed microscopic model, certain kinds of gaps in the electronic energy spectrum at the Fermi surface lead to the low-frequency electromagnetic behavior of a superconductor; in particular, they give rise to the characteristic diamagnetism. Qualitatively, the thermal properties also follow from an energy gap model; in fact, the existence of an energy gap was originally inferred from the temperature dependences of the specific heat[5] and of the thermal conductivity[4] at low temperatures.

It is the purpose of this paper to describe in detail an experiment on the temperature and frequency dependence of the microwave absorption in superconducting aluminum, previously reported in preliminary form.[11,2] The range of frequencies was selected in order to observe the changes in absorption that occur as the photon energy becomes greater than the expected energy gap. This absorption change was found to be sufficiently abrupt to permit a determination of the magnitude of the energy gap. Furthermore, the observed temperature dependence of the absorption curves has permitted us to deduce the temperature dependence of the gap. Finally, a comparison of our results with the theory of Bardeen, Cooper, and Schrieffer[7] (BCS) and with recent thermal measurements on aluminum reveals general qualitative and, in some cases, quantitative agreement.

The range of frequencies where direct excitation of electrons across the gap becomes evident ($\nu>kT_c/h$) is just above the range in which extensive superconducting absorption studies were made a decade ago.[12] In this lower frequency range, energy is absorbed by the electrons that have been thermally excited across the energy gap. A typical curve for microwave absorption at frequencies well below the energy gap has the form given in Fig. 1. The abscissa is the reduced temperature, $t\equiv T/T_c$, where T_c is the superconducting transition temperature. The ordinate is the surface resistance[13]

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[1] P. L. Richards and M. Tinkham, Phys. Rev. Letters **1**, 318 (1958).

[2] M. A. Biondi and M. P. Garfunkel, Phys. Rev. Letters **2**, 143 (1959).

[3] For a general review see Biondi, Forrester, Garfunkel, and Satterthwaite, Revs. Modern Phys. **30**, 1109 (1958).

[4] B. B. Goodman, Proc. Phys. Soc. (London) **A66**, 217 (1953).

[5] Corak, Goodman, Satterthwaite, and Wexler, Phys. Rev. **102**, 656 (1956).

[6] A. G. Redfield and A. G. Anderson, *Proceedings of the Kamerlingh Onnes Conference on Low-Temperature Physics, Leiden, June, 1958* [Physica **24**, S150 (1958)].

[7] Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957); hereafter referred to as BCS.

[8] Bogoliubov, Tomalchev, and Shirkov, *A New Method in the Theory of Superconductivity* (Academy of Sciences U.S.S.R. Press, Moscow, 1958).

[9] M. Tinkham and R. A. Ferrell, Phys. Rev. Letters **2**, 331 (1959).

[10] R. A. Ferrell, Bull. Am. Phys. Soc. Ser. II, **4**, 225 (1959).

[11] Biondi, Garfunkel, and McCoubrey, Phys. Rev. **108**, 495 (1957).

[12] A. B. Pippard, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1954), Vol. 6, pp. 1–45. This paper gives a detailed review of the low-frequency microwave work in both normal metals and superconductors.

[13] The surface resistance is the real part of the surface impedance, Z, defined as $Z\equiv4\pi(E/H)_0$, where $(E/H)_0$ is the ratio of

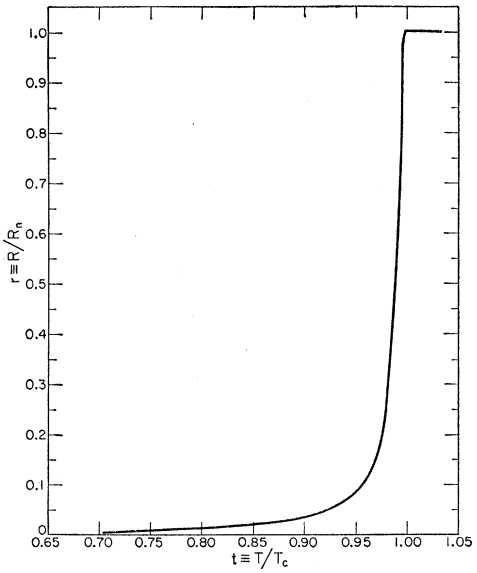

FIG. 1. Surface resistance ratio r as a function of reduced temperature t at microwave frequencies. This is the form of the curve for superconducting aluminum at a wavelength at 25 cm (after Faber and Pippard, reference 23).

ratio, $r \equiv R/R_n$, where R_n refers to the surface resistance in the normal state just above T_c. For the high conductivity of pure metals r is accurately equal to the ratio of the absorptivities in the two states. The rapid drop in absorption just below the transition temperature is largely caused by the rapid reduction in the penetration of the electromagnetic field into the superconductor. The drop to zero at $T=0$ is the result of the disappearance of thermally excited electrons.

II. EXPERIMENTAL METHOD

The objectives of the experiment involved the determination of the absolute values of absorptivity over a wide range of frequencies on a single sample whose surfaces were sufficiently good to approximate the behavior of an ideal bulk superconductor. In addition, it was desirable to carry the measurements to temperatures sufficiently below T_c that very few thermally excited (normal) electrons remained. These objectives were achieved by use of (a) a sample in the form of a one-piece wave guide with chemically brightened surfaces, (b) a calorimetric determination of absolute absorption of microwave energy by monitoring the temperature rise produced in the sample, and (c) a double Dewar apparatus employing liquid He^3 in the inner section which reached $\sim 0.35°K$ by pumping. A detailed description of the experimental techniques is given below.

electric to magnetic fields at the surface of the metal. In general, $Z \equiv R + iX$ is complex; the imaginary part is the surface reactance.

