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Experimental Evidence for an Energy Gap in Superconductors

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CONTENTS

I. INTRODUCTION

DURING the past few years a number of experiments have added greatly to our knowledge of the properties of metals in the superconducting state. Among the many experiments performed, several have suggested that there is a gap in the electron energy spectrum of superconductors. This paper reviews the relevant experiments and sums up the situation regarding evidence for an energy gap without going into a detailed review of the theoretical work.[1] More general reviews of the experimental aspects of superconductivity

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[1] A review of the theoretical work up to 1956 has been given by J. Bardeen, *Encyclopedia of Physics* (Springer-Verlag, Berlin, Germany, 1956), Vol. XV, pp. 274–368.

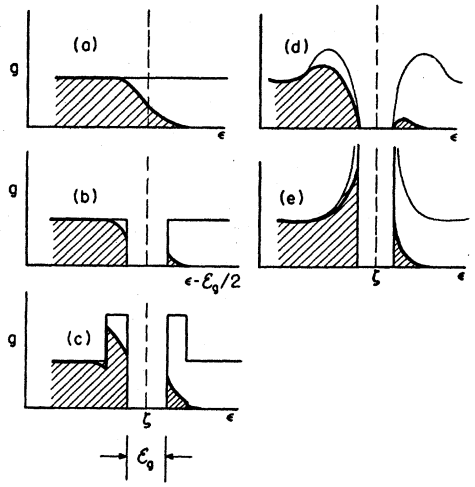

FIG. 1. Density of one electron states, g, as a function of energy, ϵ. ζ is the Fermi level. (a) represents the metal in the normal state. (b) is an energy gap model which cannot correspond to a superconductor since it has the same energy as (a) at $T=0$. (c), (d), and (e) are possible energy gap models; (e) has the form given by the theory of Bardeen, Cooper, and Schrieffer (BCS). The shaded region is that occupied by electrons at a nonzero temperature.

are given in the book by Shoenberg[2] and a review by Serin.[3]

To establish the existence of a gap in the energy spectrum of superconductors would not, of itself, solve the problem of superconductivity. It would remain to show that such a gap leads to the characteristic properties of the superconducting state, e.g., infinite conductivity and perfect diamagnetism in bulk specimens. Bardeen, in his review,[1] has presented an approximate calculation which has the above objective. Within the limitations of the approximations he shows that the perfect diamagnetism and infinite conductivity follow from the existence of a gap. More recently, Bardeen, Cooper, and Schrieffer[4] (BCS) have proposed a detailed theory of superconductivity. One of its important features is that it predicts an energy gap for individual particle excitations which decreases to zero as the temperature is increased from zero to the superconducting transition temperature T_c.

Most of the relevant experiments have been done since 1950, so the earlier work is treated rather sketchily as historical background. More recent experiments are reviewed critically to evaluate their contribution to the evidence for an energy gap.

The concept of an energy gap refers to the one electron energy spectrum unless otherwise specified. This does not mean that we believe that superconductivity can necessarily be described by a one electron theory; it is possible that such a model may be misleading.[5] In fact, the theory of BCS[4] is not a single electron theory but deals with pairs of electrons, although even in this case a one electron representation of the energy spectrum is adequate in many instances. Since it seems very likely that many of the properties of superconductors can be understood in terms of a one electron model, the simplicity of such a model makes it undesirable to resort to more complicated descriptions until forced to do so by the facts of superconductivity.

The metals which become superconducting generally have a highly complex band structure. Even so, the density of states in the *normal* state is essentially constant over a region of the order of kT_c about the Fermi energy. On the other hand, for an energy gap model the onset of superconductivity is associated with the disappearance of the states in the vicinity of the Fermi energy. These displaced states may then be replaced on either side of the resulting gap or they may be removed to infinity. In Fig. 1 are plotted schematic graphs of the density of states for several energy gap models.

The energy gap that has just been introduced is not to be confused with the concept of a condensation energy per electron, β, which is a feature of the Gorter-Casimir two fluid model.[6] The two fluid model was initially introduced to provide a basis for understanding the thermodynamic properties of the superconducting state. In this phenomenological theory it is assumed that the electrons in a superconductor are divided into two interpenetrating gases: the superconducting electrons, which have zero entropy, no electrical resistance, and can absorb no energy; and the normal electrons, which have the usual properties of the electrons in a normal metal. The normal electrons give up the condensation energy, β, when they become superconducting. In contrast to the energy gap models, there is no mention of a zero in the density of states; in fact, it is difficult to see how an energy spectrum could be constructed consistent with the two fluid model. Furthermore, in the two fluid model, as the temperature goes from the superconducting transition temperature T_c to absolute zero, all the conduction electrons go from normal to superconducting, while in an energy gap model [e.g., Fig. 1(c), 1(d), or 1(e)] the electrons in any condensation are just those that are displaced from the region of the gap. Thus, the fraction of electrons involved in an energy gap model is of the order of the ratio of the gap width to the Fermi energy. This means that the condensation energy per particle differs in the two models by just this ratio.

The earliest evidence for an energy gap dates from about 1940. An experiment by H. London[7] showed that, for radio-frequencies $\sim 10^9$ cps, the absorptivity of a superconductor approaches very small values as the temperature approaches absolute zero. On the other

[2] D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, England, 1952).
[3] B. Serin, *Encyclopedia of Physics* (Springer-Verlag, Berlin, Germany, 1956), Vol. XV, pp. 210–273.
[4] Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957).
[5] See, for example, G. V. Chester, Phys. Rev. **104**, 883 (1956).
[6] C. J. Gorter and H. G. B. Casimir, Physik. Z. **35**, 963 (1934).
[7] H. London, Proc. Roy. Soc. (London) **A176**, 522 (1940).

hand, for visible and even the near infrared frequencies ($>10^{14}$ cps), reflectivity experiments[8,9] showed no difference in absorption between the metal in the normal and in the superconducting states. Thus, in the range of frequencies between 10^9 and 10^{14} cps, the absorption at absolute zero appeared to go from zero to something equal to the normal state absorption. This is suggestive of the onset of some quantum effect, possibly excitation of electrons across a forbidden gap. However, it might also result from relaxation effects. Because of the sparsity of the data and the haziness of the ideas regarding a microscopic theory, very little was actually concluded from these experiments regarding an energy gap.

After 1945, a number of experiments were performed which added to the evidence. A series of experiments[10–13] performed on the microwave absorptivity of superconductors showed that the absorption of superconductors approaches zero at $T=0$ up to frequencies of 10^{10} cps. At the same time, experiments on the transmission of visible light through superconducting thin films[14] and on the absorption by bulk superconductors[15,16] of radiation in the visible and in the infrared down to frequencies of 2×10^{13} cps showed no difference between a metal in the normal and in the superconducting states. Following these results, it was suggested that there might be an energy gap[17] in the uninvestigated region of the frequency spectrum ($10^{10}-2\times10^{13}$ cps).

Prior to 1950, the only other experiments that might have given evidence for an energy gap were those on the electronic specific heat of superconductors and the thermodynamically related quantity, H_c, the magnetic field necessary to destroy superconductivity. However, the accuracy of the electronic specific heat data was not high, and the critical magnetic field data were not very sensitive in the important low temperature region. Empirically, the specific heat had been fitted by a cubic temperature dependence and the critical magnetic field by a quadratic, to agree with the Gorter-Casimir two fluid model.

When we discuss the more recent experiments on the thermal properties, we will see that almost all of the results can now be shown to be consistent with an energy gap. In fact, thermal conductivity and specific heat data provided the first strong experimental evidence for an energy gap in superconductors.

The question of the existence and magnitude of a superconducting energy gap has been approached by measurements on widely different physical phenomena, but, it is important to realize, all of these give only two essentially different kinds of information relating to an energy gap. One type of information is obtained through quantum effects and the other through statistical effects.

By quantum effects we mean behavior due to the direct excitation of electrons across a gap such as those of Fig. 1(c), 1(d), or 1(e). We shall see that in several experiments on the absorption, reflection, and transmission of electromagnetic radiation, evidence has been found for an absorption edge indicative of quantum effects.

By statistical effects, on the other hand, we refer to properties which are due to the thermal distribution of electrons among the available energy levels. The electronic specific heat C_e is one such quantity. It may be expressed by

$$\frac{C_e}{T}\propto\int_0^\infty\left(\frac{\epsilon-\zeta}{kT}\right)^2 g(\epsilon)\frac{\partial f}{\partial\epsilon}d\epsilon, \tag{1}$$

where f is the Fermi function at temperature T and energy ϵ, $g(\epsilon)$ is the number of one electron energy states per unit energy range, and ζ is the Fermi energy (the terms involving temperature derivatives of ζ and g are omitted in this simplified example). Examples of other quantities which can also be represented as an average of these functions across the width of the Fermi shell are the Knight shift, the fractional difference in resonant frequency between a nucleus in a free ion and that same nucleus in a metal, representable by

$$\frac{\Delta\nu}{\nu}\propto\int_0^\infty g(\epsilon)\frac{\partial f}{\partial\epsilon}d\epsilon; \tag{2}$$

and the nuclear spin relaxation rate $\mathfrak{R}$ due to interactions with conduction electrons and expressible by

$$\frac{\mathfrak{R}}{T}\propto\int_0^\infty[g(\epsilon)]^2\frac{\partial f}{\partial\epsilon}d\epsilon. \tag{3}$$

A discussion of the nature and limitation of Eqs. (1) to (3) is deferred to the sections in which we discuss these properties. We only wish to emphasize here the similarity in the conclusions that can be drawn from these experiments. It can be shown that for the type of energy gap models suggested in Fig. 1, all of these quantities are dominated by an exponential in $1/T$ at low temperatures. In cases where sufficient data exist for comparison, this exponential behavior is observed,

[8] E. Hirschlaff, Proc. Cambridge Phil. Soc. **33**, 140 (1937).
[9] Daunt, Keeley, and Mendelssohn, Phil. Mag. **23**, 264 (1937).
[10] A. B. Pippard, Proc. Roy. Soc. (London) **A191**, 370, 399 (1947); **A203**, 98, 195 (1950).
[11] W. M. Fairbank, Phys. Rev. **76**, 1106 (1949).
[12] Marcus, Maxwell, and Slater, Phys. Rev. **76**, 1332 (1949).
[13] A thorough review of the microwave work before 1954 is given by A. B. Pippard in *Advances in Electronics and Electron Physics* (Academic Press, Inc., New York, 1954), Vol. VI, pp. 1–45.
[14] A. Wexler, Phys. Rev. **70**, 219 (1946).
[15] K. G. Ramanathan, Proc. Phys. Soc. (London) **A65**, 532 (1952).
[16] N. G. McCrum and C. A. Shiffman, Proc. Phys. Soc. (London) **A67**, 368 (1954).
[17] In reference 2, p. 207, Shoenberg suggests that in the intermediate frequency region "···we might expect quantum processes to set in···," and in reference 13, p. 41, Pippard says "···we might expect quantum energies greater than this [$\sim kT_c$] to give rise to a kind of internal photoelectric effect···."

although in the case of the Knight shift there appears to be some contradictory evidence.

The presentation of experimental results in terms of reduced variables, e.g., critical magnetic field as $H_c(T)/H_c(0)$ and energy gap $\mathcal{E}_g$ as $\mathcal{E}_g/kT_c$, is a convenient way of making comparisons among different superconductors. The surmise that all measurables, when so expressed, are universal functions of the reduced temperature T/T_c is known as the law of corresponding states. While this rule does seem to be approximately obeyed, there appear to be discrepancies, particularly in the thermal properties.

II. THERMAL PROPERTIES

A. Thermodynamics and Two Fluid Models

In order to discuss the evidence for an energy gap in superconductors from their thermal properties, it is first necessary to describe those properties and their interrelation. The property which can be most easily related to the electronic energy level spectrum is the specific heat. The critical magnetic field, H_c, is thermodynamically related to the difference between the specific heat in the normal state, C_n, and that in the superconducting state, C_s, so that measurements of the critical field as a function of temperature may be considered indirect measurements of the specific heat. Under ideal conditions H_c-T curves can be measured quite accurately and supplement specific heat data for metals for which electronic specific heats cannot be determined with high accuracy.

The thermal conductivity, which is also related to the specific heat, is complicated by the fact that there are several mechanisms of heat transfer operating simultaneously. In practice it is sometimes possible to choose conditions so that one mechanism predominates, in which case the relationship between the thermal conductivity and the specific heat is reasonably straightforward. Under the best circumstances, however, there are uncertainties in the evaluation of the specific heat from the thermal conductivity.

The idea of relating, thermodynamically, the thermal and magnetic properties of superconductors had occurred to several authors.[18–21] Relations for the thermodynamic functions were derived on the assumption that the transition between normal and superconducting states was reversible when induced by a change in either temperature or magnetic field. The expression of particular interest at present is that relating the difference in specific heat between the normal and superconducting states to the critical magnetic field of a superconductor,

$$C_s-C_n=\frac{VT}{4\pi}H_c\frac{d^2H_c}{dT^2}+\frac{VT}{4\pi}\left(\frac{dH_c}{dT}\right)^2, \tag{4}$$

where V is the volume and H_c the critical magnetic field.

Associated with the superconducting transition is a discontinuity in the specific heat. On lowering the temperature through the transition temperature T_c the specific heat increases discontinuously, though without a latent heat, indicating a second-order transition. It is a characteristic of a second-order transition that as the temperature is lowered there is a critical point at which order starts to set in, the degree of order increasing with decreasing temperature.

The original two fluid model of Gorter and Casimir[6] was proposed to explain the specific heat anomaly and other thermodynamic properties of superconductors. They proposed that below T_c a fraction $(1-x)$, where x depends on T, of the conduction electrons occupies a set of lower "condensed" energy states with which are associated the superconducting properties, while the fraction x remains uncondensed.

The free energy function for the whole electronic assembly is made up of two terms; one, G_u, is similar to the electronic free energy of a normal metal and the other, G_c, corresponds to a condensation energy associated with the condensed states;

$$G_u=-\tfrac{1}{2}\gamma T^2, \quad G_c=-\beta, \tag{5}$$

where γ is the normal electronic specific heat coefficient and β is a constant representing the condensation energy. It was observed that the total free energy could not vary linearly with x; otherwise a first-order transition would result.

Gorter and Casimir assumed that the phases were not independent and proposed the following free energy function:

$$G=x^{\frac{1}{2}}G_u(T)+(1-x)G_c(T). \tag{6}$$

The coefficient for $G_u(T)$ was chosen as $x^{\frac{1}{2}}$ to fit available specific heat and critical field data. No attempt was made to justify it on a theoretical basis.

The equilibrium value of x at any temperature is found by setting $(\partial G/\partial x)_T=0$. Then, since x must equal unity at $T=T_c$,

$$\beta=\gamma T_c^2/4, \tag{7}$$

and

$$x=(T/T_c)^4\equiv t^4, \tag{8}$$

t being the reduced temperature. By inserting these values for β and x into the free energy expression, Eq. (6), and by making use of the thermodynamic relations, $C=T(dS/dT)$ and $S=(\partial G/\partial T)_H$, the reduced electronic specific heat is found to be

$$C_{es}/\gamma T_c\equiv 3t^3. \tag{9}$$

If it is assumed that the lattice specific heat is un-

[18] W. H. Keesom, Report and Discussions, Fourth Congress of Physics Solvay, p. 288 (1927).
[19] P. Ehrenfest, Koninkl. Ned. Akad. Wetenschap. Proc. **36**, 153 (1933).
[20] A. J. Rutgers, Physica **1**, 1055 (1934); **3**, 999 (1936).
[21] C. J. Gorter and H. Casimir, Physica **1**, 306 (1934).

changed through the superconducting transition, then Eq. (4) gives the reduced critical field,

$$H_c/H_0=1-t^2, \tag{10}$$

where H_0 is the limiting value of H_c as the temperature approaches 0°K. Although some deviations from the above expressions were noted before 1950, they were generally accepted as adequately describing these properties of superconductors.

A modification of the two fluid model of Gorter and Casimir was proposed by Marcus and Maxwell[22] to provide better agreement between the two fluid theory and some new precise critical field measurements. The modification was to add another adjustable parameter so that the free energy function became

$$G=-\tfrac{1}{2}x^{\alpha}\gamma T^2-(1-x)\beta, \tag{11}$$

where α could be adjusted from metal to metal. It does not now appear that this sort of modification contributes to an understanding of superconductivity.

Another model which has had some success in explaining experimental results is that of Koppe,[23] based on the theory of Heisenberg[24] which attempted to explain superconductivity on the basis of a condensation arising from Coulomb interactions among the electrons. The basic assumptions of the Heisenberg theory have been criticized,[25] and it fails to predict correctly certain phenomena of superconductivity, notably the observed variation of T_c with isotopic mass.[26,27] The Koppe model, though inspired by the Heisenberg theory, is not necessarily limited by the shortcomings of the latter.

From the Koppe treatment one gets an expression for C_{es} which is dominated at very low temperatures by a term of the form $\exp(-\epsilon/kT)$. Goodman[28] has suggested that this type of specific heat is typical of an assembly for which there is a gap in the energy levels available to the members of the assembly. He further interpreted the Koppe model in terms of an energy gap which decreases from $1.28\ kT_c$ in width at 0°K to zero at T_c. This interpretation has considerable similarity with more recent ideas concerning superconductivity.

B. Thermal Conductivity

The thermal conductivity of a superconductor is related to the specific heat, though the relationship is not without uncertainties. Nevertheless, a rapid decrease in the thermal conductivity of superconducting tin at very low temperatures gave the first indication that the electronic specific heat varied much more rapidly with temperature than the T^3 dependence of the Gorter-Casimir theory.

