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Ultrasonic Determination of the Superconducting Energy Gap in Thallium*

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The temperature-dependent energy gap $2\Delta(T)$ in single crystals of high-purity thallium has been determined by measurements of the attenuation in the normal and superconducting states of longitudinal acoustic waves. Determinations were made for sound-wave propagation along the [0002], [10$\bar{1}$0], and [1$\bar{2}$10] crystallographic axes. The energy gap $2\Delta(0)$ at 0°K for propagation along these axes, respectively, was found to be $3.76kT_c \pm 0.03kT_c$, $4.10kT_c \pm 0.03kT_c$, and $4.00kT_c \pm 0.10kT_c$. Ultrasonic attenuation gives a larger value for this limiting energy gap than that observed by other methods. The decrease in attenuation below T_c was found to be more abrupt than predicted by the Bardeen-Cooper-Schrieffer (BCS) theory. It is suggested that the simple BCS model does not give a complete picture of the ultrasonic attenuation in very pure superconductors.

I. INTRODUCTION

In superconducting metals, the electronic contribution to the ultrasonic attenuation decreases abruptly from that in the normal state as the temperature is lowered below the critical temperature T_c.[1,2] Ultrasonic measurements in various superconductors have shown that the ratio of the attenuation coefficient in the superconducting state α_s to that in the normal state α_n is in moderately good agreement with the prediction of Bardeen, Cooper, and Schrieffer (BCS),[3] according to which

$$\alpha_s/\alpha_n = 2(e^{\Delta(T)/kT}+1)^{-1}, \quad (1)$$

where $2\Delta(T)$, the temperature-dependent energy gap, approaches $3.5kT_c$ as the temperature (T) approaches 0°K. This equation is derived on the assumption that $ql_e \gg 1$, where q is the magnitude of the phonon propagation vector $\mathbf{q}$ and l_e is the electron mean free path. Tsuneto[4] and Levy[5] have demonstrated that the same result holds for $ql_e < 1$. However, recently Perz and Dobbs[6] have observed a frequency dependence of the gap in niobium.

The BCS formulation is based upon a simple model superconductor with a spherical Fermi surface, an isotropic energy gap and a weak electron-electron interaction $V_{kk'}$ which is constant in k space. A considerable body of experimental evidence[6–9] suggests that the energy gap is, in fact, anisotropic. Cooper[10] has intimated that anisotropy of the energy gap is consistent with the framework of the BCS theory if the BCS electron-electron interaction is regarded as anisotropic. The energy gap would then be not only a function of temperature but also a variable function in k space. Ultrasonic attenuation accrues only from those electrons which lie close to the intersection of the Fermi surface with the plane $\hbar\mathbf{k} = m^*\mathbf{v}_s$, where $\mathbf{k}$ is the wave vector of the electrons, m^* is their effective mass, and $\mathbf{v}_s$ is the velocity of sound.[9] Only those electrons with a velocity component along $\mathbf{q}$ equal to the sound velocity v_s scatter phonons. For a spherical Fermi surface, electrons satisfying this condition lie in the zone formed by the intersection with the Fermi surface of the equatorial plane normal to $\mathbf{q}$ since for most metals v_s/v is about 10^{-3}. Thus, observation of the attenuation of sound waves propagated along different crystallographic directions allows direct observation of the anisotropy of the superconducting energy gap.

An experimental study has been made of the attenuation of longitudinal acoustic waves along the major axes of single crystals of thallium with a view to determining the anisotropy of the energy gap. Magnetoacoustic measurements in thallium have shown that the extremal dimensions of the Fermi surface are in reasonable agreement with the free electron model.[11] It is of interest to examine how closely the BCS theory represents the acoustic attenuation in a material with an almost spherical Fermi surface in view of recent experimental evidence for other metals[12,13] which differs substantially from the theoretical predictions.

An initial report of the early stages of this work has been presented elsewhere.[14]

II. SAMPLE PREPARATION

Thallium undergoes a phase transformation from the hexagonal close-packed structure to the body-centered

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[3] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[4] T. Tsuneto, Phys. Rev. **121**, 402 (1961).
[5] M. Levy, Phys. Rev. **131**, 1497 (1963).
[6] E. R. Dobbs and J. M. Perz, Rev. Mod. Phys. **36**, 257 (1964).
[7] R. W. Morse, T. Olsen, and J. D. Gavenda, Phys. Rev. Letters **3**, 15 (1959).
[8] A. R. Mackintosh, in *Proceedings of the Eighth International Conference on Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1960), p. 240.
[9] D. H. Douglass, Jr., and L. M. Falicov, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, to be published), Vol. IV.
[10] L. N. Cooper, Phys. Rev. Letters **3**, 17 (1959).
[11] J. A. Rayne, Phys. Rev. **131**, 653 (1963).
[12] R. W. Morse, IBM J. Res. Develop. **6**, 58 (1962).
[13] H. E. Bömmel (private communication).
[14] G. A. Saunders and A. W. Lawson, Bull. Am. Phys. Soc. **8**, 593 (1963).