(a) Sample Form and Preparation

In view of the uncertainty concerning the expected value of the energy gap and of the need to measure the absorption over a rather broad frequency range which includes the gap, aluminum samples[14] were fabricated in the form of wave guides short-circuited at one end. The internal cross section of the guide was 0.020 in. $\times$0.420 in. Thus, the cutoff wavelength was 21 mm ($h\nu \simeq 0.6kT_c$) and measurements were possible over a continuous range of shorter wavelengths. The reduced height of the guides served to increase the absorption in the $\sim$3-in. long samples. Even so, the maximum absorption of the guide (in the normal state just above T_c) was only $\sim 1\%$ of the incident energy. It was therefore essential to eliminate any joints in the sample, since mechanical contacts were likely to give comparable absorption. In the final, and best, sample (Al 5c) a one-piece extruded section of aluminum[15] was used with a short-circuiting end plate heliarc welded to the end (see Fig. 2). The heliarc process provided a fused aluminum joint without adding measurable impurities. An earlier sample (Al 3a) was fabricated in two halves with a blind-ended wave-guide cross section sawed and milled to shape; the two sections were then bolted together [see Fig. 2(b)]. The cut in the wave guide occurred at zero current lines so that under ideal conditions, with the proper mode of guide excitation, no absorption should take place at the mechanical joint between the two halves.

The two types of wave guide samples were processed in similar fashion; the preparation of the one-piece sample is discussed here. The aluminum extrusion was mechanically polished on the inside wave guide surfaces and machined on the outside to form the coupling flanges, chemically etched (50% HCl solution) and rinsed, then annealed at 500°C for 4 hours. The shorting end plate, similarly cleaned, was then heliarc welded to the sample. The whole was lightly etched by drawing solution through the sample (via small holes drilled in the end plate), again annealed, and finally chemically brightened[16] on all surfaces exposed to microwave energy by means of a solution of 94% orthophosphoric acid and 6% nitric acid. This preparation, together with proper coupler design to eliminate spurious absorption, resulted in a sample whose residual absorption was negligible. In addition, at our longest wavelength, 19 mm ($h\nu = 0.64kT_c$) the transition region was sufficiently sharp and the data obtained on the two different samples agreed well enough that we conclude that the absorption measurements are characteristic of pure bulk aluminum.

[14] The material used was high-purity (99.99+%) aluminum ingots supplied by the Aluminum Company of America.
[15] The sample was extruded at $\sim$485°C around a steel mandrel.
[16] Chemical brighteners have a polishing action similar to that obtained by electropolishing techniques and can be used on closely spaced interior surfaces where electropolishing is not convenient.

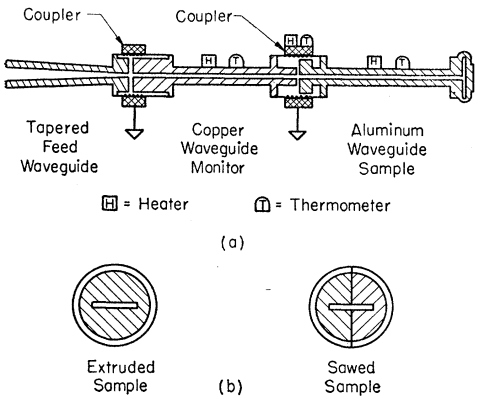

FIG. 2. Schematic representation of the measuring section of the apparatus: (a) Cross section view of the wave-guide assembly showing the aluminum sample and the copper monitor. The couplers provide alignment of the sections but maintain thermal isolation. They are constructed of thin-walled stainless steel tubing, silver soldered to a central ring of heavy copper. The inner surface of the copper is coated with a 0.005 in. thick layer of aquadag to absorb leakage radiation (see text). The ∇ symbols represent thermal "grounding" of the couplers to the liquid He^3 bath. Electrical heaters H, and carbon resistance thermometers T, are mounted on the two wave guides and on the copper ring of the coupler. (b) End view of the two wave-guide samples; the extruded sample, Al 5*c* and the sawed sample, Al 3*a*.

Two additional checks on sample quality were made. A sample in suitable form for dc conductivity measurements was cut from the same stock and processed in similar fashion to the wave-guide section. The ratio of resistances at 300°K and 4°K was 700, corresponding to a residual resistivity of 4.4×10^{-21} esu. Also, upon completion of the experiment, the extruded sample was opened for examination. The surface showed a few polishing scratches and varied from a shiny finish over most of the surface to a matted finish in patches.

(b) Measuring Section

The measuring section of the apparatus consists of the aluminum wave-guide sample and a copper wave-guide monitor suitably coupled together to prevent leakage of microwave energy, yet essentially thermally isolated from each other (see Fig. 2). These sections are fed by a tapered wave-guide section which transforms from the ordinary K-band guide size 0.170 in.×0.420 in. to the measuring section size 0.020 in.×0.420 in.