The various contributions to the thermal conductivity of a superconductor and how they compare with similar contributions in a normal metal were sorted out by Hulm.[29] A thorough discussion of thermal conductivity of superconductors is included in a recent review article by Klemens.[30] The thermal conductivity in the normal state, K_n, can be written as the sum of a lattice contribution K_{gn} and one due to the conduction electrons K_{en}, where

$$\frac{1}{K_{en}}=cT^2+\frac{\rho_0}{L_0T}, \tag{12}$$

and

$$\frac{1}{K_{gn}}=\frac{A}{T^2}+\frac{B}{T^3L_b}. \tag{13}$$

Here cT^2 represents the scattering of conduction electrons by thermal vibrations of the crystal lattice and ρ_0/L_0T that by impurities and lattice defects; A/T^2 represents the scattering of lattice waves by conduction electrons and B/T^3L_b that by the crystal boundaries. L_0 is the Lorenz number, ρ_0 is the residual resistivity, L_b is the mean free path of the lattice waves for boundary scattering, and c, A, and B are constants of the sample.

In order to explain the thermal conductivity on the basis of a two fluid model, it is generally assumed that the superconducting electrons have no entropy and can neither carry energy nor scatter lattice waves. Thus, the thermal conductivity in the superconducting state may be thought to consist of a set of contributions similar to the above, each modified by some function of (T/T_c) to account for the change with temperature of the number of normal electrons.

In order to gain information about the electronic behavior of a superconductor the best experimental situation is one in which the conductivity is predominantly due to the electrons and the scattering is predominantly by static imperfections. In this case we would expect the normal thermal conductivity, K_n, to be characteristic of the residual resistance range where

$$K_n=L_0T/\rho_0. \tag{14}$$

In the superconducting state, then, we would expect a similar expression modified by a function of the reduced temperature as follows:

$$K_s=\frac{L_0T}{\rho_0}\phi(T/T_c); \tag{15}$$

[22] P. M. Marcus and E. Maxwell, Phys. Rev. **91**, 1035 (1953).
[23] H. Koppe, Ann. Physik **1**, 405 (1947); Z. Naturforsch. **3a**, 1 (1948).
[24] W. Heisenberg, Z. Naturforsch. **2a**, 185 (1947); *Two Lectures* (Cambridge University Press, New York, 1949); Z. Naturforsch. **3a**, 65 (1948).
[25] See reference 1, pp. 343–344.
[26] E. Maxwell, Phys. Rev. **78**, 477 (1950).
[27] Reynolds, Serin, Wright, and Nesbitt, Phys. Rev. **78**, 487 (1950).
[28] B. B. Goodman, Proc. Phys. Soc. (London) **A66**, 217 (1953).
[29] J. K. Hulm, Proc. Roy. Soc. (London) **A204**, 98 (1950).
[30] P. G. Klemens, *Encyclopedia of Physics* (Springer-Verlag, Berlin, Germany, 1956), Vol. XIV, pp. 266–276.

thus

$$\phi(T/T_c)=K_s/K_n. \tag{16}$$

The electronic thermal conductivity of a normal metal can be expressed in terms of a mean free path for the electrons, l, their Fermi velocity, v, and an electronic specific heat, C_e, in the following way:

$$K_n \propto C_e v l. \tag{17}$$

If a similar expression can be written for the superconducting state, the function $\phi(T/T_c)$ should be dependent upon the ratios C_{es}/C_{en}, v_s/v_n and l_s/l_n. The Fermi velocity is not expected to change appreciably in going from the normal to superconducting state. For the case which we are considering, electronic conduction with scattering by static imperfections, Heisenberg[24] estimated the variation of the free path for normal electrons with temperature, below T_c, as a result of the decreasing number of energy states into which the electrons could be scattered. His expression,

$$l_s=2l_n/(1+x), \tag{18}$$

was based on the two fluid model where x, the fraction of the total number of electrons still normal, is equal to $(T/T_c)^4$. From this expression l_s varies rapidly with temperature between l_n and $2l_n$ near T_c, but at very low temperatures l_s becomes independent of temperature and equal to $2l_n$. Hence any variation of ϕ with T at a low temperature should indicate a similar variation in C_{es}/C_{en}. The Gorter-Casimir model predicts at low temperatures that

$$\phi \propto C_{es}/C_{en} \propto (T/T_c)^2. \tag{19}$$

Goodman measured the thermal conductivity of several specimens of tin of varying purity from 1°K to approximately 0.2°K. For his purest samples he found that $\phi=K_s/K_n$ decreased much more rapidly than $(T/T_c)^2$ over an appreciable range of temperature and

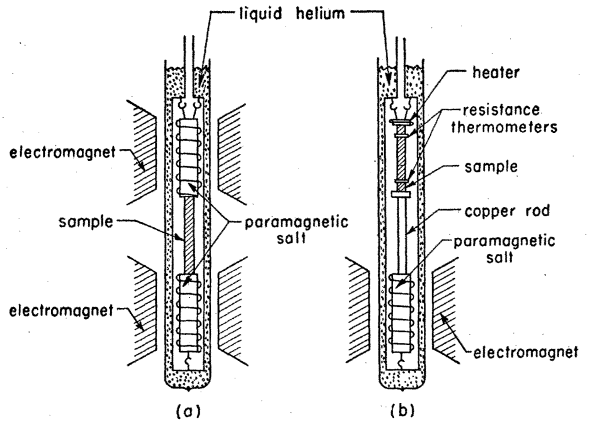

FIG. 2. Schematic diagrams of apparatuses for measurement of thermal conductivity below 1°K; (a) Goodman's rate of approach to equilibrium method, (b) steady-state method of Laredo and others.

in fact could be represented by a term of the form $\exp(-bT_c/T)$. The temperature dependence of ϕ resembled quite closely the temperature dependence of C_{es}/C_{en} from the Koppe treatment, giving support to Goodman's interpretation of that treatment. At the lowest temperature, where K_{es} became quite small, the thermal conductivity varied as T^3, characteristic of conductivity by lattice waves scattered by the boundaries of the specimen.

For his experiments, Goodman used two pills of paramagnetic salt with the specimen suspended between them making thermal contact by means of copper fins imbedded in the salts. His method is shown diagrammatically in Fig. 2(a). The two pills were brought to different temperatures by demagnetizing from different magnetic fields. The rate of approach to equilibrium was observed by measuring, as a function of time, the magnetic susceptibility of the two pills which, in turn, could be related to the temperature by means of known susceptibility-temperature characteristics of the salt. The thermal conductivity was derived from the rate of approach to thermal equilibrium. The accuracy of experiments of this type is limited by uncertainties in (a) the susceptibility-temperature relationship, (b) the specific heat of the salt, and (c) the thermal relaxation time in the salt itself.

More recently, Laredo[31] has measured the thermal conductivity of a series of tin samples of comparable purity with those of Goodman over the same temperature range. He used a steady-state method, illustrated in Fig. 2(b), less subject to uncertainties than the method of Goodman, and consequently was able to claim much higher precision. One end of the specimen made thermal contact with a pill of salt by means of a long rod of high conductivity copper. The salt served as the refrigerant and the heat sink; the copper rod held the specimen out of the magnetic field used in cooling the salt. For the measurements a steady-state heat current was maintained by a heater at the other end of the specimen and the temperature difference was measured between two carbon resistance thermometers placed near the ends of the specimen. The thermal conductivity was then related to the power in the heater, P, the temperature difference between the two thermometers, ΔT, the cross-sectional area of the sample, s, and the distance, d, between thermometers by

$$K=Pd/s\Delta T. \tag{20}$$

The measurements of Laredo disagreed with those of Goodman in many respects; however, a very rapid temperature variation of the thermal conductivity was again observed in a region of temperature where the electronic thermal conductivity was expected to dominate (see Fig. 3). Laredo could not distinguish between an exponential temperature dependence and one proportional to a power of T of the order of T^7.

[31] S. J. Laredo, Proc. Roy. Soc. (London) **A229**, 473 (1955).

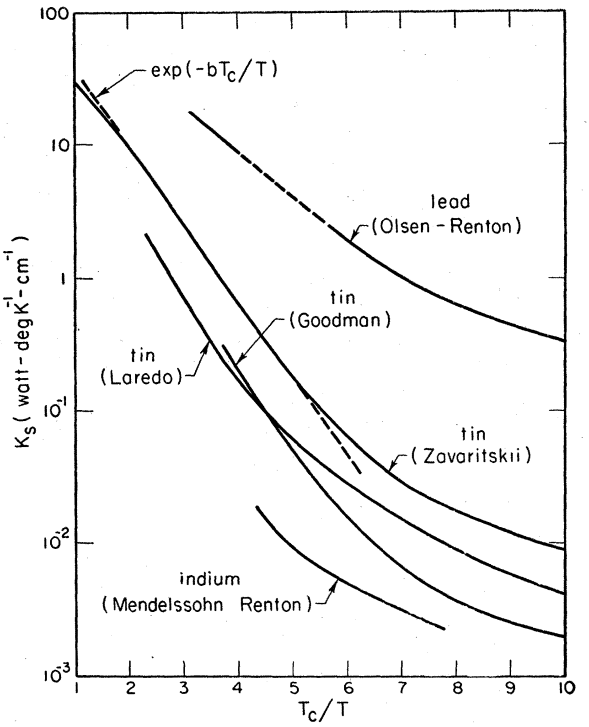

FIG. 3. Thermal conductivity curves for several superconductors. At low temperatures (large T_c/T values) the curves exhibit a T^3 dependence characteristic of lattice conductivity.

The fact that, well below T_c, K_s/K_n varies much more rapidly with temperature than predicted by the Gorter-Casimir theory, has been observed by a number of others as well. For lead below 1°K Olsen and Renton[32] found that, above a low temperature T^3 region, the temperature dependence of the superconducting thermal conductivity rose much more rapidly with increasing temperature. Mendelssohn and Renton[33] found K_s/K_n to rise quite steeply, possibly exponentially, for tin, indium, and lead over a range of temperature below 1°K. Both of the above investigations were made using a method similar to that used by Laredo.

In a recent study of the thermal properties of tin, Zavaritskii[34] measured the thermal conductivity of superconducting tin over a wide range of temperature by a method similar to that of Laredo. He found that over the range from 0.1 T_c to T_c, data on all his samples could be represented by an expression of the type $K_{es} \propto \exp(-bT_c/T)$, where $b=1.45\pm0.05$. The validity of his claim that this is in agreement with earlier measurements below 1°K is illustrated in Fig. 3, where the differences in thermal conductivity are no larger than expected from differences in sample purity and geometry.

As in the case of other statistical properties, an energy gap model implies that K_{es} would vary as $\exp(-c/T)$ at low temperatures. The rapid variation, at least approximating this temperature variation for tin, indium, and lead at very low temperatures, may be considered evidence for an energy gap. In the case of indium and tin these data corroborate and supplement specific heat and critical field data. In the case of lead they provide the only thermal evidence for an energy gap.

C. Specific Heat

Accurate measurements of the specific heat of a number of metals in both the normal and superconducting states have been reported in recent years. Superconducting state values have been obtained from measurements in the absence of a magnetic field, whereas the normal state values result from similar measurements made in a field greater than critical.

Although the specific heat determinations of interest extend over two ranges of temperature for which the techniques are quite different, they are similar in principle. Schematic diagrams are shown in Fig. 4, illustrating typical apparatuses for measuring specific heats in (a) the liquid helium region (1–5°K), and (b) the region below 1°K reached by adiabatic demagnetization. The metallic specimen is suspended in a vacuum vessel with some means of making and breaking thermal coupling between the specimen and its surroundings. An electrical heater and a sensitive thermometer are mounted directly on the specimen. In preparation for making measurements the sample is cooled to the desired temperature and thermally isolated. The actual measurement of the specific heat consists of measuring the heat supplied to the sample during a heating period and the rise in temperature as a result of the heat supplied.

In the region of temperature attainable with liquid helium the techniques are fairly standard. The temperature of the liquid helium bath surrounding the vacuum

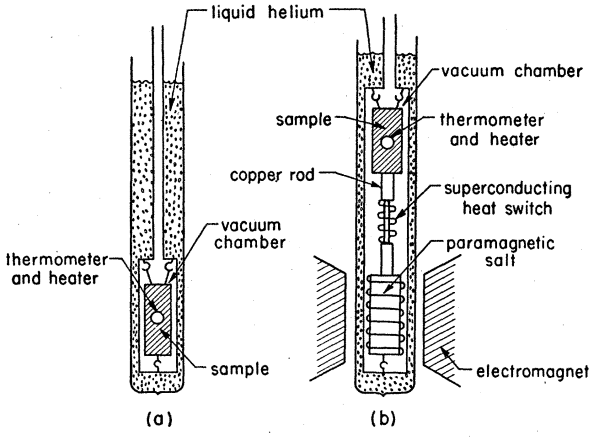

FIG. 4. Schematic diagrams of specific heat apparatuses; (a) for use in the liquid helium region, 1–5°K, and (b) for use below 1°K.

[32] J. L. Olsen and C. A. Renton, Phil. Mag. 43, 946 (1952).
[33] K. Mendelssohn and C. A. Renton, Phil. Mag. 44, 776 (1953).
[34] N. V. Zavaritskii, J. Exptl. Theoret. Phys. (U.S.S.R.) 33, 1085 (1957).

vessel is controlled by varying the pressure of gas above it. The specimen is usually thermally coupled to its surroundings by admitting helium gas at low pressure to the vacuum vessel and isolated by pumping it out. Some investigators have used mechanical contact, thus avoiding the possibility of errors due to adsorption and desorption of the exchange gas on the surface of the sample.

Temperatures in this region are derived from the vapor pressure of liquid helium. A secondary thermometer, used in the actual measurements, is calibrated against the vapor pressure of the helium bath or, preferably, against the vapor pressure of liquid helium contained in a vapor pressure thermometer. Carbon resistance thermometers have become widely used as secondary thermometers in this region of temperature because of their high sensitivity.

For the range of temperature below 1°K, adiabatic demagnetization of a paramagnetic salt is used for cooling. Thermal coupling between the pill of paramagnetic salt and the specimen is through a metallic connector. In this thermal path is included a superconducting heat switch for isolating the sample from the salt. The magnetic susceptibility of the paramagnetic salt is used as the temperature standard against which the carbon thermometers are calibrated. The calibration is related to the thermodynamic temperature scale by the known susceptibility-temperature characteristics of the salt.

It is generally assumed that the specific heat is made up of two independent contributions, one, C_L, due to the crystalline lattice and the other due to the conduction electrons. Furthermore, the lattice contribution is assumed to be unchanged by the onset of superconductivity.[35] Thus, from the difference between normal, C_n, and superconducting, C_s, specific heats it is possible to deduce the *electronic* contribution in the superconducting state, C_{es}.

The accuracy with which C_{es} can be determined is dependent not only on the accuracy of the measurements but also on the relative contributions of the lattice and the electrons. From the approximate values of this ratio at the transition temperature for a number of pure superconductors, as shown in Table I, it can be seen which are best suited for a study of the temperature dependence of C_{es}. Data exist for a number of these metals from which C_{es} may be deduced.

TABLE I. Approximate ratio of electronic to lattice specific heat (C_e/C_L) in the superconducting state at the transition temperature.

Element	T_c°K	(C_e/C_L)
Titanium	0.39	2500
Zirconium	0.55	295
Aluminum	1.17	117
Rhenium	1.7	50
Zinc	0.90	33
Vanadium	5.05	19
Tantalum	4.39	8.0
Niobium	9.2	5.2
Tin	3.73	1.23
Indium	3.40	0.30
Thallium	2.36	0.20
Lead	7.2	0.068
Mercury	4.15	0.028

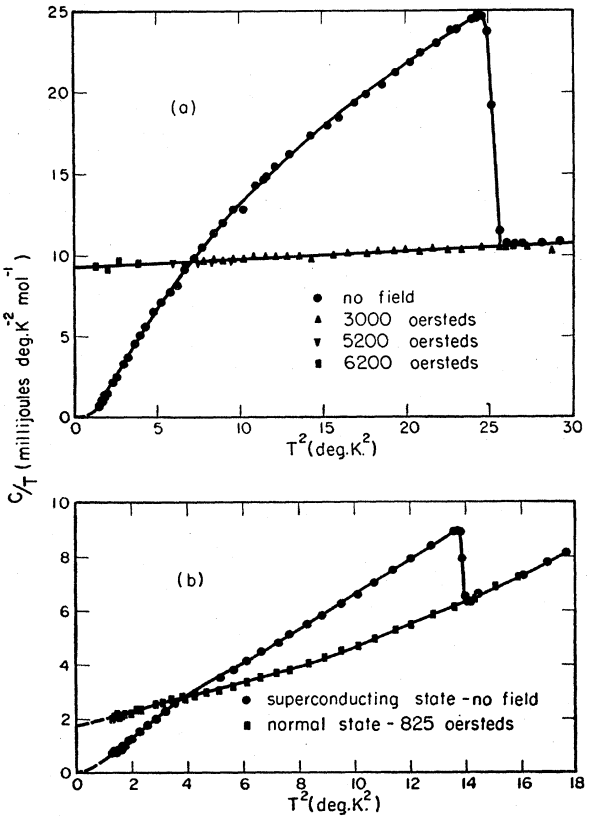

FIG. 5. C/T as a function of T^2 in both normal and superconducting states; (a) for vanadium, and (b) for tin.

