for the potential at the same point in crystal space we now have

$$\tfrac{1}{2}[\psi(\tfrac{1}{2}x,\tfrac{1}{2}y,\tfrac{1}{2}z)+\psi(\tfrac{1}{2}x,\tfrac{1}{2}y,\tfrac{1}{2}z-\tfrac{1}{2})+\psi(\tfrac{1}{2}x,\tfrac{1}{2}y-\tfrac{1}{2},\tfrac{1}{2}z)+\psi(\tfrac{1}{2}x-\tfrac{1}{2},\tfrac{1}{2}y,\tfrac{1}{2}z)+\psi(\tfrac{1}{2}x-\tfrac{1}{2},\tfrac{1}{2}y-\tfrac{1}{2},\tfrac{1}{2}z)+\psi(\tfrac{1}{2}x-\tfrac{1}{2},\tfrac{1}{2}y,\tfrac{1}{2}z-\tfrac{1}{2})+\psi(\tfrac{1}{2}x,\tfrac{1}{2}y-\tfrac{1}{2},\tfrac{1}{2}z-\tfrac{1}{2})+\psi(\tfrac{1}{2}x-\tfrac{1}{2},\tfrac{1}{2}y-\tfrac{1}{2},\tfrac{1}{2}z-\tfrac{1}{2})].$$

However, changing the definition of the cell edge changes no physical quantity (e.g., the potential) in the lattice, so that the above expression must equal $\psi(x,y,z)$. By picking particular values of $\mathbf{r}$ and making use of the full cubic symmetry of $\psi(\mathbf{r})$, the equations simplify to those of Hund. Clearly, the same type of argument also holds if the new cell side is any integer.

PHYSICAL REVIEW VOLUME 97, NUMBER 4 FEBRUARY 15, 1955

Thermal Conductivity of Indium-Thallium Alloys at Low Temperatures*

RONALD J. SLADEK†
Institute for the Study of Metals, The University of Chicago, Chicago, Illinois
(Received November 1, 1954)

The thermal conductivity of a series of homogeneous, solid solution indium-thallium alloys containing up to 50 atomic percent of thallium has been measured as a function of temperature at liquid helium temperatures and as a function of both longitudinal and transverse magnetic fields below T_c, the superconducting transition temperature in zero field. The normal-state results agree quite well with the quasi-free electron theory of metals. The superconducting-state results agree with the hypotheses that electrons in the "superconducting phase" neither transport heat nor scatter phonons.

For pure indium, it was found that $K_{es}/K_{en}=2t^2/(3+t^4)$, where K_{es} and K_{en} are the electronic thermal conductivities at a given temperature when the specimen is superconducting and when it is nonsuperconducting, respectively, and $t=T/T_c$.

For all the alloy specimens the ratio of the lattice thermal conductivities comprised a family of curves such that $t^{-3}<K_{gs}/K_{gn}<t^{-6}$.

A thermal resistivity maximum was found to accompany the isothermal destruction of superconductivity by either a longitudinal or a transverse magnetic field in specimens containing 15 percent Tl or more. When the applied field was reduced to zero, the final thermal resistivity of most of these specimens was greater than would be expected for a simple mixture of superconducting and "frozen-in" normal regions, the concentration of the latter being estimated from magnetic induction measurements. Both this effect and the maxima themselves are thought to be manifestations of an increased lattice thermal resistivity due to alteration of the mean free path of phonons when they approach the boundary between a superconducting and a normal region.

I. INTRODUCTION

THE mechanism of heat conduction in superconductors, like the phenomenon of superconductivity itself, is still very incompletely understood from a quantitative theoretical point of view. However, some progress has been made towards a qualitative understanding of the various physical processes involved particularly in the case of pure metals.[1] In order to indicate the nature of the difficulties involved, it is necessary to discuss briefly the mechanisms of heat transport in nonsuperconductors at low temperatures.

Heat is conducted through nonsuperconducting metals by the motion of conduction electrons and by the direct interactions between atoms. Since these processes can be regarded as heat paths in parallel, it is usual to assume that the separate conductivities are directly additive. For pure metals at low temperatures the electronic thermal conductivity is usually so large that the lattice thermal conductivity is negligible in comparison with it. In this case, Wilson,[2] Makinson,[3] and Sondheimer[4] have shown theoretically that at temperatures below about 0.1Θ, where Θ is the Debye temperature, the electronic thermal resistivity may be expressed in the form

$$1/K_{en}=\alpha T^2+\beta/T, \quad (1)$$

where K_{en} is the electronic thermal conductivity and α and β are constants for a given specimen. The first and second terms on the right represent thermal resistivities due to the scattering of electrons by phonons, and by impurities, respectively; the existence of both types of thermal resistivity is now well established by experiment,[5–9] and there is little doubt that the temperature dependence is close to that predicted theoretically. The experimental values of the coefficient

* Based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Physics Department of the University of Chicago.