The measurements are calorimetric in nature; that is, the absorption of energy in the wave-guide sample causes a temperature rise which is detected by carbon resistance thermometers.[17] The time constants of response of the copper and aluminum samples are adjusted by choice of the heat leaks connecting them to the temperature regulated base. Temperature rises resulting from absorption of microwave energy are reproduced, with the microwaves off, by the dc heaters.[18] By measurement of the dc power required, the absorbed microwave power is determined, without appeal to thermometer calibration. With thermal time constants of ~6 sec the minimum detectable absorbed power was 10^{-8}–10^{-9} watt. In a given run the base was set at a fixed temperature and the temperature of the aluminum sample varied over the full range ($\sim0.38° < T < 1.25$°K) by means of the dc heater attached to the sample.

The couplers are designed to eliminate spurious absorption effects in the aluminum measurements resulting from the inevitable mechanical contact between sample and coupler. In this design the energy leaking out of the space between the wave guides is made small by using the minimum practical spacing between the sections.[19] As the leakage microwave energy propagates into the coupler space it encounters the aquadag coating on the copper ring, intended to absorb and thermally "ground" energy which otherwise might reach the mechanical joint between the coupler and the aluminum. Furthermore, the energy is made to divide so that most of it is in the copper monitor-coupler space instead of the aluminum sample-coupler space (see Fig. 2). This is accomplished by using a small spacing between the aluminum flange and coupler. This design, which was evolved from several earlier versions, succeeded in reducing spurious absorption in the extruded sample measurements to the point where the residual absorption at low temperatures is less than 1% of the normal state value (see Sec. III).

(c) Double Dewar Apparatus

In order to reach temperatures very much lower than the transition temperature of the aluminum sample ($T_c=1.178$°K) a double Dewar apparatus, employing liquid He^3 in the inner section, was used (see Fig. 3). The inner section is contained in an evacuated housing. The use of a gold O-ring gasket and demountable flanges gives access to the measuring section. The outer liquid He^4 bath is reduced in temperature to ~1.3°K by pumping and serves as a radiation shield for the inner section. Connections between the outer and inner sections are limited to poor thermal conductors such as a thin-walled stainless steel section in the tapered feed wave guide and 0.003-in. diameter niobium leads for the heaters and thermometers.

The inner reservoir is initially filled with ~6 cc of liquid He^3 from a five liter volume gas reservoir at ~0.8 atmosphere. A closed pumping system is used consisting of a modified[20] Welch Duo Seal Pump, type

[17] Speer type AR 7404–1200 ohm resistors.

[18] The heaters consisted of 0.003-in. diam manganin wire having a total resistance of 100 ohms.

[19] At operating temperatures the spacing was estimated to be ~0.003 in. Using the heater and thermometer attached to the coupler, measurements of the leakage power were made. It was found to be less than 1% of the power incident on the wave guide.

[20] The Welch pump was modified by addition of rubber O-ring seals between all sections, a double shaft seal, and all "dead" volumes were reduced to minimize the quantity of oil required (~100 cc).

1405, and a Consolidated Electrodynamics Corporation type MB-10 booster pump rated at 10 liters/sec speed. With this system the inner section reaches a temperature of 0.35°K and the liquid He^3 lasts for approximately one day. The temperature of the inner Dewar is electronically regulated to within $\pm 10^{-5}$°K by means of a sensing thermometer and heater attached to the liquid He^3 reservoir.

The values of the absolute temperatures were determined and the resistance thermometers calibrated by a vapor pressure bulb attached to the He^3 reservoir (see Fig. 3). The vapor pressure bulb was connected through a 0.219 cm diam tube to a McCleod gauge at 300°K. After the thermomolecular pressure corrections[21] were made, temperatures were calculated from the He^3 vapor pressure-temperature scale.[22]

(d) Microwaves and Other Details

The sources of microwave energy were reflex klystrons rated at cw outputs of one milliwatt or greater. The available klystrons permitted us to operate over a continuous range of wavelengths from 19 mm to ~5.0 mm; then there was a gap in our spectrum. The next source covered the range 4.2 mm–3.95 mm; then there was a gap (unfortunately, in a most interesting region of this experiment—see Sec. IV) until the final source, which covered the range 3.36–3.12 mm.

In order to minimize effects on the transition temperature resulting from either the earth's or stray laboratory magnetic field a set of Helmholtz coils was used to cancel the field to ≤ 0.05 gauss over the region of the sample.

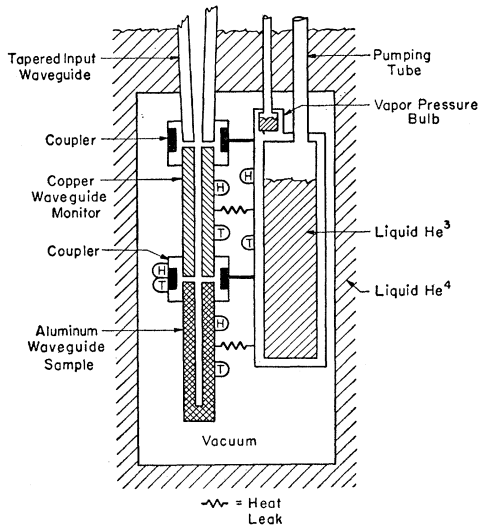

FIG. 3. Schematic diagram of the low-temperature part of the apparatus. The symbols H and T refer to heaters and carbon resistance thermometers, respectively. (See the text for the description of the functions of the various components.)

[21] T. R. Roberts and S. G. Sydoriak, Phys. Rev. **102**, 304 (1956).
[22] S. G. Sydoriak and T. R. Roberts, Phys. Rev. **106**, 175 (1957).