The first measurements of the specific heat of a superconductor for which C_{es} was observed to deviate appreciably from the T^3 dependence of the Gorter-Gorter-Casimir theory were those of Brown, Zemansky, and Boorse[36] on niobium. These authors found approximate agreement with the Koppe model but disagreement in detail. Following this, the specific heat measurements of Corak *et al.*[37] on vanadium and of Corak and Satterthwaite[38] on tin showed clearly that the temperature dependence of C_{es} is different from that

[35] G. V. Chester[5] has considered the validity of this more or less artificial separation. He has shown that, as a consequence of the similarity of the reduced critical field-temperature curves for various isotopes of the same element, the lattice contributions to the normal and superconducting states must be identical, $C_{Ln}=C_{Ls}=C_L$, as assumed.

[36] Brown, Zemansky, and Boorse, Phys. Rev. **92**, 52 (1953).

[37] Corak, Goodman, Satterthwaite, and Wexler, Phys. Rev. **96**, 1442 (1954); **102**, 656 (1956).

[38] W. S. Corak and C. B. Satterthwaite, Phys. Rev. **102**, 662 (1956).

predicted by existing theories. The features of the latter investigations which made it possible to gain a better understanding of the temperature dependence of C_{es} than from the previous measurements[39,40] were (a) higher precision, (b) smaller temperature scale errors, and (c) in the case of vanadium, lower reduced temperatures.

The superconducting and normal atomic heats of vanadium and tin are shown in Fig. 5. In the case of vanadium the normal state atomic heat may be represented by

$$C_n=C_{en}+C_L=\gamma T+\mu T^3. \quad (21)$$

C_{es} was then obtained by subtracting from C_s the cubic lattice term. For tin, however, the simple expression, Eq. (21), was not obeyed above about 2.5°K. The discrepancy was attributed to a deviation of the lattice contribution from a T^3 dependence, an effect frequently described in terms of a variation with

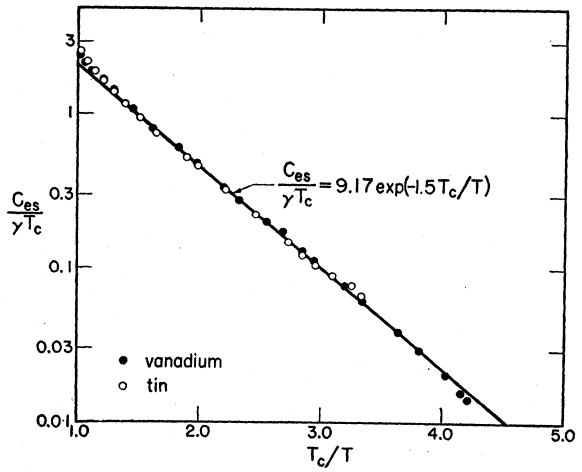

FIG. 6. Reduced electronic specific heat in the superconducting state for vanadium and tin.

temperature of the Debye Θ. In this case, C_{es} was obtained from $C_{es}=C_s-C_n+\gamma T$, where C_s and C_n were experimental values and γ was determined from the lowest temperature normal state data. For both vanadium and tin, C_{es} could be represented below about $0.7T_c$ by the following exponential expression:

$$C_{es}/\gamma T_c=9.17\exp(-1.50T_c/T). \quad (22)$$

For $T/T_c>0.7$, C_{es} was observed to rise more rapidly with temperature than indicated by the above expression. These features can be seen in Fig. 6.

As pointed out in the discussion of thermal conductivity, the above expression for C_{es} is of the sort one would expect if there were an energy gap in the one electron energy spectrum. Furthermore, the deviation

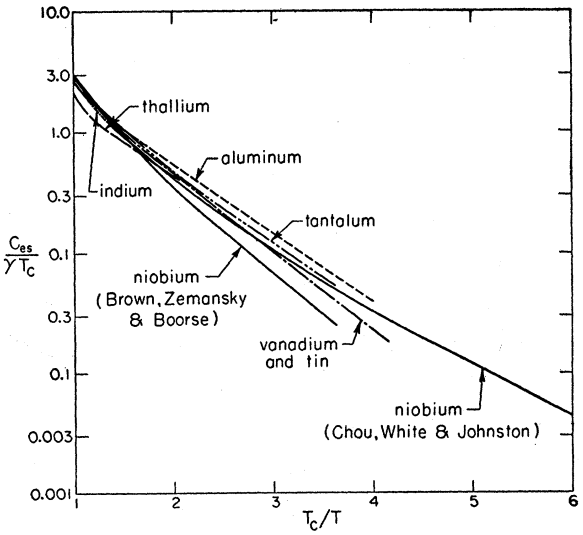

FIG. 7. Comparison of electronic specific heats of several superconductors.

near T_c is in the direction expected for an energy gap which decreases with increasing temperature.

It is of interest to review the specific heat data on other superconductors to see what further evidence there is for a predominantly exponential temperature dependence of C_{es} and to see what differences exist among superconductors. Existing data are summarized in Fig. 7.

Investigations of the specific heat of niobium have been reported by Brown, Zemansky, and Boorse[36] and, more recently, by Chou, White, and Johnston,[41] which show discrepancies in some important respects. These discrepancies (in critical temperature, in both the electronic and lattice contributions to the normal state specific heat, and in the magnitude of the superconducting state specific heat), are well outside the experimental error. These differences may arise from the purity of the samples used but perhaps to an even greater extent from the state of anneal. The work of Chou, White, and Johnston is perhaps more nearly representative of pure niobium since they used a more extensive annealing procedure and obtained consistent results with different samples. There is, however, some question as to whether they were able to quench superconductivity completely for their normal state measurements at the lowest temperature.

Curves for C_{es} obtained from both of these experiments appear in Fig. 7. The Chou, White, and Johnston data can be approximated by Eq. (22), except at the lowest temperatures, whereas the work of Brown, Zemansky, and Boorse is approximated by a slightly different exponential expression.

Worley, Zemansky, and Boorse[39] reported specific heat data on normal and superconducting tantalum

[39] Worley, Zemansky, and Boorse, Phys. Rev. **99**, 447 (1955).
[40] W. H. Keesom and P. H. van Laer, Physica **4**, 487 (1937).
[41] Chou, White, and Johnston, Phys. Rev. **109**, 788 (1958).

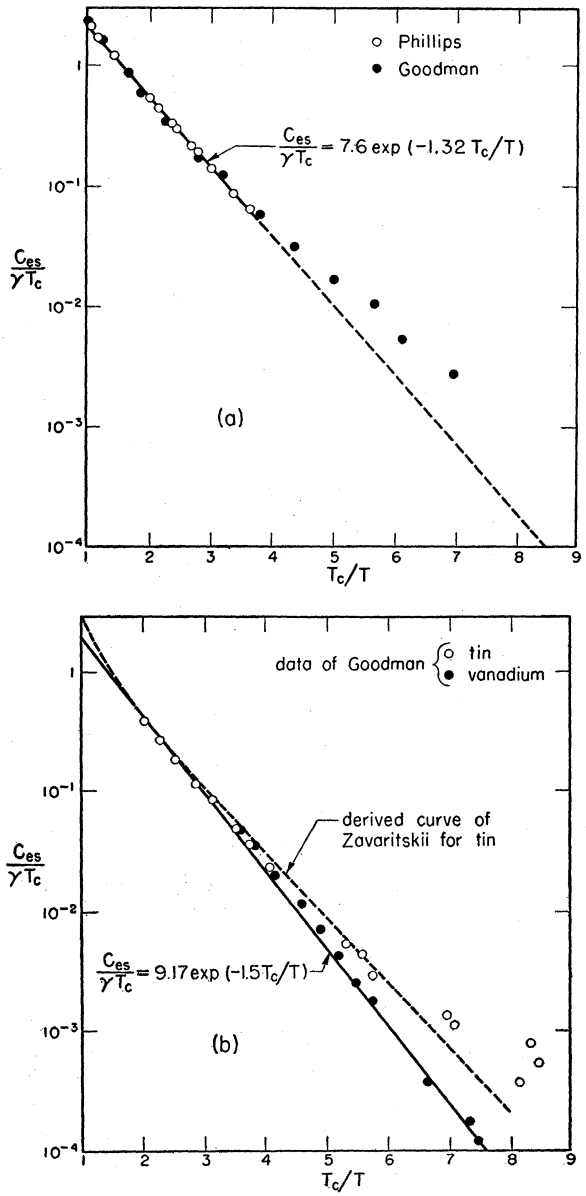

FIG. 8. Electronic specific heat of superconductors from work below 1°K; (a) for aluminum, and (b) for tin and vanadium.

and vanadium. The vanadium results were in agreement with the work of Corak *et al.* over the range of temperature common to both measurements. The values for C_{es} for tantalum deviate only slightly from the expression for vanadium and tin, Eq. (22). More recent work of White, Chou, and Johnston[42] on tantalum is in substantial agreement with the above.

Specific heat measurements on the superconductors indium[43] and thallium[44] cannot be considered very strong evidence either for or against an exponential temperature dependence of C_{es}. Both of these metals have low Debye Θ's (109.0°K for indium and 86.6 for thallium), so that C_{es} is never more than about 25% of C_s. Furthermore, neither of these investigations extended appreciably below 0.5 T_c where clear-cut information regarding an exponential temperature dependence of C_{es} can be obtained.

For the specific heat data of Clement and Quinnel on indium, an H_c-T curve was calculated which is in agreement with that derived from magnetic measurements,[45] and their values of C_{es} are in fair agreement with the vanadium and tin data over the limited temperature range covered, as seen in Fig. 7.

The determination of C_{es} for thallium from the specific heat data of Snider and Nicol is uncertain, not only because of the unfavorable ratio C_{es}/C_L (see Table I), but also because of the high experimental error. Thus, there is a wide choice of curves for C_L, C_{es}, and C_{en} as a function of temperature within their limits of error. Unfortunately, Snider and Nicol fitted their data with curves which violate the third law of thermodynamics and imply an H_c-T curve quite different from that found by direct measurement.[45] The critical field measurements indicate that $C_{es}/\gamma T_c$ for both thallium and indium should resemble quite closely comparable values for vanadium and tin.

Recently, two investigations of the specific heat of superconductors below 1°K have been reported in preliminary form. Goodman[46] has extended measurements on vanadium and tin down to $T_c/8$ and has measured C_s for aluminum from T_c to $T_c/7$, and Phillips[47] has reported measurements of the specific heat of superconducting aluminum from the transition temperature to approximately $T_c/4$ ($\sim$0.3°K). The former are particularly significant because they extend to lower reduced temperatures than previously reached, and the latter because of their high precision for this range of temperature. The results of these two experiments are shown in Fig. 8.

Over the common temperature range the two sets of data on aluminum are in agreement with the exponential expression proposed by Phillips,

$$C_{es}/\gamma T_c = 7.6 \exp(-1.32 T_c/T). \qquad (23)$$

Goodman's values for C_{es} for vanadium, while differing slightly from the higher temperature work in the region of overlap, are in essential agreement with Eq. (22) to the lowest temperatures. For tin, however, his lowest temperature values are a factor of ten higher than predicted by Eq. (22), and for aluminum his lowest temperature values are a factor of four higher than predicted by Eq. (23). In the case of tin, C_{es} becomes a very small fraction of the total, C_s, at the

[42] White, Chou, and Johnston, Phys. Rev. **109**, 797 (1958).
[43] J. R. Clement and E. H. Quinnel, Phys. Rev. **92**, 258 (1953).
[44] J. L. Snider and J. Nicol, Phys. Rev. **105**, 1242 (1957).
[45] E. Maxwell and O. S. Lutes, Phys. Rev. **95**, 333 (1954).
[46] B. B. Goodman, Compt. rend. **244**, 2899 (1957).
[47] N. Phillips, *Proceedings of the Fifth International Conference of Low Temperature Physics and Chemistry*, Madison, Wisconsin (August, 1957) (to be published).

lowest temperature so that a small systematic error in the measurements or a small error in the calculated lattice contribution would result in a large error in C_{es}. This is not true in the case of aluminum for which even at the lowest temperatures, C_{es} constitutes a very large fraction of the total heat capacity. However, the deviations in aluminum occur in the region of temperature below 0.3°K where uncertainties in the magnetic temperature scale may be relatively large. Furthermore, the thermal conductivities of the cooling salts become so low at these low temperatures that one cannot be certain of attaining thermal equilibrium.

From measurements of the thermal conductivity and the thermal diffusivity, D, using the relation $D=K/\eta C$, where η is the density, Zavaritskii[34] obtained values of the specific heat of superconducting tin over a wide range of reduced temperature. Although there is agreement with Corak and Satterthwaite over the range of temperature common to both investigations, the claim is made that the simple expression of the form of Eq. (22) or (23) is inadequate, and that the data require a generalization to

$$C_{es}=A(T)\exp(-bT_c/T). \tag{24}$$

The accuracy of the work of Zavaritskii is limited because C_{es} is a small fraction of the total specific heat of tin at low temperatures and because the derived values for C_{es} include errors in both the thermal conductivity and the thermal diffusivity. Therefore, although Eq. (24) may ultimately be required, present results do not seem to warrant this refinement.

Recently Bernardes[48] has shown that the electronic specific heats of vanadium and tin can be derived from an *ad hoc* energy gap model of the same form as that shown in Fig. 1(c). To obtain agreement in detail, he used an energy gap whose width varied with temperature as shown in Fig. 9. Good agreement is also obtained with the specific heat calculated from the BCS theory,[4] as shown in Fig. 10.

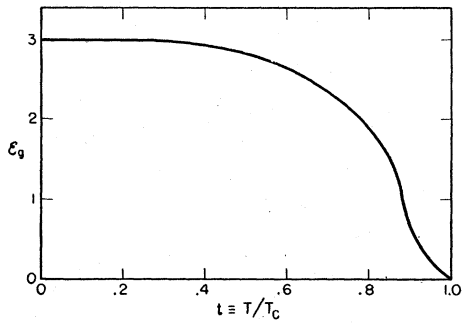

FIG. 9. Energy gap variation with temperature used by Bernardes to obtain agreement with the experimental specific heats of tin and vanadium.

[48] N. Bernardes, Phys. Rev. **107**, 354 (1957).

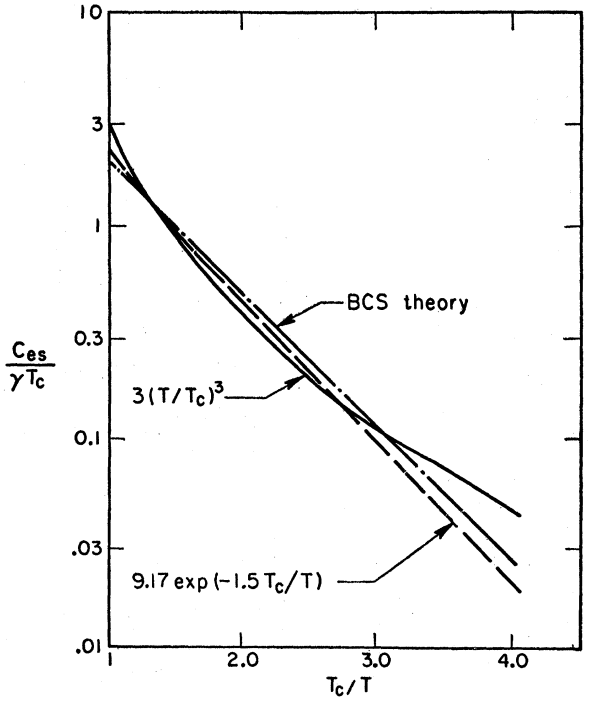

FIG. 10. A comparison of the electronic specific heat for superconductors predicted by the theory of Bardeen, Cooper, and Schrieffer with the exponential expression found to fit the data for tin and vanadium. The prediction of the Gorter-Casimir theory, $3(T/T_c)^3$, is also shown.

D. Magnetic Properties

From the thermodynamic relationship between the specific heat and the critical field, Eq. (4), it is possible to get some information about the electronic specific heat from H_c-T data for metals which exhibit reversible magnetic behavior. It is of particular interest to examine the magnetic properties of those metals for which C_{es} is so small relative to the lattice specific heat that it cannot be determined calorimetrically.

To determine an H_c-T curve for a superconducting sample, one observes the magnetic susceptibility while varying either the magnetic field or temperature, the other being held constant. For a needle-like specimen parallel to the field, the magnetic susceptibility increases abruptly from zero to unity when the magnetic field is increased above the critical field at a given temperature, or when the temperature is increased above a critical temperature for a given magnetic field. Since the change in susceptibility is quite large in crossing the critical curve on the $H-T$ plane, it is sufficient to use a relatively insensitive method of measuring the susceptibility in the determination of these curves. Generally, this method involves observing the change in inductance of coils surrounding the sample.

It would be possible to obtain values of C_{es} from critical field data using Eq. (4) if some assumption were made about the normal state specific heat. For

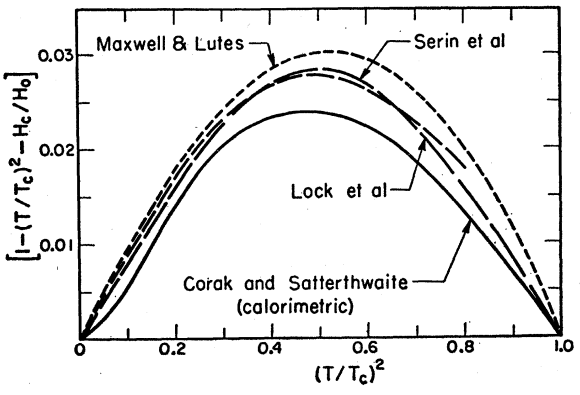

FIG. 11. Comparison of the critical field of tin derived from specific heat measurements with several directly measured values. The curves are plotted in a form which exhibits deviations from the Gorter-Casimir theory.

the purposes of comparison, however, it is equally satisfactory to compare the reduced critical field curves directly since we know that if these are similar the variation of $C_{es}/\gamma T_c$ with temperature must be similar. It must be noted that the critical field becomes a very insensitive measure of the electronic specific heat at low temperatures since the fractional change in H_c per unit change in temperature decreases whereas the fractional change in C_{es} increases with decreasing temperature.