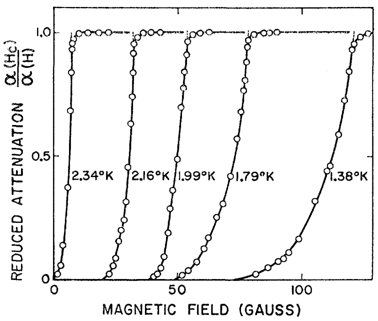

FIG. 1. Reduced attenuation of longitudinal waves along the [1$\bar{2}$10] axis of thallium as a function of the magnetic field applied perpendicular to the [1$\bar{2}$10] axis. This figure illustrates the determination of the critical magnetic field by extrapolation to a reduced attenuation $\alpha(H_c)/\alpha(H)$ equal to unity. $\alpha(H_c)$ is the attenuation in the normal state while $\alpha(H)$ is the attenuation in a magnetic field less than H_c.

cubic structure at 234°C, i.e., 69°C below the melting point.[15] Therefore, large single crystals are not readily grown from the melt. A strain anneal technique was used to grow single crystals from 99.9999% purity, zone-refined thallium. Cylindrical ingots of the metal were compressed about 1% in length, sealed under vacuum in pyrex tubes and annealed for about ten days at 220°C, just below the transition temperature. Preferential grain growth occurred providing large enough single crystals for ultrasonic measurements.

Single crystals were aligned along one of the major axes to within 1° by use of Laue back-reflection patterns and then cut by spark erosion into right circular cylinders about 2 cm in diameter and about $1\frac{1}{2}$ cm long. The end-faces were planed flat and parallel to within 0.0001 in. with the spark-cutter on its lowest cutting speed. Surface damage was removed by etching with concentrated nitric acid followed by washing with distilled water. The ratio of the room-temperature resistivities to those at helium temperatures was about 850. Assuming free-electron-like behavior for thallium[11] and Shoenberg's data for the carrier density,[16] this indicates that ql_e was of the order of 100 for our crystals. This estimate is consistent with the values obtained by Rayne.[11]

III. APPARATUS AND EXPERIMENTAL PROCEDURE

Measurements were made at 60 Mc/sec, the fifth harmonic of $\frac{1}{2}$-in. diam, x-cut, quartz transducers gold-plated in the manner suggested by Huntington.[17] Transducers were bonded to the flat end-faces of the thallium crystals with Dow Corning No. 200 silicone fluid of viscosity 2.5×10^6 centistokes. For the specimens cut with the [0002] axis along the cylinder axis, some difficulty was experienced in bonding but the problem was resolved by using a less viscous (1.5×10^5 centistokes) silicone.

Relative attenuation measurements were made by the double-ended pulse-echo technique.[18] 60 Mc/sec, 150-V peak-to-peak input pulses of 1 to 2 μsec duration were applied at a repetition rate of 60 cps, to the quartz transducer by an Arenberg pulsed oscillator. Pick-up signals from the receiving transducer were amplified and detected by the low noise, Airborne Instruments Laboratory receiver and displayed on a Tektronix 585 oscilloscope, the horizontal sweep of which was triggered in synchronism with the transmitter. The rf amplifier and the oscilloscope were calibrated with a standard step attenuator. Pulse heights were analyzed using the Tektronix type-Z oscilloscope plug-in unit as a differential comparator, a calibrated dc potential being applied by this unit to cancel out most of the detected signal on a given echo so as to allow accurate measurements of peak voltage. To eliminate any nonlinearity in the system, a comparison pulse with a variable delay was passed through the receiver and presented on the oscilloscope alongside the echo being measured. The attenuation coefficient was determined by the best exponential fit of the pulse-echo pattern.