The reduced temperature scale used to display the experimental results was based on a transition temperature, $T_c = 1.178$°K, determined from the 19-mm wavelength absorption curve. The transition region, even at this rather substantial photon energy ($h\nu = 0.64kT_c$), was sufficiently sharp, ~0.001°K, to permit this determination with some confidence. This value of T_c for aluminum is in essential agreement with the value 1.17°K obtained by longer wavelength microwave studies of Faber and Pippard[23] but disagrees substantially with the value 1.196°K obtained by critical magnetic field measurements of Cochran and Mapother.[24]

III. MEASUREMENTS

The experimental determinations of the absorptivity of the aluminum are conventionally expressed as curves of surface resistance ratio $r \equiv R/R_n$ *versus* reduced temperature $t \equiv T/T_c$. (R is the surface resistance; the subscript n refers to the normal state value at T_c or slightly above.) The surface resistance is directly proportional to the absorptivity; thus the measurements of the power, P, absorbed in the aluminum wave guide relative to that absorbed in the copper monitor wave guide yield r through the relation

$$r(t) = \frac{P_{\mathrm{Al}}(t)/P_{\mathrm{Cu}}}{P_{\mathrm{Al}}(t \geq 1)/P_{\mathrm{Cu}}}. \tag{1}$$

Measurements were carried out at thirteen wavelengths ranging from 19 mm to 3.1 mm ($0.64kT_c \leq h\nu \leq 3.9kT_c$). The curves obtained with the one-piece extruded sample at six representative wavelengths are shown in Fig. 4. These data are plotted as measured, with no normalization or other adjustment. As will be discussed shortly, this condition is essential if we are to draw conclusions concerning the existence and value of the suggested energy gap from our experimental observations, without appeal to theory.

The curve obtained at the longest wavelength, 19.05 mm, resembles the lower frequency microwave data (Fig. 1) in that there is a rather abrupt decrease in the absorption as the temperature falls slightly below T_c and the absorption tends essentially to zero as t approaches zero. At successively shorter wavelengths (higher photon energies) the absorption falls more and more slowly as the temperature is reduced below T_c. However, for all photon energies less than $3.08kT_c$ the absorption effectively approaches zero as $t \to 0$. In terms of an energy gap picture, the absence of absorption at absolute zero indicates that these photon energies ($h\nu \leq 3.08kT_c$) are too small to span the gap. Similarly, the substantial absorption at absolute zero indicated by the curves for $h\nu \geq 3.63kT_c$ indicates that

[23] T. E. Faber and A. B. Pippard, Proc. Roy. Soc. (London) **A231**, 336 (1955).
[24] J. F. Cochran and D. E. Mapother, Phys. Rev. **111**, 132 (1958).

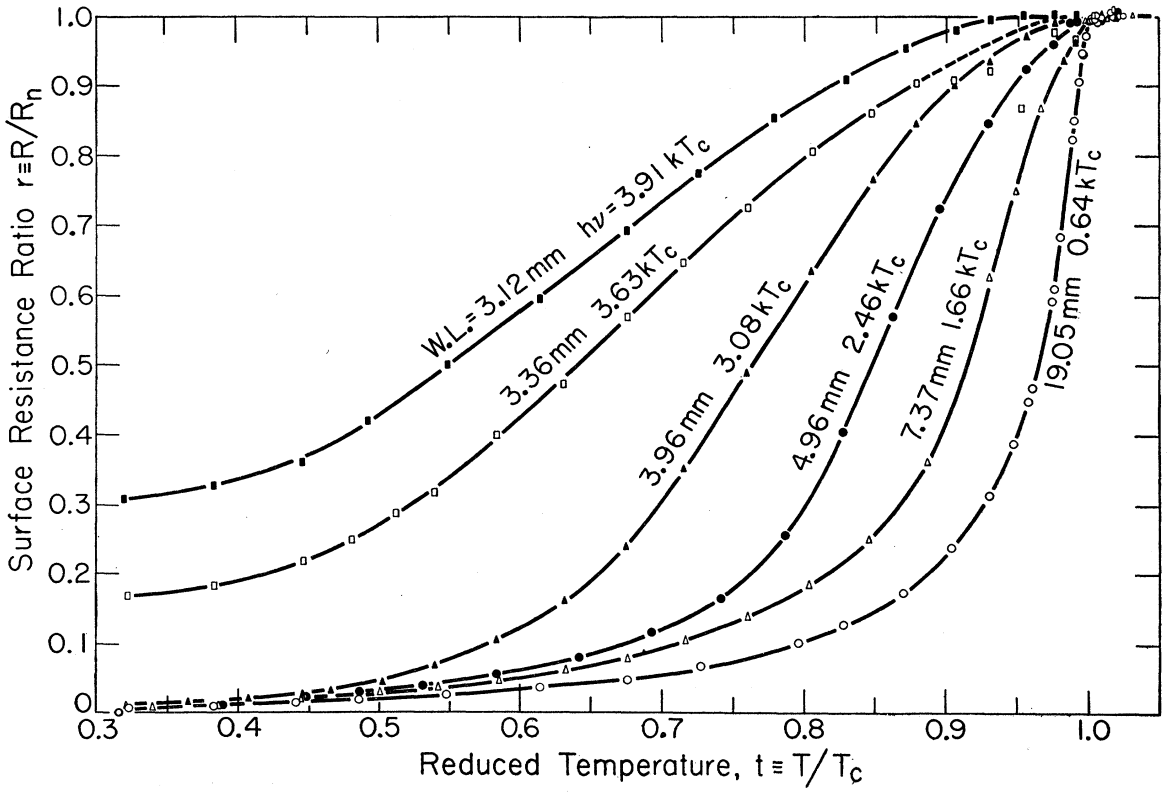

FIG. 4. Measured values of the surface resistance ratio r of superconducting aluminum as a function of the reduced temperature t at several representative wavelengths. The wavelengths and corresponding photon energies are indicated on the curves.

these photon energies induce transitions of electrons across the forbidden gap.