A comparison can be made among superconductors by plotting deviations from the parabolic expression for H_c of the Gorter-Casimir theory, Eq. (10). Such a comparison is shown in Fig. 11 between H_c calculated from the calorimetric data of Corak and Satterthwaite[38] and several magnetically determined values[45,49,50] for tin.

On a similar deviation plot (Fig. 12), H_c-T curves for vanadium and tin determined from calorimetric measurements are shown with those for thallium, indium, and mercury reported by Maxwell and Lutes[45] and the recent curves for lead of Decker, Mapother, and Shaw.[51] The similarity among vanadium, tin, indium, and thallium indicates that they must have quite similar electronic specific heats in terms of reduced variables. The fact that mercury shows no deviation (in agreement with earlier work of Reynolds, Serin, and Nesbitt[52]) is evidence that C_{es} for mercury differs from that for vanadium and tin. In fact, it approximates quite closely the T^3 dependence of the Gorter-Casimir theory over the range of temperature for which accurate determinations of specific heat can be obtained from critical field data. The deviation of lead in the opposite direction indicates that C_{es} for lead differs to an even greater extent than mercury from the other metals. Figure 13 shows a sketch of the approximate behavior of C_{es} for mercury and lead compared to that for vanadium and tin as inferred from the H_c-T curves.

If superconductivity is characterized by an energy gap in the electronic energy level spectrum, then even for mercury and lead, one would expect C_{es} to be dominated by an exponential term at low temperatures. It may be that for these two metals, for which the ionic lattices are relatively highly excited in the superconducting temperature range, the interactions which are responsible for superconductivity may be changing with temperature, giving rise to the anomalous behavior of C_{es} and H_c.

Direct determination of C_{es} to low reduced temperatures on these metals would be quite interesting, but, unfortunately, C_{es} would be expected to make so small a contribution to the total specific heat ($<3\%$ for mercury and $<7\%$ for lead at T_c) that accurate measurements of C_{es} would be extremely difficult.

From the bulk of thermal and magnetic data it appears that an exponential variation in C_{es} with $1/T$, for temperatures well below T_c, is a general property of superconductors. Such a temperature dependence is characteristic of an activation energy $\mathcal{E}_A$, where $\mathcal{E}_A/k$ is the coefficient of $1/T$ in the exponent. If we interpret the activation as excitation of particles across an energy gap, the gap width is related to the number of statistically independent particles; e.g., if a hole and electron are simultaneously excited, the gap width $\mathcal{E}_g$ will be $2\mathcal{E}_A$.

It is now clear that the law of corresponding states, i.e., that the superconducting properties are universal functions in terms of reduced variables, is only approximate. It cannot, therefore, be concluded that the energy gap, in units of kT_c, is a universal function of temperature.

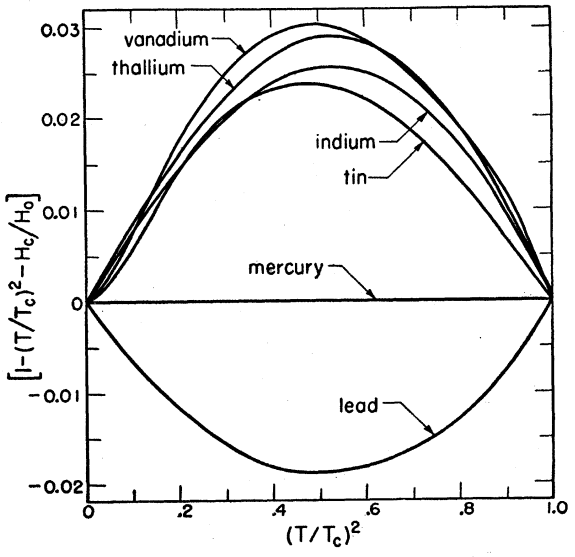

FIG. 12. Comparison of reduced critical fields for various superconductors.

[49] Lock, Pippard, and Shoenberg, Proc. Cambridge Phil. Soc. 47, 811 (1951).
[50] Serin, Reynolds, and Lohman, Phys. Rev. 86, 162 (1952).
[51] Decker, Mapother, and Shaw, *Proceedings of the Fifth International Conference of Low Temperature Physics and Chemistry*, Madison, Wisconsin (August, 1957) (to be published).
[52] Reynolds, Serin, and Nesbitt, Phys. Rev. 84, 691 (1951).

The critical field data for mercury and lead do not appear to give an exponential variation of C_{es} with $1/T$. However, for lead a very rapid (probably exponential) variation of the thermal conductivity with temperature has been observed at very low reduced temperatures, which implies a corresponding variation in C_{es}.

Furthermore, because of the insensitivity of the H_c-T curves, the critical field data do not preclude that, at very low temperatures, C_{es} for both lead and mercury assume a temperature dependence of the form $\exp(-c/T)$.

III. INTERACTION OF CONDUCTION ELECTRONS WITH ATOMIC NUCLEI

A. Nuclear Resonance

The technique of nuclear resonance has been found to give information about the conduction electrons in a metal through their effect on the nuclear energy levels and thus on the resonant frequency. The Knight shift, the fractional difference in resonant frequency between a nucleus in a free ion and that same nucleus in a metal, is directly proportional to the spin susceptibility of the conduction electrons which, in turn, is proportional to the density of states[53,54] near the Fermi energy, as expressed in Eq. (2). Implicit in this relation is the assumption that the wave function of the electrons at the nuclei are independent of energy. In equating the change in the Knight shift to the change in the integral of Eq. (2), it is assumed that the electron wave functions near the nuclei are the same in the normal and in the superconducting states. This seems reasonable.

Reif[55] and Knight, Androes, and Hammond[56] have independently made studies of the nuclear resonance in superconducting mercury. The experiments must be conducted in a magnetic field; the greater the field, the greater the sensitivity. The magnetic fields used in these experiments were as large as 5000 oersteds, a value much larger than the critical field of bulk mercury at absolute zero. This was made possible by the use of particles a few hundred angstroms in diameter, since the critical field for small particles is much greater than for the bulk material.[57] The use of these small particles also reduces difficulties associated with the exclusion of the magnetic field from all but a small penetration layer of about 500 A thickness at the surface. The surface area, and therefore, the useful volume is much greater than for bulk superconductors; and, if the particles are smaller than the penetration depth, the magnetic field is more uniform and the resonance lines narrower.

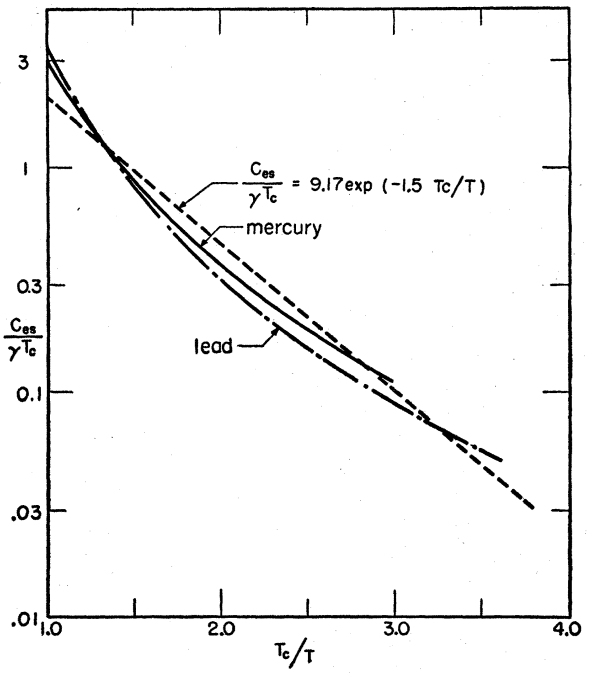

FIG. 13. Approximate behavior of the electronic specific heat inferred from the critical field data for lead and mercury.

One must then ask whether the results are characteristic of *bulk* superconductors. This is a particularly important question since the size of the particles is very small compared to a characteristic dimension of the superconducting state, the so-called coherence length.[58] Until important differences arise, however, it seems reasonable to assume that the essential features of superconductivity are the same in small samples as they are in bulk superconductors.

A detailed description of the technique of nuclear resonance is available in the paper by Reif, as well as a description of the preparation of the colloidal particles. The particles of which his sample was composed were spheres of radius a, such that $0.1\lambda_0 \lesssim a \lesssim \lambda_0$, where λ_0 is the penetration depth at $T=0°K$. This variation in size, as well as the inhomogeneity in magnetic field in a single particle, seriously complicates the interpretation of the results.

In Fig. 14 is shown a sample of the nuclear resonance data obtained by Reif at one temperature and magnetic field value. Two resonances appear, (a) due to normal metal and (b) due to superconducting metal. (The normal line arises from particles so large that they are quenched in the field.)

Since the broadening of the normal line is believed to be symmetric, its center is taken to be the center of symmetry. The asymmetric broadening of the superconducting line was attributed to the variation in magnetic field intensity over the volume of the particles. From the general features of the variation of field

[53] W. D. Knight, *Solid State Physics* (Academic Press, Inc., New York, 1956), Vol. 2, pp. 97–98.
[54] A. H. Wilson, *Theory of Metals* (Cambridge University Press, New York, 1953), second edition, pp. 150–151.
[55] F. Reif, Phys. Rev. **102**, 1417 (1956); **106**, 208 (1957).
[56] Knight, Androes, and Hammond, Phys. Rev. **104**, 852 (1956).
[57] This can be shown to follow from a thermodynamic argument involving the decrease of field energy due to the penetration of field into the sample. See reference 2, pp. 171–174.
[58] A. B. Pippard, Proc. Roy. Soc. (London) **A216**, 547 (1953).

within superconducting particles, Reif has given a plausible argument for selecting the minimum as the center of the unperturbed line.[59]

The results of Reif's measurements are presented in Fig. 15. The region near the transition temperature has been shown as a dashed curve because measurements could not be made in that region. At fields less than 2300 oersteds, Reif's extrapolated value of the Knight shift to 0°K is 1.6%. In contrast, the experiment by Knight, Androes, and Hammond[56] at 5000 oersteds showed a Knight shift of $<0.5\%$ for $t=T/T_c<0.5$. Although the two experiments are similar in most respects, there are differences which might suggest reasons for the difference in the results. The particle sizes in Reif's experiment were somewhat larger and had a different distribution than those in the experiment of Knight *et al.* Furthermore, the density of particles used in Reif's sample was greater. Both of these differences would require corrections to obtain the local magnetic field from the applied field in the experiment by Reif. However, it does not seem that the magnitude of the corrections can account for the difference in results. Finally, the magnetic field used by Knight and collaborators was more than twice that of the largest field used by Reif. Again, it is difficult to imagine how this could account for the discrepancy. It seems that more data are needed either to establish or dispel the differences in the results of these experiments.

Only the result of the experiment by Knight, Androes, and Hammond seems to give support to the concept of an energy gap. That is, if the Knight shift goes to zero as $T\rightarrow 0$°K, then the density of states would seem to be zero at the Fermi level as required in an energy gap model.† At the lowest temperatures, the Knight shift should vary exponentially with $1/T$, the magnitude of the exponent giving a measure of the gap width at 0°K. Knight *et al.* give no data to check this point.

Since Reif's result does not indicate that the Knight shift goes to zero, it would seem to rule out the possibility of the density of states being zero at the Fermi surface. In terms of a one electron model, it suggests a sharp drop in the density of states, but not to zero.

The information obtainable from the Knight shift should be very similar to that from specific heats (both are related in much the same way to the density of states near the Fermi level). Since the specific heat data seem to give consistent evidence that the density of states at the Fermi surface goes to zero at 0°K in a superconductor, and since there is a disagreement in the two available results on the Knight shift, we will draw no conclusions from these results.

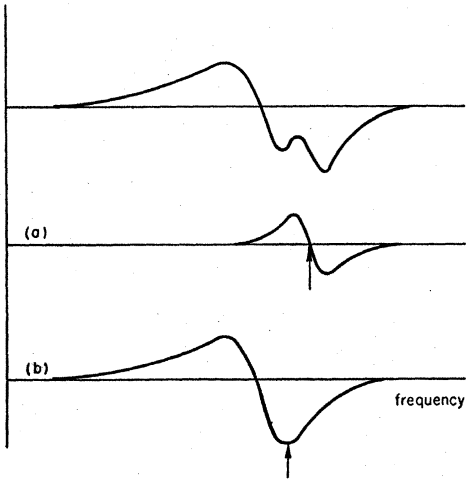

FIG. 14. Sketch of the derivative of the nuclear resonance absorption lines for colloidal mercury. The upper curve is the observed curve at one temperature and magnetic field value. This curve is then decomposed into (a) the normal resonance line and (b) the superconducting resonance line. The arrows indicate the center of each of the lines (see text).

[59] Because of the complexity of the argument and because errors of approximation are unlikely to cause any major errors in the conclusions, details of the analysis are omitted.

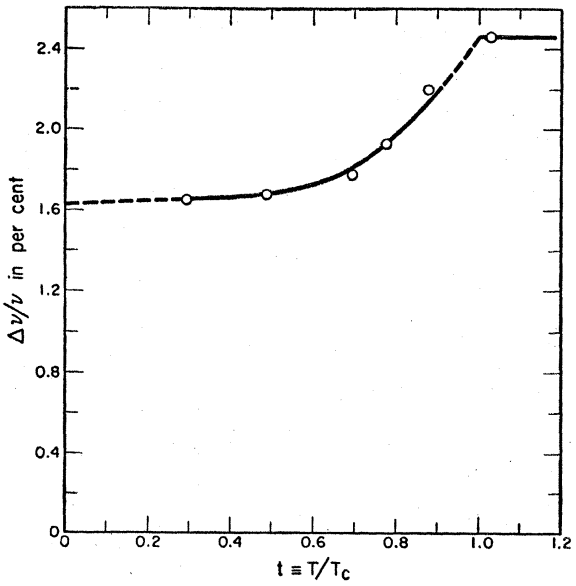

FIG. 15. Knight shift as a function of temperature for superconducting mercury as measured by Reif.

B. Nuclear Relaxation

The relaxation of the nuclear spin system in a metal occurs predominantly by interactions between the

† *Note added in proof:* In a recent paper Kei Yosida [Phys. Rev. **110**, 769 (1958)], has calculated the paramagnetic susceptibility of a superconductor according to the BCS theory. His conclusion that the susceptibility approaches zero exponentially in $1/T$ is in agreement with our conclusion about a one electron energy gap model. On the other hand, it may be possible to modify the BCS theory in a way that would give a nonzero spin paramagnetism at $T=0$. Pippard (private communication) has suggested that the BCS interaction between electrons of exactly opposite spin and momentum is highly idealized, since it is not possible in a real specimen to specify the electron momentum accurately enough to have only two electrons involved in the interaction. Pursuing this argument, we see that the energy gap of the BCS theory is not a real energy gap for individual electron spin reversal and that a spin paramagnetism may exist at absolute zero.

nuclei and the conduction electrons in the tail of the Fermi distribution. In particular, when a nucleus changes its spin direction, an electron also changes its spin to conserve the total spin. When the metal becomes superconducting, we might expect a change in the number of electrons available[60] for this exchange of spin and, therefore, a change in the nuclear relaxation rate.

Hebel and Slichter[61] have measured the nuclear spin-lattice relaxation rate, $\mathfrak{R}$, in superconducting aluminum. In principle, the technique they used was to observe the rate of approach to thermal equilibrium of the nuclear spin system after the magnetizing field was suddenly switched off. This rate of approach was obtained from the change in amplitude of the nuclear magnetic resonance absorption. Because there are difficulties in obtaining penetration of the field in a superconductor, the relaxation in the superconducting state was deduced from measurements in the normal state by the following technique. The nuclei were aligned and equilibrated in a field of 500 oe, enough to destroy superconductivity in the powdered sample used, and the amplitude of the resonance was determined. The field was then dropped rapidly to zero, allowing the sample to become superconducting with a net nuclear spin alignment. The nuclei were then left to relax toward thermal equilibrium in this state for a specified interval of time before the magnetic field was again brought rapidly to 500 oe, adiabatically warming the spin system. The amplitude of the resonance was then observed and the change analyzed in terms of the relaxation time in the superconducting state.

The results that were obtained by Hebel and Slichter consisted only of points between 0.94°K and the transition temperature, 1.17°K, ($t=0.8$ to 1.0). They found that the relaxation rate in the superconducting state, $\mathfrak{R}_s$, was greater than that in the normal state, $\mathfrak{R}_n$, obtained by extrapolation from above the transition temperature. In fact, at $t=0.8$, $\mathfrak{R}_s \approx 2\mathfrak{R}_n$. Hebel and Slichter include an unpublished result of Reif on the relaxation rate of mercury at $t=0.27$, namely $\mathfrak{R}_s \approx 0.1\mathfrak{R}_n$. Now, if one accepts the law of corresponding states and adds this result to the aluminum results, one has the superconducting relaxation rate greater than the normal relaxation rate just below T_c, and much smaller than the normal relaxation rate far below T_c. The full curve may look somewhat like Fig. 16.