Measurements were made at liquid-helium temperatures with the sample in a holder suspended by two rigid, stainless-steel, coaxial lines in a standard cryogenic system. Temperatures down to 1.2°K were obtained by fast pumping on the liquid helium and controlled by regulation of the helium vapor pressure to within 0.5% by a Cartesian manostat.[19] Oil and mercury manometers were used to measure the temperature by estimation of the helium vapor pressure in the usual way.[20]

Normal-state attenuation measurements below the

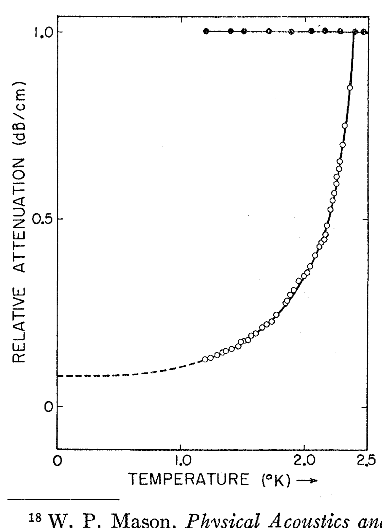

FIG. 2. Attenuation of 60 Mc/sec longitudinal acoustic waves along the [10$\bar{1}$0] axis of thallium in the normal (●) and superconducting (○) states.

[15] W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, Inc., New York, 1958), p. 878.
[16] D. Shoenberg, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. II, p. 255.
[17] H. B. Huntington, Phys. Rev. **72**, 321 (1947).
[18] W. P. Mason, *Physical Acoustics and the Properties of Solids* (D. Van Nostrand Company, Inc., New York, 1958), p. 95.
[19] R. Gilmont, Ind. Eng. Chem. Anal. Ed. **18**, 633 (1946).
[20] G. K. White, *Experimental Techniques in Low Temperature Physics* (Oxford at Clarendon Press, Oxford, 1959), p. 100.

critical temperature of thallium were made by destroying the superconducting state with a magnetic field provided by Helmholtz coils. Critical-magnetic-field determinations were made by finding the attenuation at a given temperature as a function of magnetic field as measured by a Hall probe gaussmeter to within 1%. Typical results are illustrated in Fig. 1. As the critical field was approached, the sharpness of the attenuation decrease diminished, probably due to some residual trapped regions of superconductivity at points of strain within the specimen. The critical field was found by extrapolating the curve of the reduced attenuation $\alpha(H)_c/\alpha(H)$ to unity, as shown by the dotted lines. Penetration of the magnetic field and consequent formation of the intermediate state did not occur until an external field H_e was reached, such that[21,22]

$$H_e \gg (1-D)H_c, \quad (2)$$

where D is the demagnetization coefficient. For a short cylinder of length 1.28 cm and diameter 1.40 cm, the demagnetization coefficient was estimated as 0.35. As would be expected the demagnetization coefficient was not a function of temperature.

IV. RESULTS

Ultrasonic attenuation measurements were made for propagation of the sound waves along the [10$\bar{1}$0], [1$\bar{2}$10], and [0002] axes of single crystals of thallium Typical experimental results for the temperature dependence of attenuation of longitudinal acoustic waves in the normal and superconducting states for thallium are illustrated in Figs. 2 and 3. The critical temperature, determined as that temperature at which a sharp decrease in attenuation occurred, was found to be 2.38°K in good agreement with the value of 2.394°K measured by Maxwell and Lutes.[23] The attenuation in the normal state increased very slightly with decreasing temperature while that in the superconducting state decreased abruptly below T_c in the usual way. The attenuation curves for the superconducting state were extrapolated to 0°K using Eq. (1). Since the electronic attenuation approaches zero in the superconducting state as the temperature approaches 0°K, this extrapolation allowed removal of the nonelectronic component of the attenuation. This zero of electronic attenuation was used as the reference point for determination of electronic attenuation at finite temperatures. The energy gap was then calculated as described below, the value replaced in Eq. (1), and the complete procedure repeated. This reiterative process was practiced until a self-consistent answer for the energy gap was obtained.

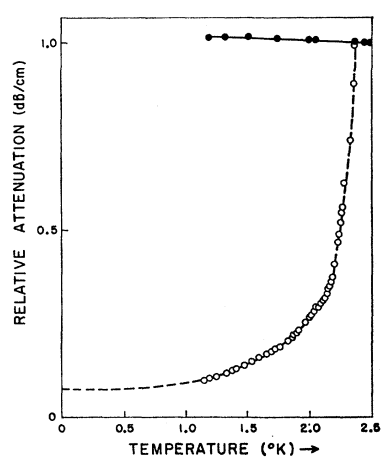

FIG. 3. Attenuation of 60 Mc/sec longitudinal acoustic waves along the [0002] axis of thallium in the normal (●) and superconducting (○) states.

