

the magnetization vector is not aligned with the applied magnetic field.

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Thermal Conductivity of Indium-Thallium Alloys in the Normal and Superconducting States*†

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Thermal conductivity measurements have been made on three indium-thallium alloys between 0.15° and 0.8°K. Temperature gradients were measured using carbon resistance thermometers. The alloys were of the type which show an increase in thermal conductivity on entering the superconducting state. At temperatures below 1°K the superconducting state thermal conductivity decreases rapidly with decreasing temperature, becoming roughly proportional to T^3 and to the grain size in the specimens at the lowest temperatures. The data are interpreted as meaning that phonon conductivity limited by boundary scattering is important in this region.

I. INTRODUCTION

THE thermal conductivity of metals can be separated into two terms—an electron conductivity K_e and a lattice or phonon conductivity K_g . The total conductivity K is then given by the sum of K_e and K_g . Experimental and theoretical results show that in the liquid helium temperature region K_e may be represented by¹

$$1/K_e = \rho_0/L_0T + \alpha T^2, \quad (1)$$

where ρ_0 is the residual electrical resistance, L_0 is the Lorenz number $\frac{1}{3}(\pi k/e)^2$, α is a constant which depends on the strength of the phonon-electron interaction, and T is the temperature. The first term on the right-hand side of Eq. (2) represents the contribution to the thermal resistance of scattering of electrons by impurities, and the second term is the resistance due to scattering of electrons by phonons. At a given temperature the relative importance of the two terms depends on the impurity content and on the Debye temperature. For impure metals and alloys at low temperatures impurity scattering is always dominant, but for pure metals with a low Debye temperature phonon scattering may be

important. For pure metals, K_e is the order of a few watt units at 1 or 2°K, but this value is reduced by the presence of strains or impurity atoms, and is two or three orders of magnitude smaller for alloys.

In the same temperature region K_g is usually limited by scattering of the phonons by conduction electrons and is proportional to T^2 . At lower temperatures the mean free path of the phonons would be comparable to the crystal dimensions and presumably would be determined by the scattering of phonons at crystal boundaries. In this case K_g should have the same temperature dependence as the lattice specific heat and should be given by Casimir's formula.² A dependence of K_g on T^3 has been found in superconductors below 1°K^{3,4} and in dielectric crystals over a wider temperature range.⁵ In most pure metals K_g is very much smaller than K_e , and phonon conductivity is important only in alloys and in metals having a very small number of conduction electrons.

If the additional subscripts s and n denote the superconducting and normal states, then

$$K_s = K_{es} + K_{gs} \quad (2a)$$

$$K_n = K_{en} + K_{gn}, \quad (2b)$$

where K_s and K_n are the total thermal conductivities of the same specimen in the two different states. K_n will be determined by the same factors considered above

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¹ For a review of thermal conductivities of metals at low temperature see: J. L. Olsen and H. M. Rosenberg, *Advances in Phys.* **2**, 28 (1953).

² H. B. G. Casimir, *Physica* **5**, 595 (1938).

³ J. L. Olsen and C. A. Renton, *Phil. Mag.* **43**, 946 (1952).

⁴ K. Mendelsohn and C. A. Renton, *Phil. Mag.* **44**, 776 (1953).

⁵ R. Berman, *Advances in Phys.* **2**, 103 (1953).

for normal metals, and the behavior of K_s will depend on which combination of heat transport mechanism and scattering process is important. For pure metals, in which $K_{en} \gg K_{gn}$, K_s/K_n decreases rapidly as T is decreased below T_c , the temperature of the superconducting transition in zero magnetic field. The experimental ratios are in reasonable agreement with Heisenberg's calculations for the case in which the electron mean free path is limited by impurity scattering. For impure metals the ratio K_s/K_n does not decrease as rapidly with decreasing T as it does for pure metals, and for several alloys values of $K_s/K_n > 1$ have been reported. Mendelssohn and Olsen⁶ have suggested that K_s/K_n may be greater than unity in alloys because of the presence of a circulation heat flow, analogous to that in liquid helium, when the alloy is in the superconducting state. However, Klemens⁷ has pointed out that this mechanism for heat transport would be present even in pure metals and would in any case be too small to explain the observed values of K_s . An alternative explanation suggested by Hulm⁸ is that the superconducting electrons do not interact with the lattice and make no contribution to scattering of the phonons. On the basis of this suggestion K_{gs} would be greater than K_{gn} , and when the specimen enters the superconducting state the increase in K_g might more than compensate for the decrease in K_e . This could happen only in alloys for which K_{gn} is comparable in magnitude with K_{en} .