In order to understand this result in terms of an energy gap model, it is first necessary to consider how the interaction of conduction electrons with the nuclei affects the relaxation rate. Hebel and Slichter assume that the wave functions (or at least the matrix elements for electron spin reversal) do not change appreciably in the transition to the superconducting state and are independent of energy near the Fermi surface. They are then able to obtain the expression for the relaxation rate given by Eq. (3). Because of the nature of the factor $\partial f/\partial\epsilon$ in the integral of Eq. (3), $\mathfrak{R}$ is seen to be, effectively, an average of $[g(\epsilon)]^2$ over the range kT about the Fermi surface. In the normal metal $g(\epsilon)$ is almost constant near the Fermi surface and $\mathfrak{R}$ is just proportional to the factor, kT. In the superconducting state, with an energy gap, the situation is more complicated. Near T_c, if the states that have been removed are piled on the edge of the gap as in Fig. 1 (c), 1(d), or 1(e), and if the gap is small compared to kT, then clearly the average of $[g(\epsilon)]^2$ will be greater for the superconducting state than for the normal state. But, at low temperatures $\partial f/\partial\epsilon$ becomes very small where $g(\epsilon)$ has nonzero values, causing the value of the integral to fall rapidly with decreasing temperature. In fact, one would expect that the relaxation rate, at least from interactions with the conduction electrons, would go to zero exponentially as T approached zero with any kind of a gap at the Fermi level. This explanation is consistent with the variation of $\mathfrak{R}$ shown in Fig. 16. Hebel and Slichter point out that it is difficult to see how a two fluid model could describe values both

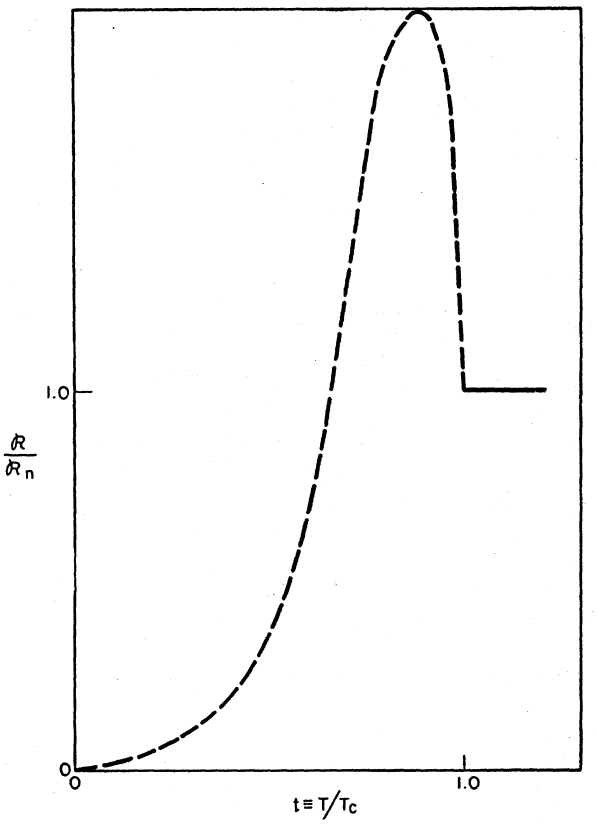

FIG. 16. Schematic representation of the reduced nuclear relaxation rate as a function of reduced temperature in a superconductor suggested by Hebel and Slichter.

[60] The electrons that can be considered available are those which can find an empty final state of the proper energy.

[61] L. C. Hebel and C. P. Slichter, Phys. Rev. 107, 901 (1957).

greater than and less than the normal state value as the temperature is varied between zero and T_c. Furthermore, they have compared the relaxation rate data with the predictions of the BCS theory[4] and find quantitative agreement.

In evaluating the conclusions of this experiment one wishes that there were more data. In particular, it seems important to obtain the nuclear relaxation rate over a sufficiently large temperature range on a single metal so that it is not necessary to invoke the questionable law of corresponding states. Similarly, it would be desirable to use a single measurement technique over the whole temperature range. It appears that more data are needed to establish firmly the conclusions of Hebel and Slichter and to establish the actual temperature dependence of the decrease in relaxation rate. It is this temperature dependence which would enable one to deduce the size of the gap. However, the present results add information to that obtained from electronic specific heat, since these involve an averaging of the *square* of the density of states. The increase of the relaxation rate just below the transition temperature enables the authors to ascribe a rather sharply peaked function, such as in Fig. 1(e), to the density of states curves on either side of the gap.

IV. ULTRASONIC ABSORPTION

There are a number of measurable quantities for which expressions of the type given by Eqs. (1) to (3) can be written and from which additional evidence for an energy gap can be sought. Among these are ultrasonic attenuation, low-frequency microwave absorption, and the dc penetration depth in superconductors.

Measurements of the ultrasonic absorption in superconductors can be used to determine the number of thermally excited electrons. The attenuation of ultrasonic waves is the result of scattering by the lattice, by static imperfections, and by the conduction electrons. On the assumption that the lattice and imperfection scattering is temperature independent at low temperatures and that the electron scattering goes to zero at absolute zero, the electronic contribution at any temperature is determined by subtracting the residual absorption at 0°K. The variation with temperature of the ultrasonic absorption is then primarily the result of changes in the number of thermally excited (normal) electrons.

Absorption measurements[62–64] have been made by observing the decrease in amplitude of an ultrasonic pulse on transmission through a specimen of the bulk superconductor. Quartz transducers affixed to the sample are used to generate and to detect the ultrasonic energy.

Recently, Morse and Bohm[65] have claimed to measure an energy gap from ultrasonic attenuation in superconducting tin and indium. They suggest that a calculation of the quantity $\mathcal{E}$ from the formula

$$\alpha_s/\alpha_n = 2[\exp(\mathcal{E}/2kT)+1]^{-1}, \tag{25}$$

derived in the BCS[4] theory, where α is the ultrasonic attenuation coefficient, constitutes a direct determination of the temperature dependence of the superconducting energy gap. They further compare their normalized values of α_s/α_n with the prediction of the BCS theory and conclude that "the agreement of the theory with experiment on the whole is remarkably good." These conclusions are not justified for the following reasons: (a) The expression for α_s/α_n, Eq. (25), was derived from the BCS theory‡ and has not been shown to have more general validity. Therefore, the calculation of $\mathcal{E}_g$ from experimental data using this equation only provides a method of comparison with the BCS theory. It does not provide a direct way of measuring an energy gap, nor even demonstrate its existence. (b) Although the agreement between experiment and the BCS theory appears reasonably good, it cannot be considered a strong confirmation of the theory since the temperature dependence of α_s/α_n over the measured range is not sensitive to the particular choice of model of superconductivity. Furthermore, the "shorting out" effect‡ may introduce large uncertainties in any theoretical treatment of ultrasonic attenuation in superconductors.

If one examines the ultrasonic measurements in terms of more general energy gap models, one expects at low temperatures an exponential variation of the attenuation with $1/T$ as a result of a corresponding variation in the number of electrons thermally excited across the gap. We have examined some of the existing data and find that they are consistent with this sort of temperature dependence.

Low-frequency microwave absorption,[10–13] which also depends on the number of normal electrons, should also exhibit the activation characteristic of excitation across a gap. Preliminary examination of these various measurements indicates that again, at low temperatures, they are consistent with an exponential variation with $1/T$, leading to an activation energy of $\sim kT_c$. Unfortunately, neither the ultrasonic absorption nor the microwave experiments that have been reported cover a sufficiently wide temperature range with enough accuracy to give evidence comparable to that obtained from the specific heat.

[62] H. E. Bömmel, Phys. Rev. **96**, 220 (1954).
[63] L. Mackinnon, Phys. Rev. **100**, 655 (1955).
[64] Morse, Tamarkin, and Bohm, Phys. Rev. **107**, 1610 (1956).
[65] R. W. Morse and A. V. Bohm, Phys. Rev. **108**, 1094 (1958).

‡ It has been pointed out to us by Holstein and by Pippard that the expression for ultrasonic attenuation in superconductors [Eq. (25)] does not include an internal shielding effect arising from the ability of superconducting electrons to partially short out the deformation fields associated with an ultrasonic wave. This "shorting out" effect would lower the deformation fields acting upon the normal electrons and decrease their absorption of energy. It is not yet clear whether or not this effect is significant, particularly for longitudinal waves.

V. QUANTUM EFFECTS IN MICROWAVE AND INFRARED STUDIES

A. General Remarks

Although the frequency range given by $h\nu \sim kT_c$ had been suggested some time ago as an interesting region for studying the nature of the superconducting state, the experimental difficulties resulted in several years' delay before such experiments were undertaken. Then, independently, a number of laboratories took up the problem, working with bulk materials,[66–72] where the radiation is confined to a small layer near the surface, or with films so thin[73–75] that an appreciable fraction of the power is transmitted.

All of the information concerning the interaction of electromagnetic radiation with bulk superconductors can be expressed in terms of the surface impedance, $Z \equiv R + iX \equiv (E/H)_0$, the ratio of electric to magnetic field at the surface of the metal. For metals, where $|Z|$ is much less than Z_0, the impedance of free space, the surface resistance R is directly proportional to the fraction of the incident power which is absorbed.[76]

Measurements of the surface resistance and the surface reactance of bulk superconductors had been made before 1955, but only at photon energies less than $0.5kT_c$[10–13] and greater than $140kT_c$.[8,9,14–16] Schematic curves of the surface resistance ratio, $r \equiv R/R_n$, where R_n is the normal state value, are shown in Fig. 17. While the dc curve, (*a*), drops abruptly to zero at the transition temperature, the curves at microwave frequencies, (*b*) and (*c*), only gradually approach zero as the temperature approaches zero.[77] The curve at infrared frequencies, (*d*), is unaffected by the superconducting phase transition. The fact that there is no difference between the surface resistance in the normal state and in the superconducting state at very high frequencies ($h\nu > 140kT_c$), cannot be understood in terms of the two fluid model in which the superconducting electrons are described by the London theory.[78] However, it can be understood in terms of an energy gap model, provided that the gap is small compared to $140kT_c$.

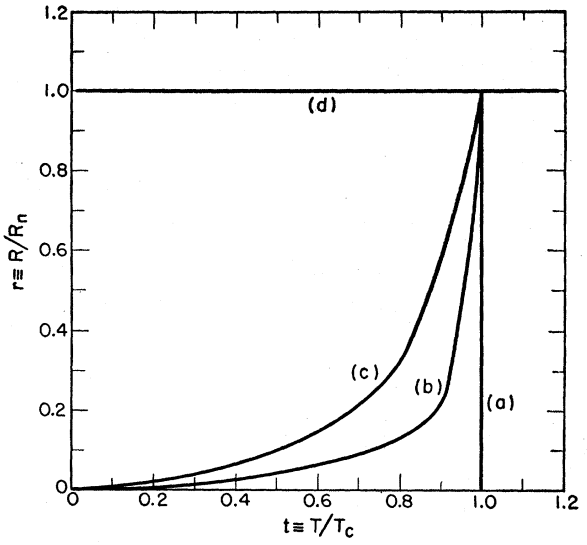

FIG. 17. Sketch of surface resistance ratio as a function of reduced temperature for several frequencies; (*a*) dc, (*b*) and (*c*) two microwave frequencies, and (*d*) infrared frequencies.

The microwave work below $0.5kT_c$ has already been adequately discussed.[2,13] Some of the more relevant features of the analysis are reviewed here in order to understand the limitations on the conclusions to be drawn from experiments at $h\nu \sim kT_c$.

The two fluid model gives a simple explanation of the temperature dependence of the microwave absorption at frequencies below $0.5kT_c/h$. The absorptivity can be described in terms of two quantities, the volume absorptivity and the effective penetration depth of the electromagnetic field. The volume absorptivity depends only on the normal electrons. The penetration depth, however, depends both on the normal and superconducting electrons, although in practice, except for a very small temperature region close to T_c, the penetration is limited almost exclusively by the superconducting electrons. The rapid fall in the surface resistance just below the transition temperature can be largely ascribed to the rapid change in penetration depth resulting from the corresponding change in the number of superconducting electrons. At low temperatures, however, the penetration depth becomes constant and the fall to zero absorptivity as $T \to 0$ must be associated with the disappearance of the normal electrons.

The frequency dependence of the absorptivity ratio can also be qualitatively understood in this way at low temperatures. When the penetration depth is dominated by the frequency independent superconducting penetration depth λ, the absorptivity in the super-

[66] A. Galkin and P. Bezuglii, Doklady Akad. Nauk S.S.S.R. **97**, No. 2, 217 (1954).
[67] Bezuglii, Galkin, and Levin, Doklady Akad. Nauk S.S.S.R. **105**, No. 4, 683 (1955).
[68] Blevins, Gordy, and Fairbank, Phys. Rev. **100**, 1215 (1955).
[69] G. S. Blevins, thesis, Duke University (1957); Blevins, Gordy, and Fairbank, Bull. Am. Phys. Soc. Ser. II, **3**, 183 (1957).
[70] Biondi, Garfunkel, and McCoubrey, Phys. Rev. **101**, 1427 (1956).
[71] Biondi, Garfunkel, and McCoubrey, Phys. Rev. **108**, 495 (1957).
[72] Biondi, Forrester, and Garfunkel, Phys. Rev. **108**, 497 (1957).
[73] R. E. Glover and M. Tinkham, Phys. Rev. **104**, 844 (1956).
[74] M. Tinkham, Phys. Rev. **104**, 845 (1956).
[75] R. E. Glover and M. Tinkham, Phys. Rev. **108**, 243 (1957).
[76] Generally the fraction of incident power absorbed is $A = 4RZ_0/(Z^2 + 2RZ_0 + Z_0^2)$. For $|Z| \ll Z_0$, this reduces to $A = 4R/Z_0$.
[77] The characteristic extrapolation to $R=0$ at $t=0$ is only approached when care is taken in the preparation of the surface and if the measurements are carefully made. However, it is generally believed that under ideal conditions this limiting resistance is actually zero.
[78] For a thorough description of the London theory, see F. London, *Superfluids* (John Wiley and Sons, Inc., New York, 1950), Vol. 1, Chap. B. In this theory and its extensions the superconducting electrons have only inertial properties and are therefore lossless at all frequencies.

conducting state is expected to be proportional to ν^2.[79] On the other hand, the frequency dependence of the absorptivity in the normal state is much smaller, $\nu^{2/3}$ for the cases where the anomalous skin effect[80] is applicable. Thus, the ratio, $r=R/R_n$, should become proportional to $\nu^{4/3}$ at low temperature. Although this frequency dependence is not accurately observed,[13] a rapid increase of r with frequency at low temperatures is characteristic of the microwave work.

For a quantitative treatment of the absorptivity as a function of temperature, it is necessary to use a detailed model of the superconductor. One such model is the Gorter-Casimir two fluid model, using the London theory for the superconducting electrons and the anomalous skin effect for the normal electrons.[81] Since the Gorter-Casimir theory predicts the details of the temperature variation of the numbers of normal and superconducting electrons, the whole shape of the surface resistance ratio-temperature curve can be derived. Unfortunately, the derived curves do not agree in detail with the experimental curves. One possible source of the disagreement is the assumption that the total number of electrons, superconducting and normal, is independent of temperature. If one gives up this assumption, then the shape of the curve is not determined by the model. Rather, the experiments can be fitted, fixing only the temperature variation of *either* the number of normal *or* the number of superconducting electrons. Since the number of superconducting electrons is fixed by the experimentally determined superconducting penetration depth λ, the number of normal electrons at any temperature can be determined from the surface resistance.

In terms of an energy gap model, it is the volume absorptivity in which we would seek a sudden rise with frequency as evidence of the onset of absorption by superconducting electrons. Since the penetration depth might be expected to change when the photon energies are close to an absorption edge,[82] an uncertainty is introduced into the value of an energy gap deduced from surface absorptivity, unless there is available a way of estimating the variations in penetration depth. At 0°K, however, a rise of R from zero at some onset frequency would unambiguously give the width of the gap. Furthermore, even at finite temperatures, data on the surface absorptivities of superconductors exhibit a behavior suggestive of the excitation of electrons across a gap. The temperature and frequency dependence of the absorption give a measure of the energy gap as a function of temperature.

[79] T. Holstein (private communication) has shown that for the special model in which the superconducting electrons are described by the London theory the frequency dependence is somewhat smaller, approaching ν^2 only at temperatures below those usually attained.

[80] In a metal, when the electron free paths become large compared to the penetration depth, the point relationship between current and field (Ohm's law) must be replaced by a more sophisticated treatment; e.g., G. E. H. Reuter and E. H. Sondheimer, Proc. Roy. Soc. (London) **A195**, 336 (1948).

[81] This model has been worked out in reference 12, and by T. Holstein in an unpublished extension of Dingle's calculation of the anomalous skin effect [R. B. Dingle, Physica **19**, 311 (1953)].

[82] The Kronig-Kramers integral transform defines a relation between the real and imaginary parts of any impedance or admittance. From this the imaginary part of the admittance, which largely determines the penetration depth, anticipates the onset of an absorption edge.

B. Bulk Material Work

1. Experimental Methods

Experimental determinations of the surface resistance ratio, $r\equiv R/R_n$, of bulk superconductors in the millimeter wave region have been made by several techniques. In each case measurements were made over an extended wavelength range with a single sample to eliminate effects resulting from variations in sample preparation. However, the various experiments differed markedly in the methods of preparation of the sample surfaces, thus complicating the problem of obtaining meaningful comparisons of results.