† U. S. Atomic Energy Commission Fellow, 1951–53; now at Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania.

[1] D. Shoenberg, *Superconductivity* (Cambridge University Press, London, 1952), second edition, pp. 78–86.

[2] A. H. Wilson, Proc. Cambridge Phil. Soc. **33**, 371 (1937); also *Theory of Metals* (Cambridge University Press, Cambridge, England, 1953), second edition.

[3] R. E. B. Makinson, Proc. Cambridge Phil. Soc. **34**, 474 (1938).

[4] E. H. Sondheimer, Proc. Roy. Soc. (London) **A203**, 74 (1950).

[5] J. K. Hulm, Proc. Roy. Soc. (London) **A204**, 98 (1950).

[6] R. Berman and D. K. C. MacDonald, Proc. Roy. Soc. (London) **A209**, 368 (1951); **A211**, 122 (1952).

[7] Andrews, Webber, and Spohr, Phys. Rev. **84**, 994 (1951).

[8] K. Mendelssohn and H. M. Rosenberg, Proc. Phys. Soc. (London) **A65**, 385 (1952).

[9] G. K. White, Proc. Phys. Soc. (London) **A66**, 559 and 844 (1953).

β in the impurity term appear to agree fairly well with the theoretical value ρ_0/L_0 calculated from the residual electrical resistivity ρ_0 and the Lorenz constant, $L_0=\frac{1}{3}(\pi k/e)^2$. However, the theoretical value of α, $95.3N_a^{\frac{2}{3}}/K_\infty\Theta^2$, where N_a is the number of conduction electrons per atom and K_∞ is the limiting value of the thermal conductivity at high temperatures, is found to be between 5 and 10 times larger than the actual experimental values, a result for which no adequate theoretical explanation has yet been forthcoming.

When a pure metal is in the superconducting state, both thermal resistivity terms in Eq. (1) are found to be larger than when it is in the normal state at the same temperature. This result has been explained qualitatively by McLennan[10] employing the two-fluid model of superconductivity proposed by Gorter and Casimir.[11,12] According to this model, when a metal is superconducting a certain fraction of the thermally excited conduction electrons are transferred to a "superconducting phase" in which they are not scattered by impurities or by phonons. Thus, since there are a reduced number of thermally excited electrons remaining in the "normal phase," less heat is transported than when the specimen is nonsuperconducting. Heisenberg[13] attempted to put this idea on a more quantitative basis for the case of impurity scattering, while Hulm[5] suggested that the experimental results for the superconducting state be represented, in analogy to Eq. (1), by the expression

$$1/K_{es}=\alpha T^2/g(t)+\beta/[Tf(t)], \qquad (2)$$

where K_{es} is the electronic thermal conductivity when the specimen is superconducting and $g(t)$ and $f(t)$ are characteristic functions of the reduced temperature t or T/T_c. The observed impurity function $f(t)$ for tin may be quite well represented by Heisenberg's theoretical expression,[13] which has the approximate form $2t^2/(1+t^4)$. No corresponding empirical or theoretical expression exists for $g(t)$.

It should be remarked that all the experiments indicate that $f(t)$ and $g(t)$ decrease from unity at the transition temperature towards zero as the absolute zero is approached. Assuming that the thermal conductivity is proportional to CLv, where C is the heat capacity of the electrons, L is their mean free path, and v is the Fermi velocity, it might at first sight appear that the thermal conductivity should follow the total electronic heat capacity in exhibiting a discontinuity when the specimen becomes superconducting and that $f(t)$ and $g(t)$ should be greater than unity. However, careful measurements[5] have failed to reveal the slightest evidence of a discontinuity in thermal conductivity at the transition temperature. This seems to indicate that the process of transferring electrons to the "superconducting phase," which gives rise to the discontinuity in heat capacity, does not contribute to the thermal conductivity.[14]