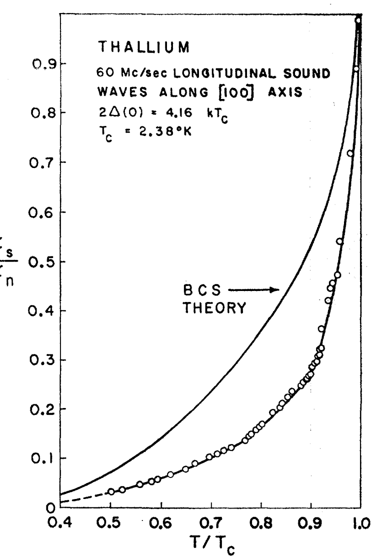

FIG. 4. Ratio of acoustical attenuation along the [10$\bar{1}$0] axis of thallium in the superconducting and normal states as a function of the reduced temperature. The theoretical curve from the BCS theory is illustrated for comparison.

Using the extrapolated attenuation at 0°K in the superconducting state as the zero reference, the relative attenuations in the normal state (α_n) and in the superconducting state (α_s) were estimated. Some data for the ratios α_s/α_n are shown in Figs. 4 and 5 as a function of the reduced temperature (T/T_c). The observed decrease below T_c is more abrupt than that predicted by the BCS theory. Similar results have been observed for other superconductors especially it appears for those in a very high state of purity.[12,13,24–26]

The temperature dependence of the superconducting energy gap for the [10$\bar{1}$0] and [0002] directions in thallium was estimated using the inverted form of Eq. (1):

$$\Delta(T)/kT_c = T/T_c \ln(2\alpha_n/\alpha_s - 1). \quad (3)$$

Results, illustrated as reduced values of the energy gap $\Delta(T)/\Delta(0)$, are shown in Fig. 6 as a function of the reduced temperature T/T_c. The experimentally determined temperature-dependent energy gap is in all cases

[21] R. Peierls, Proc. Roy. Soc. (London) **A155**, 613 (1936).
[22] F. London, Physica **3**, 450 (1936).
[23] E. Maxwell and O. S. Lutes, Phys. Rev. **95**, 333 (1954).
[24] R. W. Morse, *Progress in Cryogenics* (Heywood and Company, Ltd., London, 1959), Vol. 1, p. 221.
[25] R. David, H. R. van der Laan, and N. J. Poulis, Physica **23**, 330 (1962).
[26] R. E. Love and R. W. Shaw, Rev. Mod. Phys. **36**, 260 (1964).

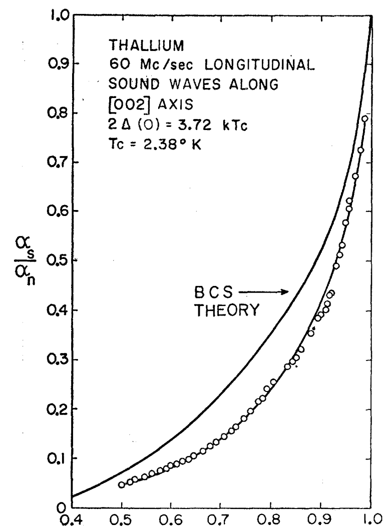

FIG. 5. Ratio of acoustical attenuation along the [0002] axis of thallium in the superconducting and normal states as a function of the reduced temperature. The theoretical curve from the BCS theory is illustrated for comparison.

TABLE I. The limiting energy gap at 0°K in thallium from acoustic attenuation.

Direction of propagation of ultrasonic waves	Measured $2\Delta(0)/kT_c$	Average value of $2\Delta(0)/kT_c$
[10$\bar{1}$0] Sample 1	4.06	
	4.14	
[10$\bar{1}$0] Sample 2	4.14	
	4.10	
	4.08	4.10±0.03
[1$\bar{2}$10]	4.0	
	4.0	4.00±0.10
[0002]	3.72	
	3.80	
	3.75	
	3.76	3.76±0.03

was found to be 179±5 G in reasonable agreement with that of 172.8 G found by Maxwell and Lutes.[23] The major source of error in this method arises from the necessity of extrapolating $\alpha(H_c)/\alpha(H)$ to unity.

rather larger than that predicted by the BCS theory.