The measurements are of the following three types: (a) measurements of the Q of a microwave cavity[68,69]; (b) studies of the transmission of electromagnetic radiation through a length of wave guide[68,69,72]; and (c) measurements of the heating of a sample as a result of the absorption of electromagnetic energy[70,71] (calorimetric method). In principle, each of the methods is capable of yielding accurate determinations of r from the measurable quantities.

(a) *Cavity Q measurements.*—The Q of a resonant cavity is related to the surface resistance R of the cavity walls by the relationship,

$$R=2\pi\nu_0\mathbf{L}/Q, \tag{26}$$

where Q is the "unloaded" or intrinsic Q of the cavity, ν_0 is the resonant frequency of the cavity, and $\mathbf{L}$ depends only on the geometry of the cavity. Thus, the surface resistance ratio of a superconducting sample in the form of a cavity is given by

$$r(T)=Q_n/Q(T), \tag{27}$$

where Q_n is the Q of the cavity in the normal state. The unloaded Q may be determined from the measured resonant frequency, from the half-power frequency width $\Delta\nu$, and from the voltage standing wave ratio at resonance, ρ_0, in the line leading to the cavity. The relationship may be expressed as

$$Q=\left(1+\frac{1}{\rho_0}\right)\nu_0/\Delta\nu. \tag{28}$$

Measurements by Blevins, Gordy, and Fairbank[68] of the Q of a tin-plated TE_{01n}-mode cavity at 3 and 4 mm wavelength were made using the type of apparatus shown in Fig. 18. Power at the desired frequency was generated by a crystal harmonic generator and was

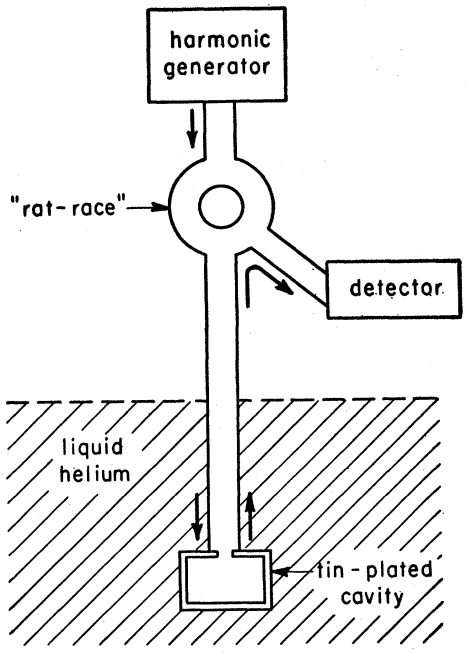

FIG. 18. Schematic diagram of apparatus of Blevins, Gordy, and Fairbank (Duke University group) used to determine the Q of a tin-plated cavity. The "rat-race" is a device which transmits power from the generator to the cavity and the reflected power from the cavity to the detector.

incident on the cavity held at a fixed temperature in the liquid helium bath. The reflected power was monitored by means of a crystal detector connected to one arm of a rat-race, a device which transmitted the harmonic generator power to the wave guide feeding the cavity and the reflected power from the cavity to the crystal detector. The results of the measurements are presented in the discussion section (Sec. VB2).

(b) *Wave-guide transmission measurements.*—In Fig. 19 is shown the basic element of an experiment for obtaining surface resistance ratio variations through measurements of the temperature dependence of the power transmitted by a length L of superconducting wave guide. If P_0 is the power incident on the sample and $P=P(T)$ the power transmitted by the sample, then $P=P_0\exp(-aRL)$, where a is a geometrical constant of the wave guide. It follows that the surface resistance ratio is

$$r(T)=\frac{\log[P_0/P(T)]}{\log[P_0/P_n]}, \tag{29}$$

where P_n is the power transmitted when the sample is normal. Unfortunately, because of line losses and the difficulties of measuring incident and transmitted power with exactly the same sensitivity, the expression for r in terms of the measured transmitted power P_d,

$$r(T)=1-A\log[P_d(T)/P_{dn}], \tag{30}$$

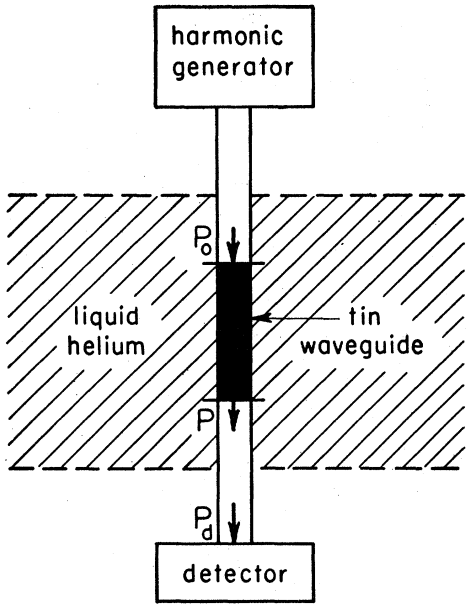

FIG. 19. Simplified diagram of apparatus used to determine the transmission of superconducting tin wave guide. The experiments of Blevins, Gordy, and Fairbank (Duke University group) and of Biondi, Forrester, and Garfunkel (BFG) are based on this method.

involves the constant

$$A=[\log(P_0/P_n)]^{-1}=aR_nL, \tag{31}$$

which, in practice, has been difficult to determine. Errors in A are exactly equivalent to adding (or subtracting) an absorptivity to the sample which is independent of temperature.

In the measurements by the Duke University group[68] the evaluation of A is made by using the results of cavity measurements to choose the normal state surface resistance of the tin. In an experiment by Biondi, Forrester, and Garfunkel[72] (BFG), the value of A is determined by comparing the measurements with those made when the tin wave guide is replaced by a very short section of essentially zero attenuation. Inaccuracies in the techniques of determining A appear to be weaknesses of both of these experiments (see Sec. VB2).

(c) *Calorimetric measurements.*—When sufficient millimeter wave power is available ($\sim$100 μw), the surface resistance of superconductors may be determined by measurements of the heating of a sample as a result of the absorption of electromagnetic energy.[76] One form of calorimetric apparatus, employed by Biondi, Garfunkel, and McCoubrey[70,71] (BGM) in studies of aluminum, is schematically illustrated in Fig. 20. Two sections of wave guide, one of copper, the other of aluminum, are connected by heat leaks to a base which is held at a fixed temperature. Absorption of microwave power (of the order of 1% of the incident power) in the guides causes temperature rises which are noted by the attached carbon resistance thermom-

eters. With the microwaves off, the temperature rises are reproduced by means of dc heaters attached to the samples. From the dc powers, the absorbed powers are determined. Since the absorption by the copper section does not depend on temperature over the range of interest, the copper serves as a power monitor. Thus, the surface resistance ratio is given by

$$r(T)=\frac{P_{\mathrm{Al}}(T)/P_{\mathrm{Cu}}}{P_{\mathrm{Al}}(T_c)/P_{\mathrm{Cu}}}, \tag{32}$$

where P represents the absorbed power in the guides.

2. *Discussion of Surface Resistance Data*

The determinations of $r(T)$ by the Duke University group for samples of electroplated tin are shown in Fig. 21. The results of the cavity measurements of Fig. 21(a) serve to determine the zero of the $r(T)$ scale in the wave-guide measurements[83] of Fig. 21(b). These curves exhibit the striking feature that the "temperature for the onset of superconductivity" is depressed as the microwave quantum energy, $h\nu$, increases. In subsequent work,[69] the authors report that the magnitude of the temperature shift is much smaller in bulk tin wave guide than in the plated samples used here.[84] In any event the authors interpret these observations as indicative of a temperature varying energy gap which increases with decreasing temperature below T_c.

These qualitative observations are consistent with the inferred energy gap behavior obtained in the work of BGM and BFG described later in the section; however, some of the quantitative aspects of the $r(T)$ curves seem open to question. For example, examination of the scatter of the data for the various measurements

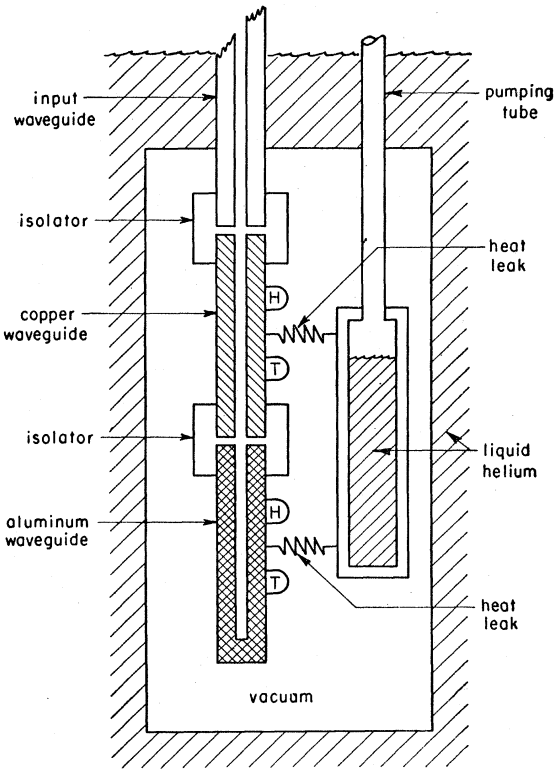

FIG. 20. Simplified diagram of the apparatus of Biondi, Garfunkel, and McCoubrey (BGM) used to measure the absorptivity of superconducting aluminum wave guide. The symbols H and T refer to heaters and thermometers, respectively, which are attached to the samples.

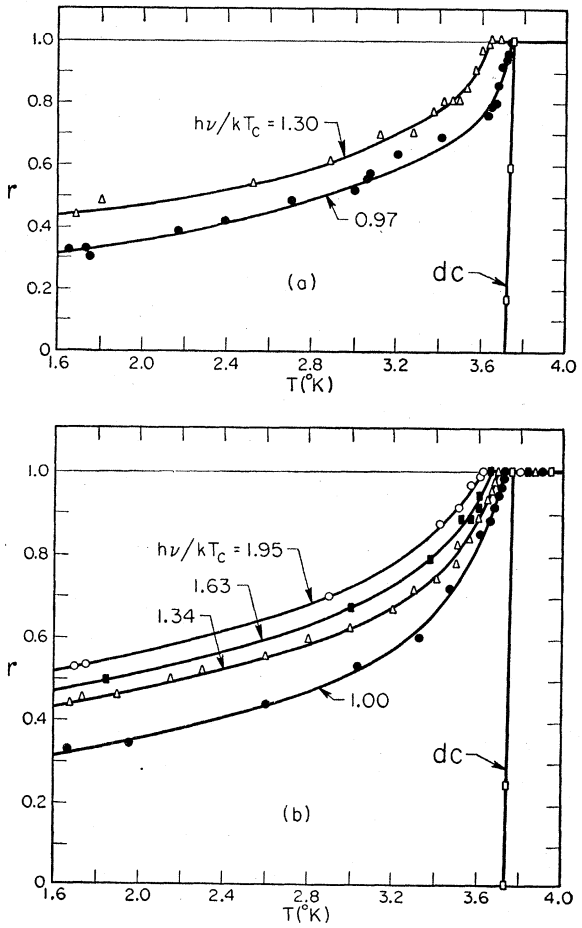

FIG. 21. Measurements by the Duke University group of the surface resistance ratio, r, as a function of temperature; (a) absolute determinations from Q measurements on a tin-plated cavity, and (b) measurements obtained from transmission data for tin-plated wave guide. In (b) the zero of the scale is determined by comparison with the cavity data.

[83] At wavelengths shorter than 3 mm, $h\nu/kT_c>1.3$, the R_n values were obtained by extrapolation of the longer wavelength measurements.

[84] Since the dc transition temperatures (measured by a magnetic susceptibility technique) of the two wave-guide samples also were somewhat different, one may argue that the different methods of sample preparation resulted in substantially different superconducting properties in each case. However, since large differences in the magnitude of the shift are also found between the tin-plated cavity and the tin-plated wave guide, the effect must be considered incompletely understood.

(see Fig. 21) suggests that the curves may well have been drawn with a smooth rounding in the vicinity of T_c rather than with the abrupt change of slope shown. Further, accurate measurements on aluminum[71] indicate that for $h\nu<2kT_c$, $r(T)\to 0$ as $T\to 0$, whereas, in all cases the curves of the Duke University group indicate nonzero values of $r(0)$. This suggests that the nonzero intercept may result from an imperfect sample surface or from systematic errors in the cavity Q determinations used to determine the zero of the $r(T)$ scale.[85] Thus, quantitative conclusions cannot be drawn from this work in its present state.

The calorimetric measurements on aluminum[71] shown in Fig. 22 involve an experimental error of $\pm 0.3\%$ in the absolute values of r. At the smallest quantum energy, $h\nu=0.65kT_c$, the curve has the essential characteristics of the lower frequency studies; that is, except for a very slight rounding, there is a sharp drop at T_c and the curve seems to extrapolate to $r(t)=0$ at $t=0$. However, at higher quantum energies the character of the curve changes in that the abrupt decrease in $r(t)$ just below $t=1$ disappears as the quantum energy increases. In their earlier measurements,[70] BGM erroneously fitted their relatively inaccurate ($\pm 3\%$ error) data[86] by curves with sharp changes of slope, patterned after the low-frequency curves (see Fig. 17). Since curves of the type deduced from the recent accurate data (Fig. 22) provide an equally good fit to the earlier data, it is clear that there is no contradiction between the data of the two sets of measurements.

As discussed earlier, at low frequencies the two fluid model is successful in predicting the observed form of the $r(t)$ curves. In this model the normal electrons alone can absorb; the superconducting electrons are lossless and act only to decrease the penetration of the electromagnetic field into the sample. The marked departure of the curves of Fig. 22 at $2.37kT_c$ and at $3.04kT_c$ from the shape predicted by the two fluid model suggests that we have encountered absorption by the superconducting electrons.

In terms of an energy gap model, we have reached quantum energies which exceed the gap with the result that transitions of superconducting electrons are induced across the gap, leading to additional absorption of energy. Unfortunately, this simple idea is complicated by the fact that, for photon energies comparable to the gap energy, the penetration depth of the field may be altered,[82] with a resulting change in absorption over the predictions of the two fluid theory. However, both quantum effects, that of increased absorption due to induced transitions of the superconducting electrons and that of increased penetration of the field, are consequences of the existence of an energy gap.

In order to evaluate the additional absorption resulting from these quantum effects, we first calculate the background absorption contributed by the *normal* electrons. This calculation[87] is based on the theory of the anomalous skin effect; the normal electron fluid provides the absorption mechanism as is the case in normal metals. The superconducting electrons are treated by the London theory[88]; since they are lossless their effect appears in the alteration of the penetration depth. A curve of $r(t)$ for a single frequency, together with the experimentally observed dependence[89] of the penetration depth $\lambda(0)/\lambda(t)=(1-t^4)^{\frac{1}{2}}$ suffices to fix all parameters needed to calculate $r(t)$ at higher frequencies.

This approach is used to predict the normal electron absorption at various frequencies from the observed absorption curve at $h\nu=0.65kT_c$. This scaling of the $0.65kT_c$ data is justified, *a posteriori*, by the inference that, over most of temperature range, the energy gap $\mathcal{E}_g$ exceeds $0.65kT_c$ and, therefore, the absorption does not involve quantum effects. An example of the results of the scaling procedure is given by the dashed curve of Fig. 22. The difference between the observed curve at $2.37kT_c$ and the calculated curve for the normal electrons represents the additional absorption due to quantum effects.

On the assumption that the additional absorption can only occur so long as the photon energy $h\nu$ exceeds the gap $\mathcal{E}_g(T)$, one finds that, at the temperature T'

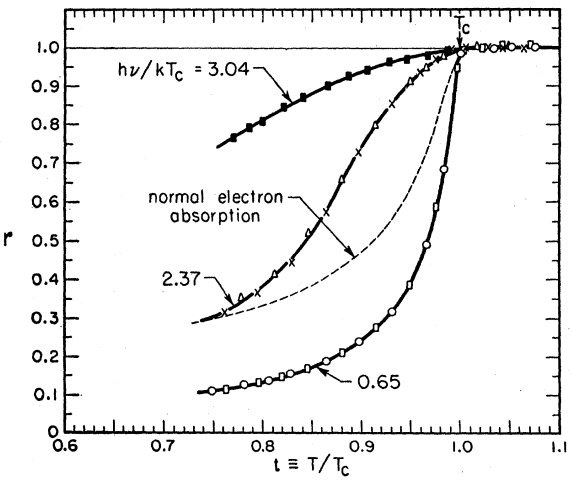

FIG. 22. Absolute measurements by BGM of the surface resistance ratio *vs* reduced temperature for bulk aluminum. The dashed curve represents the absorption by the normal electrons at $h\nu=2.37kT_c$ (see text).

[85] In order to determine the energy reflected from the cavity, it was necessary to cancel out leakage power reaching the detector from the source, introducing the possibility of serious errors in the Q measurements; see reference 69, Blevins' thesis, p. 92.

[86] The apparent "structure" in the curves was not found in their later measurements, and therefore was ascribed to experimental error.

[87] M. P. Garfunkel and T. Holstein (unpublished calculation). See also reference 81.

[88] The theory has also been developed using the nonlocal theory suggested by Pippard[58] to treat the superconducting electrons. The calculated absorption curves are sufficiently similar so that the analysis which follows is essentially the same in either case.