The coefficient β in Eqs. (1) and (2) is proportional to the impurity content of the specimen at low concentrations and thus to the residual electrical resistivity ρ_0. Hence, as the concentration of impurity is increased, the impurity scattering term gradually becomes dominant and the total electronic thermal conductivity decreases. At sufficiently large impurity content, usually about 0.1 percent, the electronic thermal conductivity becomes comparable to that due to the lattice, which has been estimated theoretically by Makinson.[3] For temperatures less than about 0.1Θ, the theoretical lattice thermal resistivity may, under certain conditions,[5] be expressed in the form

$$1/K_{gn}=A/T^2+B/T^3+CT, \qquad (3)$$

where K_{gn} is the lattice thermal conductivity when the specimen is normal (i.e., nonsuperconducting), and A, B, and C are constants for a given alloy. The three terms on the right-hand side are thermal resistivities due to the scattering of phonons by electrons, by crystal grain boundaries, and by impurities respectively. Expansion of the lattice thermal resistivity in this manner is only valid when either the first or second term on the right is large compared to the other terms.

Experiments on nonsuperconducting alloys[15–18] suggest that at temperatures of a few degrees Kelvin scattering of phonons by grain boundaries is unimportant for average grain sizes. Furthermore, scattering by electrons is usually more effective than scattering by impurities, at least at the lower temperatures. Thus, the lattice thermal conductivity is proportional to T^2. In alloys studied so far the electronic thermal conductivity is never negligible compared to the lattice thermal conductivity, but the two may be separated because of different temperature dependences.

For alloys in the superconducting state, one of the puzzling features of the early experiments of de Haas and Bremmer[19] was that for certain high-concentration alloys the thermal conductivity in the superconducting state was *greater* than that in the normal state at the same temperature, in direct contrast to the behavior of pure metals. As a possible explanation of these and similar later results on alloys, Hulm[5] has suggested that for a superconducting alloy Eq. (3) is modified to the form

$$1/K_{gs}=A/[T^2h(t)]+B/T^3+CT, \qquad (4)$$

[10] J. C. McLennan, Proc. Roy. Soc. (London) **A152**, 1 (1935).
[11] C. J. Gorter and H. B. G. Casimir, Z. tech. Phys. **15**, 539 (1934).
[12] See also reference 1, p. 194.
[13] W. Heisenberg, Z. Naturforsch. **3A**, 65 (1948); also *Two Lectures* (Cambridge University Press, London, 1949), p. 36.
[14] See reference 1, p. 215.
[15] J. Karweil and K. Schaeffer, Ann. Physik **36**, 567 (1939).
[16] J. K. Hulm, Proc. Phys. Soc. (London) **B64**, 207 (1951).
[17] R. Berman, Phil. Mag. **42**, 642 (1951).
[18] I. Estermann and J. E. Zimmerman, J. Appl. Phys. **23**, 578 (1952).
[19] W. J. de Haas and H. Bremmer, Leiden Comm. **220c** (1932); **243c** (1936).

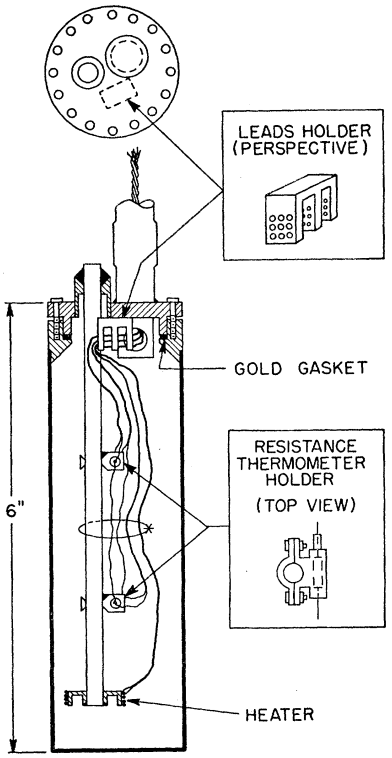

FIG. 1. The vacuum can with the specimen in place.

where $h(t)$ is yet another characteristic function of reduced temperature, which, unlike $f(t)$ and $g(t)$, exceeds unity. This hypothesis is also based upon the two-fluid model of superconductivity, but involves the additional assumption of negligible scattering of lattice waves by electrons belonging to the "superconducting phase." Since only the remaining thermally excited electrons (i.e., those in the "normal phase") are available as scattering centers, the lattice thermal conductivity when the specimen is superconducting must be greater by a certain factor $h(t)$ than when the specimen is in the normal state at the same temperature. $h(t)$ might be expected to depend mainly upon the ratio of the number of thermally excited normal electrons when the specimen is in the normal state to that when the specimen is superconducting and thus to be a characteristic function of the reduced temperature.