The limiting energy gap at 0°K, $2\Delta(0)$, was determined from plots of the reciprocal of $[\ln(2\alpha_n/\alpha_s-1)]$ as a function of the reduced temperature. Such plots are illustrated in Figs. 7 and 8. At lower temperatures this curve should approach asymptotically to a straight line through the origin, the gradient of this line being the limiting value of the energy gap.[6] Collected results are presented in Table I. These results show that the energy gap in thallium is anisotropic, the apparent gap when the propagation of sound waves is along the c axis being smaller than that measured with propagation in the basal plane. The measured limiting energy gap $2\Delta(0)$ is in both cases larger than the value of $3.5kT_c$ predicted by the BCS theory in the weak-coupling limit.

Critical-magnetic-field data are plotted as a function of temperature in Fig. 9. Assuming the Gorter-Casimir relation[27]

$$H_c(T)/H_c(0)=(1-T/T_c)^2, \qquad (4)$$

where $H_c(T)$ is the critical field at temperature T, $H_c(0)$

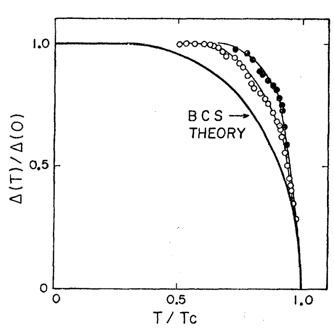

FIG. 6. The reduced energy gap as a function of the reduced temperature compared with the BCS theory. Full circles represent the data for propagation of sound waves along the [10$\bar{1}$0] axis and the open circles are data for the [0002] axis.

[27] C. J. Gorter and H. B. G. Casimir, Physik. Z. **35**, 963 (1934).

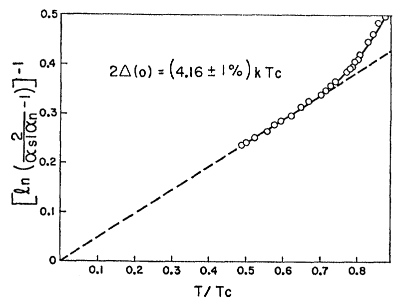

FIG. 7. Estimation of the limiting energy gap for sound wave propagation along the [10$\bar{1}$0] axis in thallium.

TABLE II. Collected data for the limiting energy gap at 0°K for thallium.

Method of measurement	$2\Delta(0)/kT_c$
Critical-field data[a]	3.5
Tunneling[b]	3.57±0.05
Specific heat[c]	2.8
Ultrasonic Attenuation	3.76–4.10

[a] See Ref. 23. [b] See Ref. 30. [c] See Ref. 31.

V. DISCUSSION

The existing data on the energy gap in thallium as determined by other techniques is compared with our ultrasonic value in Table II. The estimate of the gap from the critical-magnetic-field data was based on the precise susceptibility measurements of Maxwell and Lutes.[23] Using a standard thermodynamic procedure,[28] they estimate the value of the Sommerfeld constant γ in thallium as 3.65×10^{-4} cal/deg^2 mole. Inserting this value in Goodman's[29] formula for the energy gap,

$$2\Delta(0)=4kH_0(24\pi\gamma)^{-1/2}, \qquad (5)$$

[28] E. A. Lynton, *Superconductivity* (John Wiley & Sons, Inc., New York, 1962), pp. 17–19.
[29] B. B. Goodman, Compt. Rend. **244**, 2899 (1957); **246**, 3031 (1958).

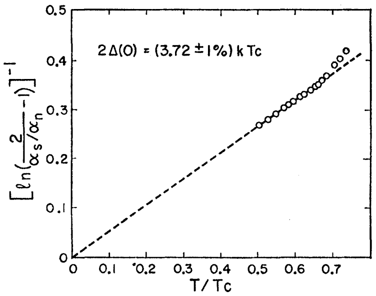

FIG. 8. Estimation of the limiting energy gap for sound wave propagation along the [0002] axis in thallium.

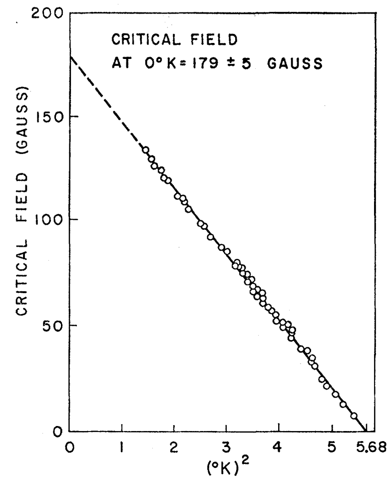

FIG. 9. Parabolic fit of the critical-magnetic-field data for a thallium single crystal. Longitudinal sound waves propagated along the [$1\bar{2}10$] axis. Magnetic field directed perpendicular to this axis.

we find $2\Delta(0)$ to be $3.5kT_c$ in exact agreement with the weak-coupling theory.