[89] See reference 2, p. 143.

at which the additional absorption just disappears, $h\nu = \mathcal{E}_g(T')$. By plotting the additional absorption as a function of temperature for various quantum energies and extrapolating to zero additional absorption to find T' in each case, BGM obtained the inferred energy gap variation shown in Fig. 24.

The data of BFG[72] obtained from measurements of the transmission of tin wave guide are presented in Fig. 23. Here the absolute values of $r(0)$ are set equal to zero at the various measured frequencies. This has been justified by (a) rough measurements, yielding $r(0)=0\pm0.25$, and (b) the conclusion that the energy gap at $t=0$ exceeds all of the photon energies used. When an analysis is made to determine the additional absorption for tin, the inferred energy gap variation is as shown in Fig. 24.

At the present time, the reason for the rather different shapes of the $r(t)$ curves for tin obtained by the Duke University group and by BFG is not completely clear. The accuracy of the data of BFG concerning the shape of the $r(t)$ curves in the vicinity of T_c indicates clearly that the curves at various frequencies break away from unity at T_c. While the scatter in the data of the Duke University group might permit curves of similar character to be fitted to their data, an exact correspondence between the Duke University results and those of BFG does not seem possible. Part of the difference may lie in the samples of tin used; electroplated in the Duke work, extruded in BFG's experiments. It is hoped that additional experiments will resolve these questions.

The results of the work on tin by both the Duke University group and BFG clearly disprove the behavior predicted by Galkin and Bezuglii,[66] and Bezuglii, Galkin, and Levin.[67] In these last two papers, the authors extrapolate their measurements of the surface resistance of tin in the frequency range $0.24<h\nu/kT_c<0.9$. Their prediction that the difference in absorption between normal and superconducting states would disappear at $h\nu/kT_c=1.2$ is contradicted by the more recent observations.

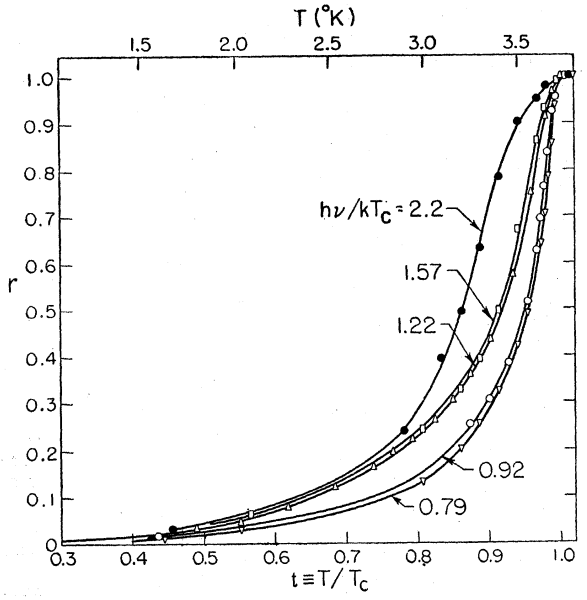

FIG. 23. Measurements by BFG of the surface resistance ratio for extruded tin wave guide. The curves are fitted so that $r(T)\to0$ as $T\to0$.

At the present time, among the microwave experiments, only those of BFG on tin and BGM on aluminum have given a measure of the temperature dependence of the energy gap $\mathcal{E}_g$. The agreement between the inferred energy gap values for aluminum and for tin is rather good (see Fig. 24). The variation of the energy gap near T_c shown by the points in Fig. 24 is also consistent with the fact that the superconducting transition is a second-order phase transition. If one invokes an energy gap model to explain superconductivity, the gap cannot vanish discontinuously at T_c.

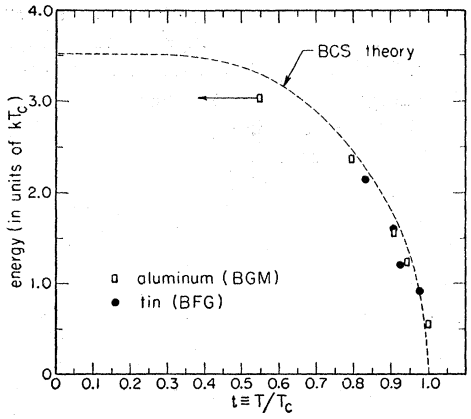

FIG. 24. Inferred variation of the energy gap with temperature. The arrow on the symbol at an energy of $3.04kT_c$ indicates that at this photon energy the gap may have been exceeded. The dashed curve indicates the prediction of the theory of Bardeen, Cooper, and Schrieffer.

Unfortunately, the use of the two fluid model and the variation of penetration depth near an absorption edge introduce some uncertainty in the separation of the absorption due to thermally excited electrons from the total absorption. The resulting uncertainties in the values of the energy gap are difficult to evaluate. However, an examination of the analysis suggests that this uncertainty is not very large, probably not causing an error in the temperature greater than $\pm5\%$ near T_c and $\pm15\%$ at the lower temperatures. The highest frequency point on aluminum is excepted in this estimate since it was obtained by extrapolating the high temperature data to lower temperatures, a procedure that is highly uncertain. It is possible that at this frequency the gap at $T=0$ has already been exceeded.

In view of these uncertainties, the agreement with the BCS theory (dashed curve of Fig. 24) is remarkably good. Furthermore, the agreement between tin and

aluminum gives additional evidence that the law of corresponding states is approximately obeyed for these superconductors.

C. Experiments with Thin Films

1. Special Features of Thin Films

The approach to the spectroscopy of superconductors through the interaction of radiation with very thin films has an advantage in the ease of interpretation of experimental data. If the film is sufficiently thin compared to the superconducting penetration depth the field intensity is constant throughout, simplifying comparisons with theory. The limitation on the mean free path of the electrons by the thickness of such thin films also simplifies calculations by forcing the current to be in phase with the field up to frequencies close to the visible region. Experimentally, thin films offer the advantage of a somewhat greater ease of studying a wide frequency range in a single experiment.

Because superconducting penetration depths are of the order of 500 A it is necessary to work with films whose thickness is of the order of 50 A. The behavior of such thin films may not be characteristic of the bulk material. It has been found[90] in the case of bulk material that strained surfaces often show absorption at 0°K. The crystalline imperfection of thin films may be as great as that occurring on the surface of a strained bulk sample, so that an absorptivity which persists to absolute zero would not be unexpected in a thin film. A more fundamental question is the effect of a film thickness which is small compared to dimensions which are characteristic of the superconducting state, the coherence length[58] and the superconducting penetration depth. Nevertheless, thin films do become superconducting, and if the superconducting state involves an energy gap it should be observable in a spectroscopic study of thin films.

All of the electromagnetic properties of a thin film, the phases and amplitudes of the reflected and transmitted waves relative to the incident wave, can be expressed in terms of the film impedance $Z=E/(H_1-H_2)=E/j$ or the admittance $Y=1/Z$, where H_1-H_2 is the difference in the magnetic field amplitudes on the two sides of the film, E is the electric field intensity (constant throughout), and j is the current per unit length in the film. We can write

$$Y=(\sigma_1-i\sigma_2)d, \tag{33}$$

where d is the film thickness and σ_1 and σ_2 the in-phase and out-of-phase components of the conductivity, respectively.

A direct approach to the study of an energy gap is through the search for an absorption edge. In terms of the conductivity, what is sought is a sudden increase in $\sigma_1(\nu)$ as the photon energy is increased. Except for the low-frequency work of Khaikin,[91] the quantity measured in thin film work has always been the transmission by the film. Unfortunately, this quantity is limited by both reflection and absorption, and is related to both components of the conductivity. However, with sufficient transmission data it is possible to draw conclusions concerning the function $\sigma_1(\nu)$.

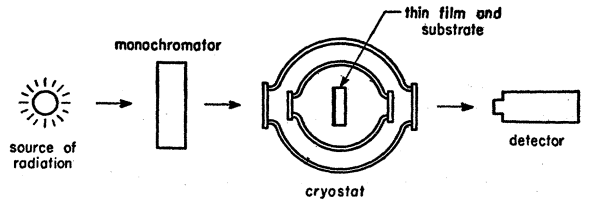

FIG. 25. Schematic representation of apparatus for measuring the transmission by a thin superconducting film.

2. Thin Film Transmission Data

An experiment for measuring the transmission by thin films is shown schematically in Fig. 25. As mentioned earlier,[14] it is found that the transmission in the visible is the same in the superconducting and normal states.

Recently, Glover and Tinkham[73–75] (GT) have extended transmission measurements to the microwave (6 to 3 mm) and long infrared (0.75 to 0.1 mm) regions for thin films of both tin and lead deposited on a quartz substrate. If the law of corresponding states may be applied, so that tin and lead data may be plotted together in terms of reduced variables, this spans the photon energy range from 0.3 to $40kT_c$ with only a small (but important) omission between 1.2 and $2.7kT_c$. This proved to be adequate to cover the spectral region over which the superconducting behavior changed from its low-frequency pattern to one indistinguishable from normal state behavior.

Glover and Tinkham obtained data at 6, 4, and 3 mm by using a crystal harmonic generator as a source. The radiation was brought into the cryostat and directed at the film by a tube. A similar tube, with protection against leakage around the film, accepted the radiation on the other side of the film and transmitted it to a Golay pneumatic detector.[92] Their source of radiation over the range 0.75 to 0.1 mm was a quartz mercury arc. Coarse gratings plus filters were used to select desired regions of the continuous spectrum. The necessity of getting significantly above noise level required the use of bands of frequencies for which the half-power widths were about 40% of the central frequency. The radiation was focused on the film and the transmitted beam was caught by a pipe which, as in the microwave case, transmitted the energy to a Golay detector.

[90] See reference 2, p. 11.

[91] M. S. Khaikin, Doklady Akad. Nauk S.S.S.R. **86**, 517 (1952).

[92] M. J. E. Golay, Rev. Sci. Instr. **18**, 357 (1947); "Golay infra-red detector," The Eppley Laboratory, Inc., Newport, Rhode Island, Bulletin No. 10 (1952).

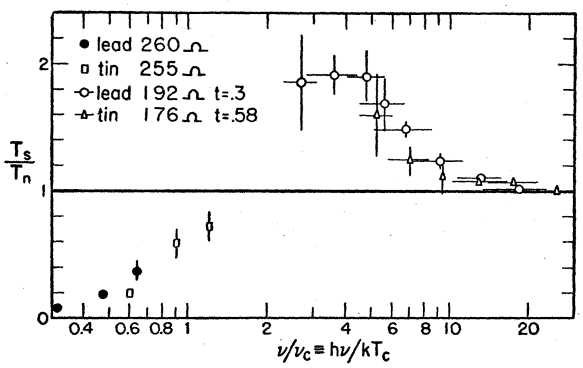

FIG. 26. Transmission ratio data obtained by Glover and Tinkham (GT). The values shown at reduced frequencies $\nu/\nu_c<1.3$ contain very large corrections (by GT) for interference effects and have been extrapolated to $T=0°K$. The resistance values given in the figure refer to the dc resistance per square of each film.

Glover and Tinkham obtained their data in the form of $\mathbf{T}_s/\mathbf{T}_n$, the ratio of the power transmitted when the film was superconducting to that transmitted when the film was above T_c. Several sets of data are shown in Fig. 26. In terms of the reduced frequency ν/ν_c, where $\nu_c=kT_c/h$, the data for the lead and tin films show similar behavior. Since the same reduced frequency ν/ν_c for lead and for tin occur at very different absolute frequencies, it is clear that the general shape of the curve cannot be attributed to systematic errors associated with frequency changes.

The transmission is observed to rise towards transparency at frequencies up to $3kT_c/h$ and decrease toward normal state transmission at higher frequencies, becoming sensibly equal to it at $\nu/\nu_c\approx 20$. The peak in transmission at $\nu/\nu_c\approx 4$, with a transmission $\mathbf{T}_s$ greater than $\mathbf{T}_n$ does not imply, *a priori*, that there is a resonance or a spanning of a gap in this region. For example, a rise to transparency with increasing frequency is to be expected on the basis of the London or Pippard theories, and the maximum may be the combination of this rise with processes which lead to normal state absorption at high frequency. The data require a careful analysis before any positive statements can be made about their implications pertinent to an energy gap.

3. *Analysis of Transmission Data*

A direct and informative approach to an understanding of the transmission data was that taken by GT through the film conductivity $\sigma=\sigma_1-i\sigma_2$. In terms of this quantity, the fraction of the power transmitted by a film of thickness d and its substrate, relative to that transmitted by the substrate alone, is

$$\mathbf{T}=\left|1+\frac{\sigma d Z_0}{n+1}\right|^{-2}, \tag{34}$$

where Z_0 is the impedance of free space and n is the index of refraction of the substrate. In this equation interference effects between the reflections at the two boundaries of the substrate have been omitted. The ratio of the transmissions given by Eq. (34) may be related to σ_1 and σ_2 through

$$\frac{\mathbf{T}_s}{\mathbf{T}_n}=\frac{1}{[\mathbf{T}_n^{\frac{1}{2}}+(1-\mathbf{T}_n^{\frac{1}{2}})(\sigma_1/\sigma_n)]^2+[(1-\mathbf{T}_n^{\frac{1}{2}})\sigma_2/\sigma_n]^2}. \tag{35}$$

The conductivity σ_n of the film in the normal state was shown by GT to be real and independent of frequency by observing that $\mathbf{T}_n$ was independent of frequency and given by the value obtained from the dc resistance of the film.

We shall see that there is a basic relation between σ_1 and σ_2, the Kronig-Kramers transforms, so that from transmission data over a wide frequency range both σ_1 and σ_2 can be determined. Furthermore, the problem of finding the components of the conductivity is simplified by the fact that, over all but a very small band of frequencies, $\mathbf{T}_s/\mathbf{T}_n$ is dominated by either σ_1 or σ_2.

Equation (35) shows that the value of σ_1/σ_n corresponding to a measured value of $\mathbf{T}_s/\mathbf{T}_n$ cannot be greater than that obtained by setting $\sigma_2=0$. Using the maximum value of $\mathbf{T}_s/\mathbf{T}_n$ in Fig. 26 we get $\sigma_1/\sigma_n<0.2$ at $\nu/\nu_c=3.6$, and it appears safe to assume that this same upper limit applies at all smaller values of ν/ν_c. This, in turn, imposes an upper limit on the term in Eq. (35) which contains σ_1/σ_n. In the region $\nu/\nu_c<1.3$ the measured $\mathbf{T}_s/\mathbf{T}_n$ values require a total denominator so large compared to this term, that it may be neglected, and the σ_2/σ_n values shown in Fig. 27 are thus obtained directly from the transmission ratio.

The universality of the behavior of σ_2/σ_n as a function of ν/ν_c, for films of different thickness and different

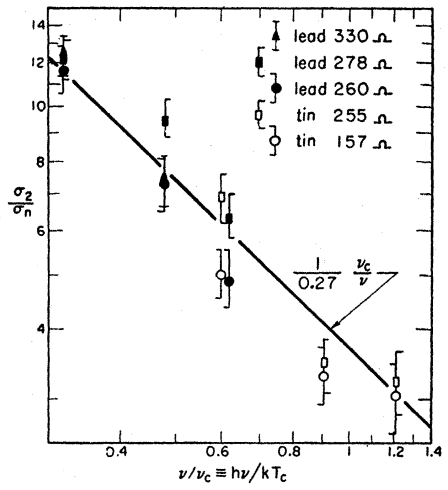

FIG. 27. Imaginary part of the reduced conductivity from GT. These are obtained from corrected $\mathbf{T}_s/\mathbf{T}_n$ values by taking $\sigma_1/\sigma_n=0$.

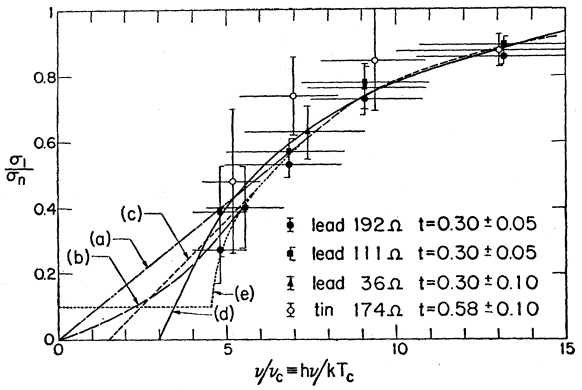

FIG. 28. Real part of the reduced conductivity from GT. These points are obtained from $\mathbf{T}_s/\mathbf{T}_n$ data by taking $\sigma_2/\sigma_n=0$. The curves shown are arbitrarily chosen functions, including curve (*d*) selected by GT.

states of anneal and for the two different materials, is one of the simplifying features of these data. Within experimental error, the data are fitted by the relation

$$\sigma_2{}^L/\sigma_n=\nu_c/a\nu, \tag{36}$$

where the superscript L indicates that this part of σ_2 has the same frequency dependence as given by the London theory.[93] On the basis of the data of Fig. 27, GT chose $a=0.27\pm0.05$. While 0.05 is much larger than the probable error or standard deviation in the mean value of a, the large corrections for interference effects which were required in the microwave region probably do place this much uncertainty on the choice of a.[94]

For the films used, Eqs. (35) and (36) show that if σ_2 continues to be inversely proportional to frequency its magnitude at $\nu/\nu_c>5$ will be too small to limit appreciably the transmission. (We shall further see that for $\nu/\nu_c>5$ the magnitude of σ_2 is very much reduced by another term.) Thus, by setting $\sigma_2/\sigma_n=0$ in Eq. (35), the values of σ_1/σ_n for $\nu/\nu_c>5$ have been obtained from the transmission data. These are plotted in Fig. 28, where an approximately universal behavior is again observed. There appears to be an appreciable difference between the tin points and the lead points. Although GT minimize the significance of this difference, it may arise from the failure of the law of corresponding states.