It may be inferred from previous experiments[5,19–21] that for scattering of phonons by electrons, the lattice thermal conductivity is greater when a specimen is superconducting than when it is in the normal state. However, these experiments provide little detailed information on the functional form of K_{gs}/K_{gn} or $h(t)$. The present work was initiated to obtain more information on $h(t)$. The indium-thallium system was chosen for three reasons: first, because homogeneous solid solutions are formed for thallium concentrations ranging from zero up to more than 50 atomic percent; second, because over this whole range of concentrations the superconducting transition temperature lies in the neighborhood of 3°K, which is low enough so that K_n has a simple form but high enough to allow determination of K_s down to $0.4T_c$ simply by using a liquid helium bath; and third, because accurate magnetic and electrical data on the superconductivity of this system were already available through the work of Stout and Guttman.[22] In fact the specimens used for our thermal conductivity measurements were the same ones investigated by Stout and Guttman and were either single crystals or large grain size polycrystals free from strain and inhomogeneities in composition.

The observed dependence of thermal conductivity upon magnetic field for these alloys has already been reported in brief.[23] In the present paper these results are discussed in greater detail along with the data on the variation of thermal conductivity with temperature when the specimen is completely normal or completely superconducting.

II. EXPERIMENTAL DETAILS

A. Apparatus

The thermal conductivity apparatus (Fig. 1) was of the conventional type in which a steady heat current is established in a uniform cylindrical specimen and the resulting temperature gradient is determined by thermometers located at two separate positions along the length of the specimen. The thermometers were modified Allen-Bradley ½-watt, 12-ohm nominal, carbon-composition resistors glued in copper holders which were in turn soldered to the specimens with Rose's metal. The specimens were mounted in a vacuum can which was immersed in liquid helium or liquid hydrogen contained in a liquid nitrogen-shielded Dewar flask.[24] Either longitudinal or transverse magnetic fields could be applied to the specimen by a solenoid and by Helmholtz coils, respectively.

It was essential to avoid distortions of the applied magnetic field other than those due to the specimen itself. Thus a minimum of Rose's metal was used in soldering to the specimen, and the vacuum can was constructed of nonsuperconducting and nonferromagnetic materials. Since the can had to be easily taken apart to permit specimen changes and could not be heated appreciably owing to the low melting point of the specimens (about 180°C), it was constructed in two portions and joined by means of a gold gasket

[20] K. Mendelssohn and J. L. Olsen, Proc. Phys. Soc. (London) **A63**, 2 (1950).
[21] J. K. Hulm, National Bureau of Standards Circular **519** (U. S. Government Printing Office, Washington, D. C., 1952), p. 37.
[22] J. W. Stout and L. Guttman, Phys. Rev. **88**, 703, 713 (1952).
[23] R. J. Sladek, Phys. Rev. **91**, 1280 (1953).
[24] See, for example, G. F. Hardy and J. K. Hulm, Phys. Rev. **93**, 1004 (1954).

seal.[25] With the rather small ($1\frac{1}{4}$-in. diameter) rings employed, the best results were obtained using spectroscopically pure gold wire.[26] The gasket was compressed satisfactorily with brass screws, although these occasionally fractured on warming up the system from low temperatures.

The thermometer and heater coil leads were small-gauge manganin wires. These passed into the vacuum can via the pumping tube and a copper heat station which made good thermal contact with the low-temperature bath. As an extra precaution against heat input down the pumping tube due to radiation or due to conduction by residual gas molecules, there was an S bend in this tube somewhat above the vacuum can and a suitable trap at its lower end.

Under typical conditions of measurement, pressures of less than 5×10^{-7} mm Hg were maintained in the vacuum can. At such pressures the heat lost from the surface of the specimen by conduction through the surrounding gas was estimated to be less than 1 percent of the lowest heater power employed.

B. Temperature Measurements

The resistance thermometers were calibrated in place on the specimen against the vapor pressure of the bath using the 1949 international helium scale[27] and the N.B.S. hydrogen scale,[28] with appropriate corrections for the hydrostatic pressure head above the specimen. Each thermometer resistance was determined using a Wenner potentiometer and measuring currents of only a few microamperes to ensure that the heat generated in the thermometer itself was small compared to the lowest heater power employed in the thermal conductivity measurements. The high sensitivity of the thermometers, particularly at the lower end of the temperature range, may be gauged from typical calibration data shown in Table I.