Sladek⁹ has measured K_s and K_n for a series of single-crystal indium-thallium alloys ranging in composition from pure indium to 20 atom percent thallium. For pure indium $K_s/K_n < 1$ for all temperatures; for the 5% thallium specimen K_s falls below K_n as T decreases from T_c , but at about 2°K the curve for K_s bends toward that for K_n and apparently crosses it at 1.3°K—the lowest temperature at which measurements were made; for the 15% and 20% specimens, K_s/K_n is greater than unity for all temperatures from T_c down to 1.3°K, and there is some indication of a minimum in K_s at about 1.4°K.

The present paper describes thermal conductivity measurements at temperatures below 1°K on some of these alloy specimens. The experiments were undertaken in the hope that a study of the dependence of K_s on temperature and crystal size would give some indication of the mechanism by which K_s becomes greater than K_n .

II. EXPERIMENTAL

The Apparatus

Figure 1 shows the essential features of the apparatus. Temperatures below 1°K were produced by adiabatic

demagnetization of the salt pill N from a starting temperature of about 1.3°K. The salt was cylindrical in shape, 10 cm in length, and 2.5 cm in diameter. Thermal contact between the salt and the thermal conductivity specimen was made by a method described by Mendoza¹⁰; the powdered salt was pressed onto a system of thin copper vanes under a pressure of about 20 tons/sq in. The tops of the vanes were connected through a thin copper disk M to a copper wire J using an alloy of copper, silver, and phosphorus as solder. The top of the copper wire was soldered to the lower end of the thermal conductivity specimen F . Two carbon resistance thermometers E and a resistance heater D were attached to the specimen as shown. The thermometers were prepared by painting a thin layer of colloidal graphite onto a Formex insulated copper wire, stripping the Formex from one end of the wire, and soldering that end to the specimen. The heater was similar to the thermometers except that the layer of carbon was replaced with a 2000-ohm coil of manganin wire held in place with varnish. Electrical leads to the heater and thermometers consisted of 20-cm lengths of number 40 manganin wire tinned with soft solder and therefore superconducting at the temperatures of measurement; they were taken out into the helium bath through Kovar seals B . The salt pill was supported by threads inside a fiber tube (not shown), and the specimen was supported from the salt by stiffening the copper wire J with a Plexiglas tube. The salt pill and specimen were contained in a glass tube R which was connected by the copper-glass seal C to a pumping

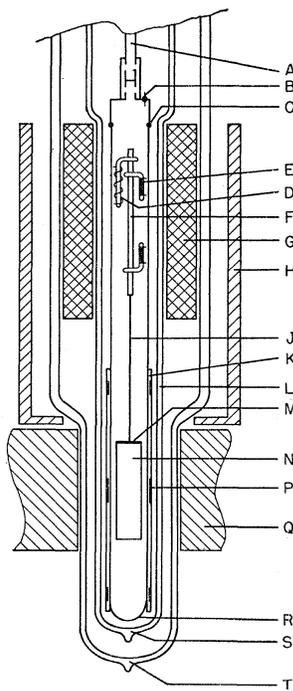


FIG. 1. The apparatus.

⁶ K. Mendelssohn and J. L. Olsen, Proc. Phys. Soc. (London) **A63**, 2 (1950).

⁷ P. K. G. Klemens, Proc. Phys. Soc. (London) **A66**, 576 (1953).

⁸ J. K. Hulm, Proc. Roy. Soc. (London) **A204**, 98 (1950).

⁹ R. J. Sladek, Phys. Rev. **97**, 902 (1955).

¹⁰ E. M. Mendoza, Ceremonies Langevin-Perrin, Paris, 1948.

tube *A*. The pumping tube led to the usual system for introducing and pumping out exchange gas. The helium and nitrogen Dewars are shown at *S* and *T*, and the magnet pole pieces at *Q*. A solenoid *G* was capable of producing magnetic fields of 1000 gauss in the region of the specimen.