In order to investigate possible sample dependence of these results, measurements were carried out on the two-piece sawed sample (Al 3*a*) at a wavelength for which only the fundamental guide mode can be excited, wavelength = 19 mm. It was hoped that possible current flow across the mechanical contacts between the two halves would thus be avoided and spurious absorption from this source eliminated. However, zero current flow, even in the fundamental guide propagation mode, requires absolute symmetry of the two halves of the sample; unfortunately, slight nonuniformities in the widths of the two sawed slots were unavoidable. The results at 19 mm obtained with the two samples are shown in Fig. 5. It will be seen that the two curves agree, within experimental error, except at the lower temperatures. Here a systematic deviation corresponding to an additional absorption of $\sim 0.5\%$ occurs in the sawed sample, and is most probably the result of the above mentioned asymmetry in the slot. Thus, we conclude that the absorption is not sample dependent but is essentially characteristic of pure bulk aluminum.

In order to obtain more accurate information concerning the value of the energy gap at absolute zero and the variation of the gap with temperature, isotherms of the surface resistance ratio as a function of the reduced energy $h\nu/kT_c$ were constructed from the measurements of Fig. 4 (see Fig. 6). The data points were obtained from the r *vs* t curves at each of the 13 measured wavelengths. If we consider the $t=0.7$ curve, it will be seen that the absorption rises slowly with increasing frequency (photon energy) until $h\nu/kT_c \sim 2.6$, following which the absorption increases much more rapidly.

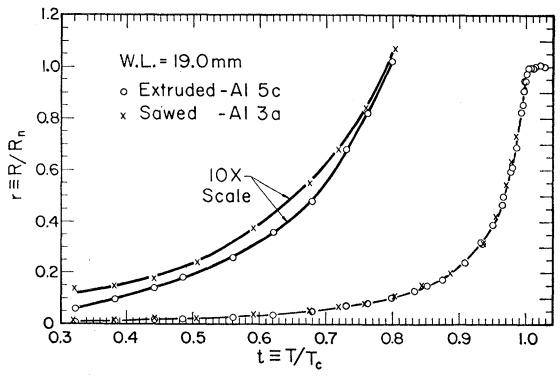

FIG. 5. Sample dependence of the measured values of the surface resistance ratio at 19 mm wavelength. The crosses refer to the sawed sample, Al 3*a*, and the circles refer to the extruded sample, Al 5*c*. The scale for the upper curves is ten times that shown on the ordinate.

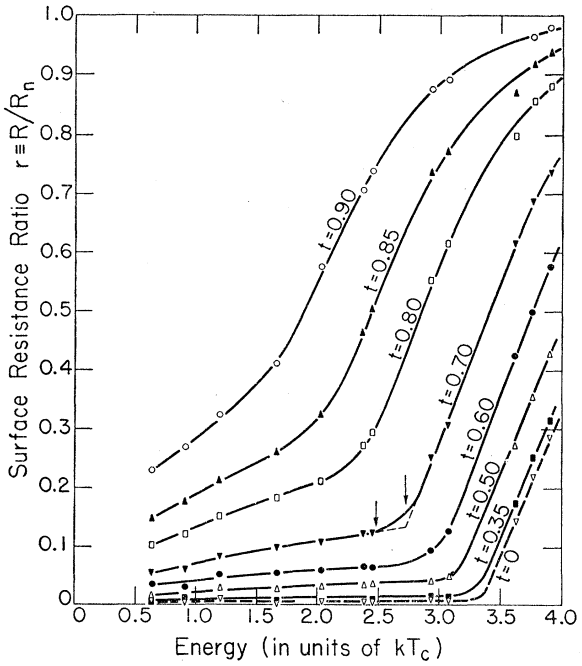

FIG. 6. Isotherms of surface resistance ratio r as a function of reduced photon energy $h\nu/kT_c$. The points are taken from the curves of Fig. 4 at each of the measured frequencies. The arrows on the $t=0.7$ curve indicate the estimated limits of uncertainty in determining the value of the energy gap.

The effect of the onset of the increased absorption is quite pronounced for the low-temperature isotherms, becoming less distinct as $t\rightarrow 1$. The curve for $t=0$ is derived through an extrapolation procedure described in the next section. If one argues that, at a given temperature, a fixed number of electrons are *thermally* excited across the forbidden gap, then the slow variation of absorption with frequency may be ascribed to these electrons, while the abrupt increase in absorption above a critical frequency can be ascribed to electronic transitions induced by photons possessing sufficient energy to span the gap. The energy gap values deduced from Fig. 6 and limitations of this approach are discussed in the next section.