Neither longitudinal nor transverse magnetic fields of the size used in this experiment had any detectable influence upon the resistance of the thermometers. The calibration curve was also found to be perfectly reproducible, within the accuracy of measurement, during a liquid helium experiment lasting several days, and could be quite well represented by an empirical expression of the type

$$\log_{10}R+C/\log_{10}R=A+B/T, \tag{5}$$

where A, B, and C are constants for a given thermometer.[29] Unfortunately, however, small, random changes of up to 2 percent in resistance were sometimes observed between separate experiments when the thermometers had been warmed up to room temperature in the intervening period. Thus, since temperature differences between the thermometers of less than 0.1°K were used in the liquid helium range, it was necessary to recalibrate them during each experiment. Instead of tediously fitting the calibration data to an expression of the type of Eq. (6) for each recalibration, temperatures were obtained directly from large-scale calibration curves.

TABLE I. Typical thermometer calibration data, Allen-Bradley $\frac{1}{2}$-watt, 12-ohm (nominal, room temperature) resistors.

T (°K)	R (ohms)	dR/dT (ohms/°K)
20.4	25	− 0.57
10.7	37	− 2.6
4.2	100	−35
1.2	1900	−5000

In a few cases, thermal conductivity measurements were carried out for a few degrees above 4.2°K by using enough heater power to raise the mean temperature of the specimen. Since direct calibration of the thermometers was not possible for this temperature range, Eq. (5) was fitted to the data for the liquid hydrogen and liquid helium I ranges and was then used as an interpolation formula for the intermediate region. The somewhat greater error in the determination of the absolute temperature of each thermometer and consequent uncertainty in the temperature difference between them was to some extent compensated by the greater temperature differences used.

C. Corrections and Errors

The thermal conductivity was calculated from the experimental variables by means of the relation

$$K=Pd/A\Delta T, \tag{6}$$

where P is the heater power, d the distance between the thermometers, A the cross sectional area of the specimen, and ΔT the temperature difference between the thermometers. Of the quantities determining the thermal conductivity in Eq. (6), ΔT was the least accurately known. As already noted, the working temperature difference was usually in the neighborhood of 0.1°K in the liquid helium range, and somewhat greater above 4.2°K. Although changes in ΔT as small as 0.0002°K could readily be detected, for example, during isothermal magnetic field transitions, the error in the absolute temperature difference was usually somewhat greater than this owing to fluctuations in the bath temperature, particularly in the helium I region. We estimate that ΔT was known to about ±2 percent over most of the range of measurement, with, however, a somewhat greater error just above the λ point and also above 4.2°K where the larger heater powers caused greater bath temperature fluctuations. The heater power P was known to about ±0.3

[25] Wexler, Corak, and Cunningham, Rev. Sci. Instr. **21**, 259 (1950).
[26] We are indebted to Dr. R. T. Webber of the Naval Research Laboratory for helpful discussions on this point.
[27] H. Van Dijk and D. Shoenberg, Nature **164**, 151 (1949).
[28] Wolly, Scott, and Brickwedde, J. Research Natl. Bur. Standards **41**, 379 (1948).
[29] J. R. Clement and E. H. Quinnell, Rev. Sci. Instr. **23**, 213 (1952).

percent after allowance was made for the heat generated in the leads. Heat conduction along the heater and thermometer leads in parallel with the specimen amounted to only about 0.1 percent of the heat flowing in the specimen itself in the worst case and so could be neglected. Owing to the finite length of the solder contacts between the specimen and thermometers, there was an uncertainty of about ± 1 percent in the effective length of the specimen. The error in A was negligible. Combining these various errors, we estimate that the thermal conductivity was determined to about ± 2.5 percent over most of the range of measurement, with a slight increase in error close to the λ point and above 4.2°K.

D. Specimens

The specimens were obtained from Stout and Guttman who have described their preparation elsewhere.[22] Nominal compositions and magnetic and electrical characteristics, obtained in most cases from Stout and Guttman's work, are listed in the first four columns of Table II. In one case, that of pure indium,

TABLE II. Characteristics of the indium-thallium specimens.