The data of Sladek on the same alloy specimens used in the present investigation have shown that it is essential not to expose the specimen to magnetic fields greater than the critical field H_c (or $\frac{1}{2}H_c$ if the field is transverse) at any time after it has become superconducting. Otherwise, it would be left with "frozen-in flux" in the superconducting state and the observed thermal conductivity would differ from the correct value. For this reason a cylindrical iron shield *H* was placed around the outside of the cryostat in the neighborhood of the specimen. The shield reduced the fringing field of the magnet at the lower end of the specimen to about 80 gauss.

Since the salt, and also the specimen, warmed up during the magnetization, it was necessary to prevent them from warming to a temperature at which the transverse field of 80 gauss would exceed $\frac{1}{2}H_c$. The temperature of the lower thermometer was followed continuously during the magnetization of the salt, and the field was increased slowly, allowing the exchange gas to conduct away the heat of magnetization so that the temperature never rose above 1.4°K. The H_c - T relation for indium-thallium alloys is approximately parabolic,¹¹ with $H_c(T=0)$ about 280 and a zero-field transition temperature of about 3.3°K. Therefore, at 1.4°K the critical field is about 230 gauss, and the presence of a transverse field of 80 gauss during the magnetization should have no effect on subsequent measurements of thermal conductivity. The shield was removed whenever magnetic measurements were made on the salt.

A mutual inductance was wound on a plastic coil former *K* (Fig. 1) fastened to the outside of the glass vacuum container. The secondary consisted of a main coil *P* of 3000 turns connected in series-opposition with two compensating coils *L* of 1500 turns each. The primary was a uniform solenoid wound over the whole length of the coil former, but with extra turns added at the ends. The number of extra turns was adjusted so that in the absence of the salt the total mutual inductance was almost zero. This arrangement also provided a uniform primary field over the length of the salt pill.

Calibration of the Salt

Susceptibility measurements on the salt were made by observing the deflection θ in a ballistic galvanometer connected to the secondary coils, when a current i was made or broken in the primary. A fixed mutual inductance in the secondary circuit was used to check

¹¹ J. W. Stout and L. Guttman, Phys. Rev. **88**, 703 (1952).

the sensitivity of the galvanometer. Below 1°K the magnetic temperature T^* was defined by the usual relation¹²:

$$\begin{aligned}(\theta - \theta_0)(T^* - \Delta) &= Ai, \\ \Delta &= \delta' + c(4\pi/3 - n) = \delta' + \delta.\end{aligned}\quad (3)$$

The constants A and θ_0 were determined by measurements of θ in the helium region, where T^* was set equal to the thermodynamic temperature T ; c is the Curie constant/cm³, and n is the demagnetizing factor for the salt. δ' corrects for deviations from Curie's law for a salt pill of spherical shape.

Chromium potassium alum and copper potassium Tutton salt were both used as cooling agents. By taking for n the value it would have for an ellipsoid of the same length and diameter, the values of Δ were as follows: for the chromium salt $\delta' = 0$ and $\delta = 0.022^\circ$; for the copper salt $\delta' = 0.035^\circ$ ¹³ and $\delta = 0.006^\circ$. Strictly speaking, the above treatment is valid only for ellipsoids; for cylinders, the demagnetizing field is not uniform and cannot be defined. However, since the length of the salt was four times its diameter and the measuring coils were well removed from the ends, the nonuniform demagnetizing field should not have introduced an error of more than a few thousandths of a degree.

Calibration of the Thermometers

Following a demagnetization to the lowest attainable temperature, the salt was allowed to warm with no power input to the heater. The residual heat leak produced a temperature rise of the order of 0.001 deg/min or less. During the warm-up period successive measurements of the thermometer resistances and ballistic galvanometer deflections were made. From the ballistic measurements a graph of temperature *versus* time was constructed, and the temperature of the salt at the time corresponding to each resistance measurement was obtained by interpolation. On the assumption that the thermometers and the salt were at the same temperature, it was then possible to make a calibration curve for each thermometer.