IV. DISCUSSION

In order to obtain an estimate of the energy gap at $t=0$ we must extrapolate the absorption curves of Fig. 4 to $t=0$. Pippard,[25] basing his argument on the two-fluid model, proposed that at low temperatures, r is a function of $f(t)=t^4(1-t^2)/(1-t^4)^2$. In view of the energy gap it would seem more reasonable to expect that r is a linear function of $g(t)\sim\exp(-\mathcal{E}_g/2kT)$. However, for the accuracy that we are interested in, these give essentially the same result for extrapolations of our data. Figure 7 shows the low-temperature portions of several of the absorption curves when plotted against $f(t)$. Most of the curves are fairly straight lines when plotted in this way, giving some justification for the method. All of the curves for $h\nu/kT_c\leq 3.08$ have an intercept at $t=0$ which is less than 1%, and the average is about 0.3%. We assume that this residual absorption is extraneous and due either to leakage into the couplers, imperfections in the sample surface, or foreign material deposited on the sample surface.[26] For photon energies such that $h\nu/kT_c\geq 3.63$ the substantial absorption at $t=0$ is assumed to result from direct excitation across the energy gap. (Extraneous absorption of the magnitude observed at the lower photon energies would make a negligible difference at these frequencies.) From the extrapolations of Fig. 7 we obtained the points for the $t=0$ curve of Fig. 6.

At low temperatures ($t<0.6$) the absorption curves of Fig. 6 show an abrupt increase in absorptivity at a fairly well defined photon energy, indicating that the energy gap has been exceeded. The major uncertainty associated with determining precisely this absorption edge results from the limited number of frequencies at which data are available. It is necessary to interpolate between $h\nu/kT_c=3.08$ and $h\nu/kT_c=3.63$ to obtain the critical photon energy (the width of the gap) at temperatures up to $t=0.6$. At the higher temperatures the interpolation range is not so large, but the more rapid frequency variation of the absorption due to the thermally excited electrons makes the determination of the onset somewhat uncertain. In addition, at finite temperatures, the determination of the value of the energy gap from the onset of increased absorption is complicated by the fact that the electromagnetic skin depth alters in the vicinity of an absorption edge. This leads to a slight increase[27] in the surface resistance at photon energies less than the energy gap.

The above considerations are taken into account in establishing the values of the energy gap and the estimated limits of error. These are indicated by the arrows on the $t=0.7$ curve in Fig. 6, and by the vertical extent of the rectangular symbols in Fig. 8, which shows the deduced values of the energy gap $\mathcal{E}_g$ as a function of reduced temperature. The solid line is the best smooth curve drawn through the points and forced to go to zero at $t=1$. The dashed curve is from the theory of Bardeen, Cooper, and Schrieffer.[7] In shape, the curves agree very well, but the absolute values of the predicted energy gaps are about 10% larger than those deduced from the experiment. This is at least as good as one

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

[26] It is conceivable that the sample has some true residual absorption at $t=0$ and photon energies less than the energy gap. This could be the result of some electrons remaining normal at $t=0$. If this were indeed the case, we estimate that the maximum number of electrons that can remain "uncondensed" is ~1% of the normal electrons at T_c.

[27] In order to show that the corrections to the deduced energy gap values resulting from this effect are relatively small, it is necessary to calculate the surface reactance X. We do this in the following paper [M. A. Biondi and M. P. Garfunkel, Phys. Rev. **116**, 862 (1959)], in which we also discuss the frequency dependence of the skin depth.

can expect for the highly idealized BCS theory. Because of the necessary interpolation between experimental frequencies, the uncertainty in the experimental value of $\mathcal{E}_g(0)$ is about $\pm 3\%$. The interpolation indicated in Fig. 6 gives the value $\mathcal{E}_g(0)=3.25\pm 0.10kT_c$.

Biondi, Garfunkel, and McCoubrey[11] (BGM) in measurements over smaller frequency and temperature ranges ($0.65<h\nu/kT_c<3.04$ and $0.75<t<1.0$) were also able to infer a temperature varying energy gap in superconducting aluminum. Because of the limited extent of the data, it was necessary to resort to a less direct method to obtain the temperature dependence of the energy gap. It was assumed that the microwave absorption is the sum of two parts; a background absorption by those electrons that have been *thermally* excited across the energy gap, and absorption resulting from *direct* excitation of electrons across the gap by sufficiently energetic photons. The background absorption, calculated as described in the Appendix, is subtracted from the total absorption, the difference being ascribed to direct excitation across the gap. It is found that at each photon energy there is a temperature below which there is no direct excitation across the gap.

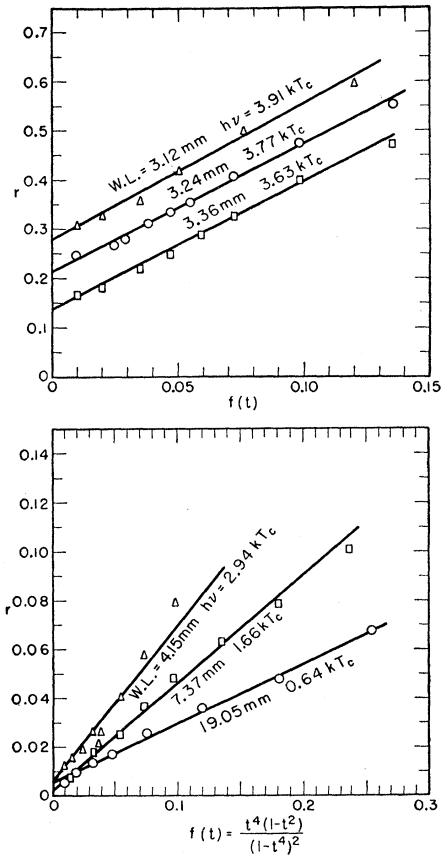

FIG. 7. The measured low-temperature values of the surface resistance ratio r as a function of $f(t)=t^4(1-t^2)/(1-t^4)^2$ for several representative wavelengths. These curves are used to extrapolate the values of r to $t=0$.