[93] Although Pippard[58] had avoided applying his nonlocal theory to the case of superconductors with dimensions of the order of or less than λ, GT observed that a universality in σ_2/σ_n is a consequence of the Pippard theory. Furthermore, the constant a which appears in Eq. (36) was found by Faber and Pippard [T. E. Faber and A. B. Pippard, Proc. Roy. Soc. (London) **A231**, 336 (1955)] to be 0.15, a value which is of the same order as that required by the GT data. The London theory yields a value approximately 1/100 of that observed by GT, very different for lead and tin, and dependent on the thickness of the film. In the microwave region the theory of BCS[4] yields a value of σ_2/σ_n very nearly the same as the Pippard theory value.

[94] R. A. Ferrell and R. E. Glover, III, Phys. Rev. **109**, 1398 (1958), point out an interesting rule relating a to the high-frequency data. They are led to a value of $a=0.21\pm0.05$.

Of the many possible curves consistent with the high-frequency data, five are drawn in Fig. 28. In order to choose among them, one must consider the $\mathbf{T}_s/\mathbf{T}_n$ data in the intermediate-frequency region where both σ_1/σ_n and σ_2/σ_n are significant. It is important to realize that $\sigma_1(\nu/\nu_c)/\sigma_n$ and $\sigma_2(\nu/\nu_c)/\sigma_n$ are related by the Kramers-Kronig (KK) integral transforms, which may be written as

$$\sigma_1(\nu)=\frac{2}{\pi}\int_0^\infty \frac{\nu_1\sigma_2(\nu_1)d\nu_1}{\nu_1{}^2-\nu^2}+C;$$
$$\sigma_2(\nu)=-\frac{2\nu}{\pi}\int_0^\infty \frac{\sigma_1(\nu_1)d\nu_1}{\nu_1{}^2-\nu^2}. \tag{37}$$

The procedure is then as follows. Choose a function σ_1/σ_n. From the appropriate KK transform obtain the imaginary part of the conductivity σ_2'/σ_n. It follows from the linear nature of the KK transforms that $\sigma_2=(\sigma_2'+\sigma_2{}^L)$[95] is also a KK transform of σ_1 and is the σ_2 that must be used to satisfy the low-frequency data. In Fig. 29 this process is illustrated using, as the selected σ_1/σ_n, curve (*d*) in Fig. 28. It is fortunate that for the functions shown in Fig. 28 $|\sigma_2'|\ll\sigma_2{}^L$ at $\nu/\nu_c<1.3$ so that $\sigma_2{}^L+\sigma_2'$ still satisfies the low-frequency data. In addition, for the functions shown in Fig. 28, σ_2' is negative and $|\sigma_2'+\sigma_2{}^L|<\sigma_2{}^L$ for all ν, so that the neglect of σ_2 at $\nu/\nu_c>5$ is better justified than on the basis of the $\sigma_2{}^L$ term alone.

The final test for the choice of σ_1 is then the match of $\mathbf{T}_s/\mathbf{T}_n$ from Eq. (35) to the $\mathbf{T}_s/\mathbf{T}_n$ data. The match to data at $\nu/\nu_c<1.3$ is assured by the proper choice of $\sigma_2{}^L$; and to data at $\nu/\nu_c>5$ by the proper choice of σ_1 in that region. The final selection among the various extensions which one can put on σ_1 then lies in the

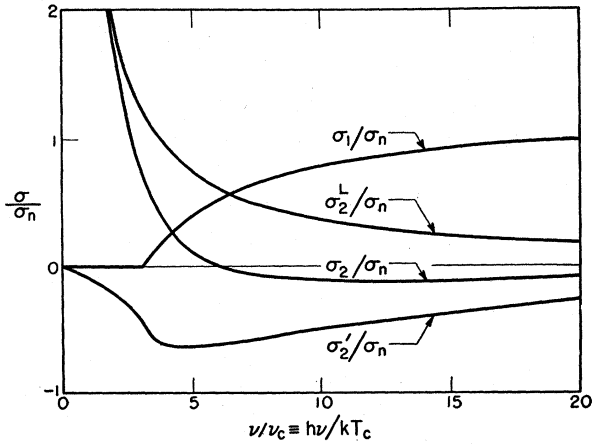

FIG. 29. Components of the reduced conductivity. The function $\sigma_2{}^L/\sigma_n$ is obtained from low-frequency data. Curve σ_1/σ_n, whose validity is to be checked by comparison with transmission data, is chosen to match high-frequency transmission. Curve σ_2'/σ_n is the KK transform of σ_1/σ_n, and σ_2/σ_n is the sum $\sigma_2{}^L/\sigma_n+\sigma_2'/\sigma_n$.

[95] Note that $\sigma_2{}^L$ is the KK transform of a real conductivity of zero, except at $\nu=0$.

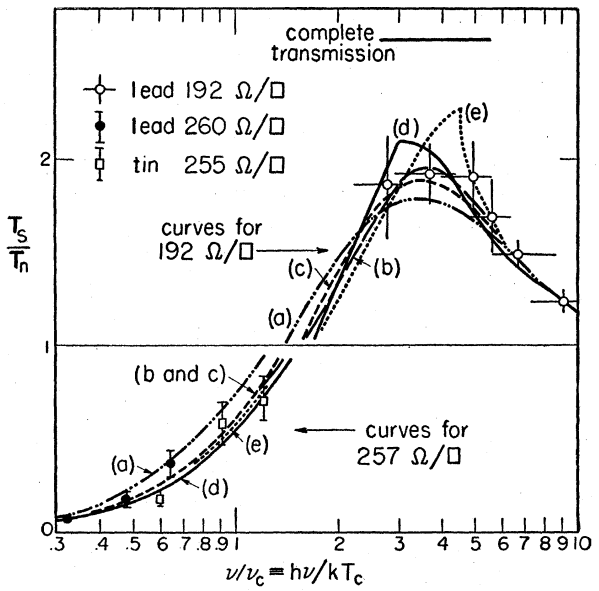

FIG. 30. Transmission ratio data as a function of reduced frequency obtained by GT. The curves correspond to the choices of σ_1 in Fig. 28 and an optimum choice of the constant a in Eq. (36). In these curves a has the values (*a*) 0.33, (b) 0.29, (*c*) 0.29, (*d*) 0.27, and (*e*) 0.29.

match to the data in the interval $1.3<\nu/\nu_c<5$. Unfortunately, there are very few points in this region and these with rather large errors and frequency bands. Indeed, if we discount two points not shown in this paper because they were taken at the relatively high reduced temperature $T/T_c=0.67$, we have only two points in this region to provide the choice among the various curves with which the data of Fig. 28 can be fitted.

In Fig. 30 data are shown in the high-frequency region for the low temperature set including the points at $\nu/\nu_c=2.7$ and 3.6, and for two sets of low-frequency data for approximately the same value of film resistance so that they can be compared with the same calculated $\mathbf{T}_s/\mathbf{T}_n$ curves. The curves shown in comparison with the data are those obtained from the five choices of σ_1 shown in Fig. 28 and an optimum choice, for each choice of σ_1, of the constant a in Eq. (30).

GT chose the σ_1 given by curve (*d*), Fig. 28, and obtained the fit to the data shown by curve (*d*), Fig. 30. In their paper, they failed to consider the insensitivity of the fit to variations in the choice of σ_1 and concluded that they had demonstrated the existence of an energy gap $\mathcal{E}_g\approx 3kT_c$ and ruled out the possibility of a gap as small as $1.5kT_c$ which would also be compatible with specific heat data. Forrester[96] has pointed out that their data are equally consistent with the σ_1 given by curve (*c*), Fig. 28, which would suggest a gap of $1.5kT_c$, and curve (*b*), not suggestive of a gap at all. The limitations of the GT experiment (the broad band widths in the infrared region, the generally large uncertainties in the transmission ratios, and the lack of data in the critical frequency region) restrict the conclusion about the width of the gap, if one exists, to $0<\mathcal{E}_g<4.5kT_c$. While this inference is much less specific, quantitatively, than results obtained from experiments previously discussed, the conclusion follows from the data in such a direct manner that it must be considered firmly established.

Tinkham and Glover[97] do not agree with our estimate of the uncertainty. They find approximate agreement between their data at $\nu/\nu_c>5$ and a formula derived from the BCS theory. The extrapolation by them of their high-frequency data to lower frequencies on the basis of this formula must, then, lead to a value of the photon energy for which $\sigma_1\to 0$ which is close to that predicted by the BCS theory, i.e., $3.5kT_c$. Forrester had noted the agreement of their high-frequency data with the BCS theory, but made the point that this does not constitute primary evidence for an energy gap.

Unambiguous evidence for an energy gap through the observation of a spectroscopic absorption edge remains to be obtained. It would appear that information from measurements on the transmission by thin films is severely limited by the insensitivity of this quantity to the absorptivity at low absorptivities. In principle, at least, a much better quantity to observe would be the energy absorbed by the film.

VI. CONCLUSION

A number of experiments have been discussed which provide evidence pertinent to energy gaps in superconductors. This evidence arises from studies of two essentially different types of properties, (a) those which depend on the statistical distribution of thermally excited electrons, which include the thermal properties, the Knight shift, the nuclear relaxation rate, and acoustic absorption, and (b) those which depend on the excitation of electrons across the gap by sufficiently energetic photons, i.e., absorption, reflection, and transmission of electromagnetic energy at frequencies, $\nu\sim kT_c/h$.

The strongest evidence for an energy gap from studies of properties which depend on the distribution of thermally excited electrons comes from measurements on the electronic specific heat and the related quantity, the critical magnetic field H_c, with support from other experiments. The rapid fall in the specific heat of superconductors at low temperatures is almost certainly dominated by an exponential in $1/T$. It may be possible that the density of states over the temperature region in which measurements were obtained is such an unusual function of temperature that the exponential

[96] A. T. Forrester, Phys. Rev. **110**, 776 (1958).

[97] M. Tinkham and R. E. Glover, III, Phys. Rev. **110**, 778 (1958).

arises from that source; however, an exponential of this sort is most likely to be associated with a gap in the electron energy spectrum. If one interprets the exponential temperature dependence in terms of an energy gap, the experiment on nuclear relaxation indicates that there is piling up of the states on either side of the gap as suggested in Figs. 1(c), 1(d), and 1(e).

The disagreement between the results of Reif[55] and those of Knight, Androes, and Hammond[56] on the Knight shift in superconducting mercury colloids at present prevents us from drawing conclusions from these experiments. However, if Reif's result should be substantiated, i.e., if it should be confirmed that the Knight shift does not go to zero as $T\rightarrow 0$ in a superconductor, then the simple one electron energy gap model would have to be questioned.

The most accurate data available for comparing one superconductor with another come from measurements of the electronic specific heat and the critical magnetic field. These have been shown to demonstrate that the law of corresponding states is only approximately obeyed, a result which is not unexpected since the scheme of reduced variables does not take into consideration many differences among superconductors, e.g., crystal structure.

We now turn to the experiments in which there is direct excitation of electrons by photons of energy near the expected gap energy. The experiments on bulk superconductors have been generally conducted with photon energies that are apparently less than the width of the gap at 0°K (excepting, possibly, the highest frequency of Biondi, Garfunkel, and McCoubrey[71]). The onset of excitation of electrons across the energy gap was found by using the two fluid model to subtract the absorption due to thermally excited electrons. This technique has been used to obtain the temperature variation of the energy gap for both tin and aluminum. There are many uncertainties associated with this treatment of the data, including the use of the two fluid model which is, at best, only approximately correct. The fact that this temperature variation of the energy gap (Fig. 24) is in good agreement with the BCS theory should not be regarded as conclusive, considering the limitations of the analysis of the experiment. At any rate this work suggests that the energy gap at $T=0$ is of the order of $3kT_c$ and seems to impose a lower limit of $2.4kT_c$.

The experiment of Glover and Tinkham[75] on the transmission of microwave and infrared radiation through thin films of lead and tin does not have the difficulty in analysis that is associated with the bulk work just discussed. This enables them to establish unambiguously that, at some photon energy less than $4.5kT_c$, there is an onset of a real component of the film conductivity, evidence that an energy gap cannot be greater than this. The uncertainty in the size of the gap results partly from the uncertainties and the sparseness of the data in the critical frequency range and partly from the insensitivity of the transmission to the real part of the film conductivity.

In making comparisons with theory, we have seen that the BCS theory has had remarkable success in predicting the properties discussed here. This fact, along with the ability of the theory to predict the bulk of the other known properties of superconductors, makes the BCS theory highly satisfactory from the experimental point of view.

There are still many questions to be resolved. As was noted earlier, mercury and lead exhibit a temperature variation of the critical magnetic field H_c which would seem to imply that the electronic specific heat is not exponential. Unfortunately, the lattice specific heat so overwhelms the electronic that calorimetric determinations of C_{es} are impractical for these metals. It seems that in these cases the experimental approach to the question of an energy gap must be through other techniques.

Another question which needs to be resolved is the disagreement between the two experiments on the Knight shift in superconducting mercury. More complete evidence from nuclear relaxation experiments may help to resolve some of these questions.

The ultimate evidence for a gap should be an observation of an absorption edge, i.e., a sudden increase of absorptivity with increasing frequency. Unfortunately, the difficulty of working in the interesting spectral region is compounded by the difficulty of allowing for background effects and therefore, the spectroscopic evidence which has been obtained to date is not, by itself, incontrovertible. The measurements on bulk superconductors need to be carried to higher frequencies and lower temperatures, and the thin film transmission measurements need to be supplemented by measurements of the power absorbed by the film.

The over-all estimate of the experimental evidence regarding a gap in the one electron energy spectrum of superconductors depends to a great extent on the large scope of the evidence. When viewed individually, each experiment has certain limitations which restrict the conclusions that may be drawn. Taken together, however, we are led to conclude that a gap in the electronic energy spectrum is one of the features of superconductivity. Furthermore, the gap at 0°K is about $3kT_c$, but there appear to be variations among superconductors. Finally, the gap must vary with temperature, decreasing from a limiting value at 0°K until it disappears at T_c.

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APPENDIX ADDED IN PROOF: SOME RECENT DEVELOPMENTS

Section II

Measurements of the electronic specific heats of zinc and of gallium have recently been reported by Seidel and Keesom.[98] For both metals liquid He^3 was used as the refrigerant, enabling them to attain temperatures down to 0.35°K. The measurements extended down to $t=0.5$ for zinc and $t=0.32$ for gallium. In both cases the electronic specific heat constituted at least 95% of the total over the range of measurements.

For gallium and zinc below about $t=0.7$ the superconducting electronic specific heats obeyed an expression of the type $C_{es}/\gamma T_c=A\exp(-bT_c/T)$, where for gallium $A=7.0$ and $b=1.35$, and for zinc $A=6.4$ and $b=1.27$. The high degree of precision of the work leads to confidence in the expression for gallium. However, since the range of reduced temperatures covered in the zinc experiments was much smaller, a larger uncertainty must be attributed to the expression for this metal.

Boorse and Hirshfeld[99] have remeasured the electronic specific heat of niobium. By annealing near the melting point of niobium under high vacuum conditions, they produced a sample which they believe to be more nearly ideal in behavior than those used in the earlier investigations.[36,41] They find that below about $t=0.7$ the electronic specific heat of their sample accurately follows an exponential temperature dependence of the type given above with the values $A=10.1$ and $b=1.63$.

[98] G. Seidel and P. H. Keesom, Bull. Am. Phys. Soc. Ser. II, 3, 17 (1958); *Proceedings of the Kammerlingh Onnes Conference on Low Temperature Physics, Leiden* (The Netherlands, June, 1958).

[99] H. A. Boorse and A. Hirshfeld, *Proceedings of the Kammerlingh Onnes Conference on Low Temperature Physics, Leiden* (The Netherlands, June, 1958).

Section III

Redfield[100] has performed an experiment on the nuclear relaxation rate in superconducting aluminum. He used essentially the same method as Hebel and Slichter[61] for relaxation measurements. However, cooling by adiabatic demagnetization of a paramagnetic salt which was in thermal contact with the aluminum specimen enabled him to extend the temperature range to about $t=0.5$. Within the accuracy of his experiment he agreed with the earlier results.[61] Furthermore, he observed that the relaxation rate went through a maximum at about $t=0.8$ and fell to about the normal state value at about $t=0.5$ as had been predicted by Hebel and Slichter.

Section V

Richards and Tinkham[101] have recently studied the relative absorption of energy by a superconducting sample in the form of a high-mode resonant cavity over a wide range of frequencies. A small absorber in the cavity served to indicate the variation in energy density in the cavity as a result of changes in the surface resistance of the cavity walls. At small reduced temperatures, a rather sharply defined decrease in energy density was observed to occur for both lead and tin at approximately the same reduced frequency; namely, $\nu\simeq 3kT_c/h$. This result was interpreted as evidence for the existence, at absolute zero, of an absorption edge at a photon energy of approximately $3kT_c$, which in turn implies an energy gap of this value. It was noted that the edge occurred at slightly different reduced frequencies for lead and for tin, again indicating the approximate nature of the law of corresponding states.

[100] A. G. Redfield, reference 99.

[101] M. Tinkham, reference 99.