Thermal Conductivity Measurements

Thermal conductivities were measured by demagnetizing the salt and then making resistance measurements on the two thermometers with a heat current flowing through the specimen. Values of the temperature difference and mean temperature were read from graphs of temperature *versus* time and were combined with the heater power to give the thermal conductivity as a function of temperature. Whenever possible, the heater current was chosen to give tem-

¹² N. Kurti and F. Simon, Phil. Mag. **26**, 849 (1938).

¹³ R. J. Benzie and A. H. Cooke, Proc. Phys. Soc. (London) **63**, 213 (1950).

perature differences of about 10% of the absolute temperature. At temperatures above 0.5°K this was not usually practical because of the combined effect of the high thermal conductivity of the specimen and the low heat capacity of the salt.

Errors

The total heat leak to the salt-specimen system was almost constant at about 1 microwatt. Because the heat capacity of the salt was so much larger than that of the specimen, any part of the residual heat leak which was directed to the specimen would have to flow to the salt. The resulting heat current would produce a temperature gradient in the specimen and copper wire and would therefore introduce an error into the thermometer calibration.

The temperature difference between the two thermometers during the calibration run can easily be shown to produce no error in the thermal conductivity measurements, if it is assumed that the distribution of the residual heat leak over the length of the specimen is the same in the thermal conductivity run as in the calibration run. This assumption seems to be justified by the fact that when the heater is turned on the temperature difference between the upper end of the specimen and the bath changes by no more than a few percent and the heat leak (exclusive of heater current) is unchanged.

The thermal resistance between the lower thermometer and the salt was measured and was found to be in rough agreement with that found for salt-metal interfaces by Mendoza¹⁰ and Goodman.¹⁴ By assuming that the fraction of the residual heat leak which goes to the specimen is proportional to its area, the temperature difference between the lower thermometer and the salt during the calibration was estimated to be about 0.002° at 0.15°K and to be negligible above 0.25°K. Even at the lowest temperatures this will not introduce an error of more than a few percent into the thermal conductivities, because the error in both thermometers is in the same direction and partially cancels in measuring temperature differences.

The ballistic galvanometer could be read to better than 1 mm, and below 1°K the primary current was adjusted to give a deflection of 60 to 80 cm. Equation (3) then shows that T^* is measured to approximately 1 part in 1000. This also represents the precision of the thermometer calibration. Therefore, when temperature differences of $0.1T^*$ were used, ΔT^* could be measured to about 2%, but as was pointed out above this was not always possible. If we neglect for the moment differences between T^* and T , the measured thermal conductivity points should be accurate to about 3% below 0.4°K but at higher temperatures the low resistance specimens may be as much as 10% in error.

¹⁴ B. B. Goodman, Proc. Phys. Soc. (London) A46, 217 (1953).

III. RESULTS

Copper Specimen

With the magnetic fields available it was not possible to cool chrome alum below 0.25°K, and measurements at lower temperatures had to be made by using copper potassium Tutton salt as the cooling agent. Unfortunately, the heat capacity of the copper salt was so small at the higher temperatures that it could not be used above 0.25°K. It will be seen from the results for indium-thallium alloys that measurements made with the two salts do not join smoothly at 0.25°K and that values of K_n obtained with the chromium salt deviate from a straight line below 0.4 or 0.5°K. The results of some measurements on a copper specimen are shown in Fig. 2 and are introduced at this point to illustrate more clearly the nature of the discrepancy. The thermal conductivity is proportional to the temperature, at least at the higher temperatures, and the value of the proportionality constant is approximately the same as that found for another copper specimen by Nicol and Tseng.¹⁵

It seems clear that the difference in the results obtained with the two salts must be a consequence of different relations between T^* and T . For copper potassium Tutton salt the difference between T^* and T is probably small above 0.1°K¹⁶; this is in agreement with the observation that the values of K obtained with this salt fall on the same straight line through the origin as the points obtained above 0.5°K with chrome