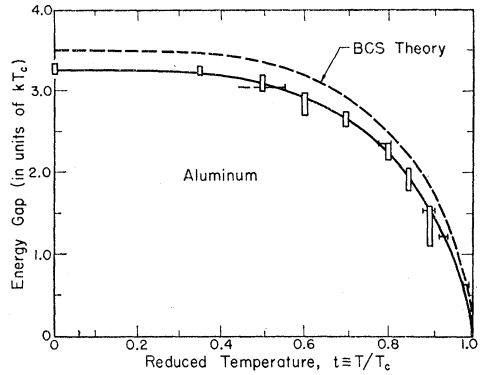

FIG. 8. The temperature dependence of the energy gap in superconducting aluminum. The solid line is the experimentally determined curve and the dashed line is from the theory of Bardeen, Cooper, and Schrieffer, reference 7. The rectangular symbols are from the measurements on Al 5*c*. They are derived from Fig. 6 as described in the text. The horizontal bars are from Biondi, Garfunkel, and McCoubrey, reference 11.

At this temperature, then, the energy gap is just equal to the photon energy. The results so obtained are plotted as horizontal bars in Fig. 8. The agreement with our present results is very good considering the uncertainties of the above procedure; especially since our present results show that the data in BGM contained some extraneous absorption—probably from leakage of microwave energy. We are thus led to conclude that the success of the BGM method results from the large effect of direct excitation, so large that the errors introduced by the sources mentioned above only have a minor effect on the estimate of the energy gap.

A more rigorous comparison between theory and experiment is provided by a detailed examination of the predicted shape of the surface resistance *vs* temperature curves. Unfortunately, the theory of microwave absorption in superconductors has not been worked out for the conditions of the experiment. The theory of Bardeen and Mattis[28] applies to certain limiting situations, namely, when $\delta/l\ll 1$ and $\lambda/\xi_0\ll 1$ (the extreme anomalous limit). δ is the skin depth and l the electron mean free path in the normal state, λ is the superconducting penetration depth, and ξ_0 the superconducting coherence length. In the case of our aluminum sample at these frequencies, the conditions above are not quite met, since $\delta/l\simeq 0.015$ and $\lambda/\xi_0\simeq 0.04$. However, it seems that we are sufficiently close to the limiting case to introduce only a small error by the assumption that we are in the extreme anomalous limit.

For this limiting case, Bardeen and Mattis[28] give the ratio of superconducting to normal surface impedance as

$$Z/Z_n=(\sigma_r/\sigma_n-i\sigma_i/\sigma_n)^{-\frac{1}{3}}, \qquad (2)$$

where $\sigma_n=$dc conductivity of the metal in the normal state and $\sigma_r-i\sigma_i=$complex conductivity in the super-

[28] D. C. Mattis and J. Bardeen, Phys. Rev. **111**, 412 (1958).

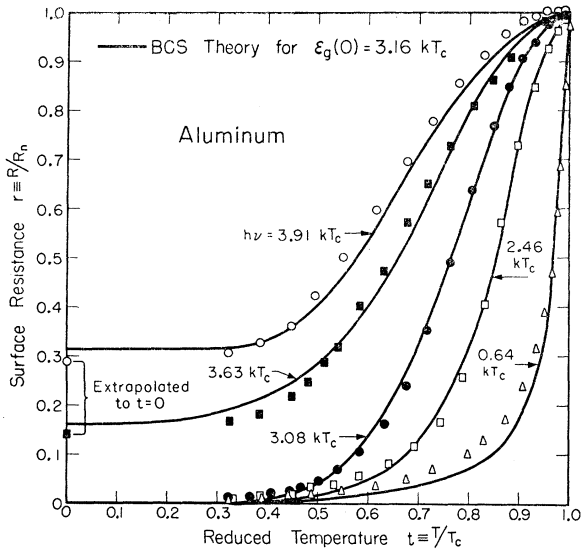

FIG. 9. Comparison of the experimental data with the theoretically predicted surface resistance curves. The curves are obtained from the theory of Mattis and Bardeen, reference 28, with the energy gap scaled to the value $3.16kT_c$, which gives the best over-all fit to the data. The points are from the present measurements.

conducting state. Tables of σ_r/σ_n and σ_i/σ_n as functions of frequency and temperature have been calculated by Bardeen.[29] From this table we have evaluated Z/Z_n, and since $Z_n=R_n(1+i\sqrt{3})$ for the limiting case we are discussing, we have been able to calculate $r\equiv R/R_n$. Since the experimentally determined value of the energy gap at absolute zero does not agree exactly with that of the BCS theory, we have taken the liberty of trying various values of the energy gap to get the best fit to our absorption curves. (The validity of this procedure has not been demonstrated.)

Scaling of the energy gap was accomplished by multiplying all the frequencies in the table[29] by a constant scaling factor. The value of the energy gap at $t=0$ that gives the best over-all fit to our data is $\mathcal{E}_g(0)=3.16kT_c$. The theoretical absorption curves[30] and the experimental points are plotted in Fig. 9. The theory clearly reproduces all of the main features of the experimental curves in this frequency region; it is therefore necessary only to remark on the shortcomings. At the lowest frequencies, the experimental data fall above the theoretical curves while at the highest frequencies the reverse is true. Therefore, if we were to try to fit only the lowest frequency curves by this technique, we would find it necessary to use a substantially smaller value for the energy gap. Similarly if only the highest frequency curves were fitted, it would be necessary to use a larger energy gap value.