The limiting energy gap from the tunneling experiments is also consistent with the weak-coupling point of view.[30]

The specific-heat measurements yield an anomalously low value for the gap of $2.8kT_c$. However, this value is probably doubtful. The low value of the Debye temperature (86.6°K)[31] makes the separation of the lattice and electronic contributions to the specific heat difficult and this problem will probably not be resolved until the measurements are extended to lower temperatures.

The range of values found for the energy gap by the ultrasonic technique are appreciably larger than those found by the other techniques. In fact, the ultrasonic gap at 0°K suggests that the strong-coupling theory, in which $2\Delta(0)$ is $4.0kT_c$,[32] is more appropriate to thallium than the weak-coupling theory. However, the deviation from the parabolic dependence of H_c on T_c is in the direction previously found[33] for weak-coupling superconductors and opposite to that found for strong-coupling superconductors. Furthermore, even the assumption of strong coupling does not explain the marked deviation in observed attenuation from the theoretical BCS curve for weak coupling illustrated in Fig. 6. The strong-coupling theory[34] indicates that $\Delta(T)/\Delta(0)$ near $T/T_c=1$ should not deviate by more than 0.1% from the behavior predicted by the weak-coupling theory.

The disparity between measurement and theory is particularly evident just below T_c where, approximately,

$$[\Delta(T)/\Delta(0)]^2 \simeq B(1-T/T_c). \qquad (6)$$

The theoretical value[6] of B in both the weak- and strong-coupling limits is 3.0. The value of B found experimentally for thallium is 4.8 for propagation of sound along the [0002] direction and 4.6 for the [$10\bar{1}0$] direction. Similar large values for B have been found for niobium[6] (5.0) and lead (8.0).[6,26]

Thus, in summary, we find that our results tend to suggest a gap in better accordance with the strong-coupling BCS theory whereas other experiments suggest that the weak-coupling theory is more appropriate. Near $T=T_c$, neither the weak- nor the strong-coupling theory explains the large value of B. We are thus left in the position of concluding that the theory is inadequate as far as explaining many features of ultrasonic attenuation. The disagreement between theory and experiment might possibly arise from the anisotropy of the energy gap. However, in the present case this would imply a very rapid change of the gap in k space since the large value for B occurs in all the major crystallographic directions.

We turn now briefly to a discussion of the anisotropy of the gap. This effect in thallium is considerably less pronounced than in tin[12,35] or lead.[8] This result might be expected in view of the fact that the Fermi surface in thallium approximates the free-electron situation,[11] whereas tin and lead possess extremely complex surfaces.[36] Recently, Pokrovskii[37] and Privorotskii[38] have discussed the relation of the gap anisotropy with the electron distribution in the effective interaction zone in k space. These theories do not predict significant deviations from the BCS theory for ultrasonic attenuation in the temperature range of concern in our experiments. In view of the discrepancies between the BCS theory and our experiments, we shall not discuss these theories further. However, they do suggest the desirability of further experiments directed towards establishing a correlation between the shape of the Fermi surface and the anisotropy of the energy gap.

[30] B. N. Taylor and E. Burstein, Phys. Rev. Letters **10**, 14 (1963).
[31] J. L. Snider and N. Nicol, Phys. Rev. **105**, 1242 (1957).
[32] J. C. Swihart, IBM J. Res. Develop. **6**, 14 (1962).
[33] D. E. Mapother, IBM J. Res. Develop. **6**, 77 (1962).
[34] D. J. Thouless, Phys. Rev. **117**, 1256 (1960).
[35] R. W. Morse and H. V. Bohm, Phys. Rev. **108**, 1094 (1957).
[36] A. R. Mackintosh, *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 233.
[37] V. L. Pokrovskii, Zh. Eksperim. i Teor. Fiz. **40**, 641, 898 (1961) [English transl.: Soviet Phys.—JETP **13**, 447, 628 (1961)].
[38] I. A. Privorotskii, Zh. Eksperim. i Teor. Fiz. **42**, 450 (1962) [English transl.: Soviet Phys.—JETP **15**, 315 (1962)].