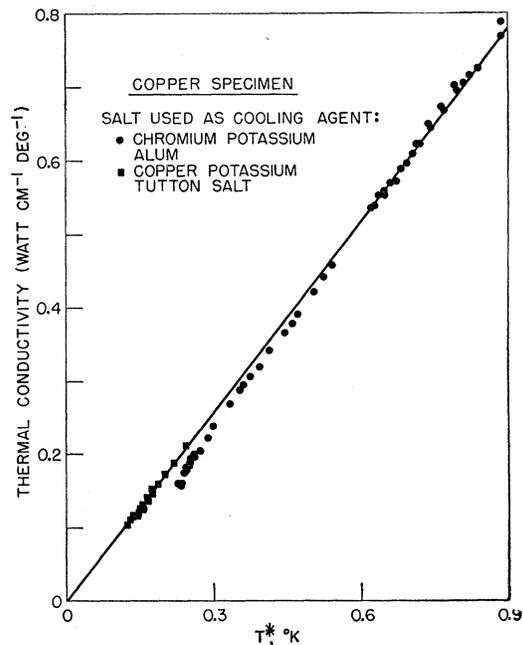


FIG. 2. Thermal conductivity of the copper specimen.

¹⁵ James Nicol and T. P. Tseng, Phys. Rev. 92, 1062 (1953).

¹⁶ C. G. B. Garrett, Ceremonies Langevin-Perrin, Paris, 1948.

alum and leads to the conclusion that this line represents K as a function of T . The difference between T^* and T for chrome alum would then have to be about twice as great at 0.25°K as measured by Bleaney using the γ -ray heating method.¹⁷ There is a considerable amount of conflicting data on the low-temperature properties of chrome alum which is sometimes thought to indicate the possibility that these properties depend on the previous treatment of the salt, and while there has been no such evidence bearing directly on the present question it is possible that this provides an explanation for the unexpectedly large deviations from a straight line of the chrome alum points.

Indium-Thallium Alloys

Measurements of the thermal conductivity in the normal and superconducting states have been made on three indium-thallium alloys—a 15% thallium polycrystalline specimen with a grain size of 1 or 2 mm, a 15% single crystal, and a 20% thallium single crystal. The measurements of K_s extend from about 0.15°K to about 0.8°K but K_n was measured only down to 0.25°K . The specimens were 6 mm in diameter and were originally prepared by Stout and Guttman,¹¹ who have reported on their magnetic and electric properties. Sladek has made thermal conductivity measurements on the two single crystals above 1°K , but, since it was not clear from his work with higher thallium content polycrystals whether or not grain size had any effect on K_s above 1°K , measurements on the 15% polycrystal in the helium region are included in the work

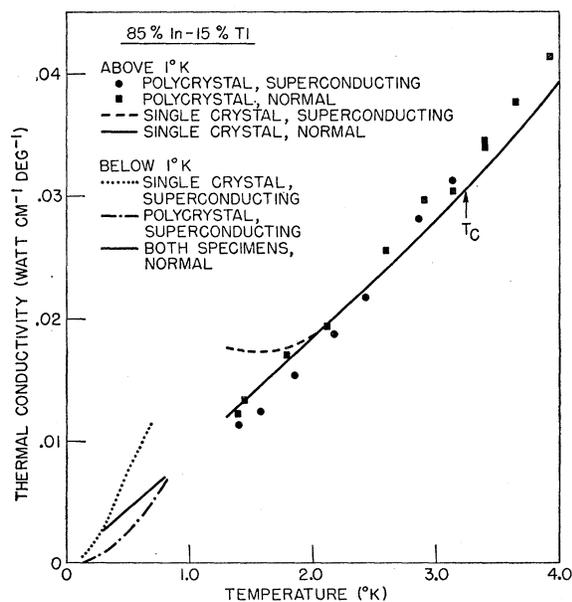


FIG. 3. Thermal conductivity of the 15% thallium single and polycrystal specimens. The curves for the single crystal above 1°K are from Sladek's measurements.

¹⁷ B. Bleaney, Proc. Roy. Soc. (London) A204, 216 (1951).

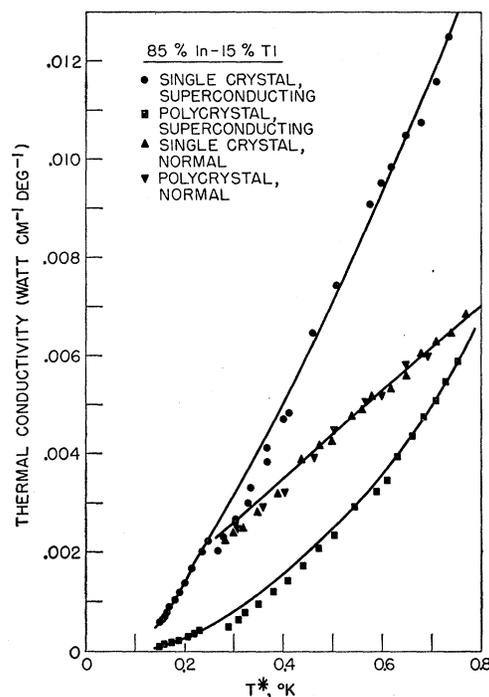


FIG. 4. Thermal conductivity of the 15% thallium specimens below 1°K .