Our values of the energy gap may be compared with those obtained from other, less direct determinations. If one uses the BCS theory to analyze the electronic specific heat data of Goodman[31] and of Phillips,[32] one obtains values of $\mathcal{E}_g(0)$ of $\sim 3.1kT_c$ and $\sim 3.2kT_c$, respectively, in essential agreement with the present results. Redfield[33] has obtained an estimate of $\mathcal{E}_g(0)$ $\sim 3.2kT_c$ from his measurements of the nuclear relaxation rate in aluminum, again in agreement with our results. However, the thermal conductivity measurements of Satterthwaite[34] and of Zavaritskii[35] are in good agreement with the theory of Bardeen, Rickayzen, and Tewordt[36] which uses a gap value $\mathcal{E}_g(0)=3.5kT_c$. Since there would appear to be less ambiguity in the determination of the energy gap by direct photon excitation, the present results are considered to give the best present estimate of the gap in aluminum.

Richards[37] and Tinkham[38] have made measurements of the energy gap at $T=0$ for a number of other superconductors by far infrared absorption techniques. Their results indicate that $\mathcal{E}_g(0)/kT_c$ varies from 4.7 for mercury to 2.8 for niobium, in contrast to the universal value of 3.52 of the BCS theory. Furthermore, they have shown that if $\mathcal{E}_g(0)/kT_c$ is plotted as a function of the Debye characteristic temperature, a smooth curve is obtained. Our result for aluminum essentially falls on their curve.

A best estimate of the energy gap is somewhat difficult to make. From our empirical determination from Fig. 7, we arrive at a value of $3.25kT_c$. But when we use the BCS theory to fit our absorption curves we find that a value of $\mathcal{E}_g(0)=3.16kT_c$ gives the best results. Probably a value of $\mathcal{E}_g(0)=3.20\pm 0.10kT_c$ is the best estimate that we can make from this experiment. The shape of the energy gap-temperature curve, within experimental error is just that of the BCS theory. Furthermore, the Bardeen-Mattis theory of the anomalous skin effect in superconductors predicts the general features of the temperature dependence of the absorption for photon energies in the range about the energy gap.

[29] J. Bardeen (private communication).

[30] In the calculation from theory [references 7 and 28], at the higher frequencies the surface resistance ratio initially rises slightly above unity as the temperature is decreased below T_c. Since the total predicted rise is $\sim 1\%$ at the experimental frequencies, it is not possible to establish or disprove this prediction from the experiment. Furthermore, the prediction of a rise may be the result of rounding errors in the table of σ_r/σ_n and σ_i/σ_n calculated by Bardeen (reference 29).

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[37] P. L. Richards, Bull. Am. Phys. Soc. Ser. II, **4**, 149 (1959).

[38] M. Tinkham, International Union of Pure and Applied Physics Conference on Superconductivity, Cambridge, England, June, 1959 (unpublished).

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APPENDIX

In this section we outline the procedure used by Biondi, Garfunkel, and McCoubrey[11] (BGM) to evaluate that part of the microwave absorption contributed by electrons which have been *thermally* excited across the energy gap, the so-called "normal" electrons. Holstein,[39] in his treatment of the surface resistance of superconductors, starts with the theory of the anomalous skin effect for normal metals and adapts it to superconductors by use of a two fluid model. The normal electrons are characterized by σ/l, the ratio of conductivity to the free path. The superconducting electrons are introduced into the expressions as a dielectric constant, and are characterized by the superconducting penetration depth, λ. With these assumptions expressions for the surface resistance are obtained as a function of the above two parameters and of the frequency. In his calculation, Holstein has treated the superconducting electrons both from the local theory[40] (London) and nonlocal theory[41] (Pippard). Although the results for the surface resistance are somewhat different in the two cases, they do not appreciably affect the estimate of the energy gap made by BGM. In the results quoted in BGM only the local theory was used.

The parameter λ in the surface resistance is represented by the experimentally observed expression[40] $\lambda=\lambda_0/(1-t^4)^{\frac{1}{2}}$ (actually only the ratio λ/λ_0 need be used). It is then assumed that, for the lowest frequency curve ($h\nu/kT_c=0.64$), the photon energy is less than the energy gap at all temperatures (except possibly for a very small temperature region near T_c) and therefore all absorption is by thermally excited electrons. With these assumptions it is then possible to determine from the curve at $h\nu/kT_c=0.64$ the temperature dependence of σ/l. These values of σ/l can then be introduced into the Holstein expressions for the surface resistance to obtain the "normal" electron absorption at higher frequencies.

The weakness of this analysis lies in the implicit assumption that σ/l and λ are independent of frequency. In the following paper it will be seen that the real part of the conductivity of the superconductor (a quantity which is directly related to σ/l at photon energies less than the gap) is in fact a function of frequency. But, fortunately, the errors introduced by this assumption are not large enough to affect appreciably the estimate of the energy gap.

An interesting side result of this analysis is the deduced form of the temperature dependence of σ/l. It turns out that, at $h\nu/kT_c=0.64$, as the temperature is decreased below T_c, σ/l first *rises* to a maximum of about $2(\sigma/l)_{t=1}$ at $t\simeq 0.8$ before falling, presumably to zero at $t=0$. This behavior is very similar to that observed in thin films by Khaikin[42] and also by Glover.[43] It can be shown to be a consequence of the piling up of the density of states on either side of the energy gap.

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