reported here. The measurements above 1°K were carried out by placing the copper wire attached to the specimen in thermal contact with the helium bath instead of with the salt.

Figure 3 shows the smoothed values of K_s and K_n for the two 15% specimens below 1°K , Sladek's smoothed curves for the 15% single crystal above 1°K , and the experimental points for the 15% polycrystal above 1°K . The experimental points for the same specimens below 1°K are shown in Fig. 4. In all figures the curves are drawn to fit the low temperature points obtained using the copper Tutton salt as the cooling agent. Figure 5 is a log-log plot of K_s versus T for the same specimens; the low-temperature points obtained with chrome alum are omitted in the belief that they do not represent the correct temperature dependence of K_s . Data for the 20% specimen are plotted in Fig. 6.

IV. DISCUSSION

It is evident from Figs. 3-5 that, although the presence of grain boundaries has no effect on K_n , it has a marked effect on K_s . The absence of an effect on K_n is easily understood in terms of the concept of thermal conductivity as a product of the heat capacity, velocity, and mean free path of the heat carriers. Sladek has analyzed the data for the 15% single crystal to give the separate contributions of the electrons and phonons to the thermal conductivity. The mean free paths of both phonons and electrons—estimated by equating Sladek's values of K_{gn} and K_{en} to the product

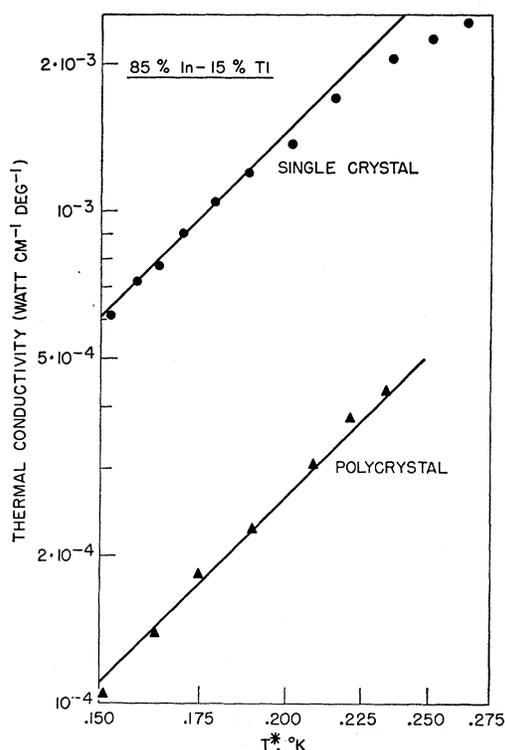


FIG. 5. Plot of $\log K_s$ versus $\log T$ for the 15% thallium specimens showing only points obtained with copper potassium Tutton salt. The straight lines are drawn with a slope of three.

of the heat capacity, velocity, and mean free path of the phonons and electrons respectively—are several orders of magnitude smaller than the grain size in the polycrystal. Therefore, it is to be expected that the presence of grain boundaries should not influence K_n . The difference in K_s between the two 15% specimens can be explained if it is supposed that the mean free path of one of the heat carriers is much longer in the superconducting state than in the normal state. Qualitatively, the experimental results agree with Hulm's suggestion that the mean free path of phonons becomes longer in the superconducting state and that it is this effect which makes $K_s > K_n$ in the neighborhood of 1°K.

On the basis of this explanation the maximum observed in K_s for the single crystals is similar in origin to the one occurring in dielectric crystals at temperatures in the helium region and above. On the high-temperature side the mean free path of the phonons decreases more rapidly with increasing temperature than their heat capacity increases (the decrease is caused by electron scattering in the present case and by Umklapp processes in the dielectric crystals). On the low-temperature side the mean free path is constant, limited only by crystal dimensions, and the temperature dependence of the conductivity is determined by the lattice heat capacity. (In the present case there is also the complication of a second heat transport mechanism being important on the high-temperature side.)

The above interpretation is very similar to that given by Laredo¹⁸ in connection with his measurements on a series of tin specimens. He concluded that at temperatures well below 1°K the contribution of electron conductivity to K_s became negligible and that the phonon mean free path was determined by boundary scattering.

A quantitative comparison with theory is possible only at the lowest temperatures. No theory has been developed for phonon conductivity under the conditions that would exist in the present case near 1°K. At lower temperatures, however, the contribution to K_s from electron conductivity probably decreases exponentially, becoming negligible at a few tenths of a degree, and if scattering of phonons by electrons decreases until only grain boundary scattering is important K_s should be given by the theory developed by Casimir for dielectric crystals.² Casimir's formula predicts a conductivity proportional to T^3 and to the diameter of the crystal (for long single crystals of uniform cross section). Figure 5 shows that for the polycrystal K_s is proportional to T^3 between 0.15 and 0.25°K and that for the single crystal the slope of $\log K_s$ versus $\log T$ increases with decreasing T but becomes equal to three below 0.2°K. Furthermore, in the region in which K_s is proportional to T^3 for both 15% specimens it is greater for the single crystal by a factor of about five, which is approximately the ratio of the diameter of the single crystal to the grain size of the polycrystal. This suggests that at the lowest temperatures K_s is entirely a lattice conductivity limited by the grain-boundary scattering of phonons. At temperatures above the T^3 region K_s falls below an extrapolation of the T^3 curve, as would be expected when another scattering mechanism

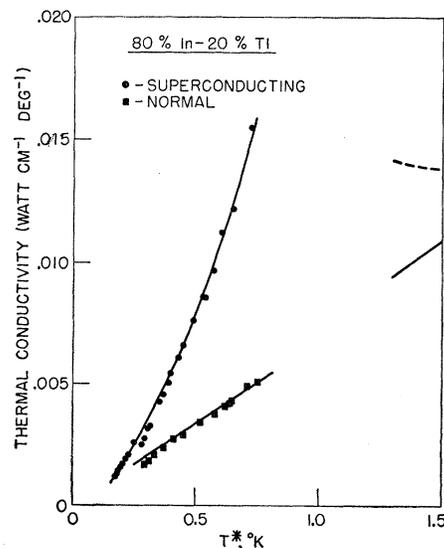


FIG. 6. Thermal conductivity of the 20% thallium specimen. The curves above 1°K are from Sladek's measurements.

¹⁸ S. J. Laredo, Proc. Roy. Soc. (London) A229, 473 (1955).

(electron scattering) becomes important. For the 20% single crystal the slope of a $\log K_s$ versus $\log T$ plot (not shown) is increasing with decreasing T but is still only 2.5 at 0.15°K.

Although K_s becomes proportional to T^3 and to grain size, the magnitude of the conductivity is about ten times smaller than the value calculated from Casimir's formula using a Debye temperature of 100. Experiments on dielectric crystals show that Casimir's formula gives values of the conductivity which are in some cases an order of magnitude too high (in some cases the agreement is good). These discrepancies are probably connected with the presence of some type of lattice imperfection and their existence shows that the lack of quantitative agreement need not exclude the interpretation of K_s given above. In addition to the usual types of imperfections there is, in the indium-thallium alloys, the additional possibility that there were small normal-state regions "frozen in" when the specimen first became superconducting (the earth's field was not compensated). There would undoubtedly be some normal regions formed at the ends of the specimen during the magnetization of the salt even though the field did not exceed $\frac{1}{2}H_c$, but it is unlikely that these extended into the part of the specimen between the thermometers to any appreciable extent. Any resistance due to these

effects cannot be too large or it would mask the observed dependence of K_s on crystal size. However, the observed factor of five between the values of K_s for the 15% specimens is not incompatible with the presence of a certain amount of resistance due to a mechanism other than boundary scattering. In this connection it must be remembered that the Casimir formula was derived for long cylinders and that in the present case the irregular shapes and range of sizes of the grains make the relation between grain size and conductivity very approximate.

V. ACKNOWLEDGMENTS

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