Nominal composition atomic % Tl (a)	T_c °K (a)	H_0 oersteds (a)	$10^3\, L_0/\rho_0$ mw−cm^{-1} deg^{-2} (a)	$10^3/\beta$ mw−cm^{-1} deg^{-2} (b)	$10^3/A$ mw−cm^{-1} deg^{-3} (b)	N_a (b)
0[c]	3.374	284.3	660[b]	664	...	...
5[c]	3.280	276.5	24.3	24.5	0.64	0.78
15[c]	3.252	281.1	8.51	8.52	0.35	1.01
20[c]	3.223	252.3	6.52	6.56	0.42	0.92
30[d]	3.304	200[b]	4.49	4.88	0.33	1.02
38[d]	2.938	178[b]	4.08	4.59	0.18	1.35
50[d]	2.652	128[b]	3.53	4.79	0.10	1.76

[a] See reference 22, except where stated.
[b] Present work.
[c] Single crystal.
[d] Polycrystal, large grains.

our thermal conductivity results differed by a factor of about two from those expected from the Wiedemann-Franz law, using Stout and Guttman's residual electrical resistivity value, 0.0632 micro-ohm cm. We therefore redetermined ρ_0 for this specimen and found the value 0.0371 micro-ohm cm, which is much more consistent with the thermal conductivity data. It seems likely that, during the two years which elapsed between these two electrical measurements, the resistivity decreased appreciably owing to a redistribution of impurities by diffusion through the indium sample at room temperature.

In the case of the high-concentration polycrystalline specimens, Stout and Guttman were unable to determine the critical magnetic fields by induction measurements because of the very gradual penetration of the field into these samples. However, we found that a slight penetration of field caused a sharp decrease in thermal conductivity for all the alloys investigated. Since for the 5, 15, and 20 percent thallium specimens, the fields at which this decrease occurred were almost identical with Stout and Guttman's critical field values, it

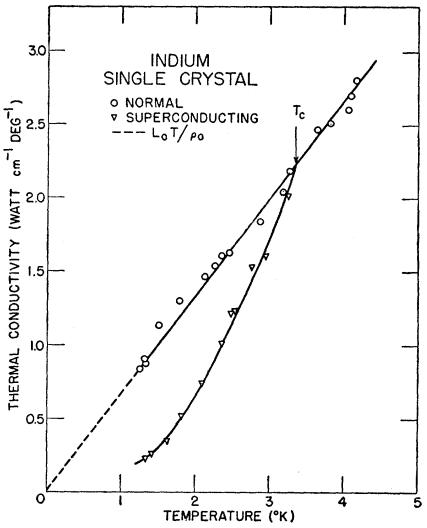

FIG. 2. Thermal conductivity of indium *versus* temperature.

seems reasonable to obtain the critical fields of the higher concentration alloys from the thermal conductivity transition curves. The data for the 30, 38, and 50 percent thallium samples given in the third column of Table II were obtained in this fashion.

III. RESULTS AND DISCUSSION

A. The Normal State

The thermal conductivity of each of the seven specimens was measured at intervals of about 0.1°K from 4.2°K down to 1.3°K, first, in almost zero magnetic field[30] in order to obtain the virgin superconducting

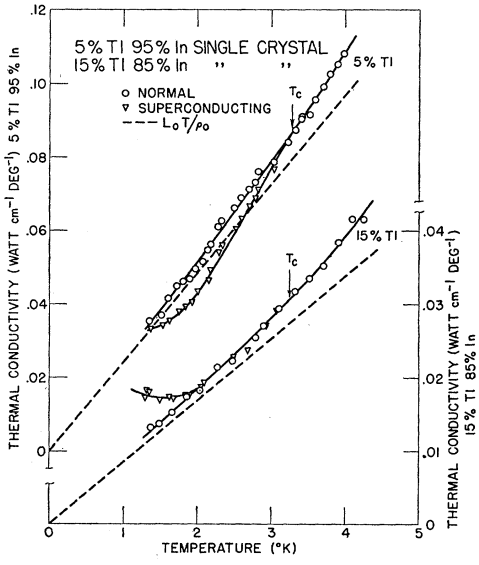

FIG. 3. Thermal conductivity of indium +5 and 15 percent thallium *versus* temperature (different ordinates for the two samples).

[30] The earth's field was present.

state curve, and second, in a longitudinal field sufficient to completely destroy superconductivity at temperatures below the transition point. The magnitude of this field was known from magnetic induction and electrical resistance data,[22] but as an additional check that the pure normal state was reached in each case it was ascertained that no change of thermal conductivity occurred with a further increase in field. For all the specimens a region of field-independent thermal conductivity was reached below about 1000 oersteds, and no evidence was found for appreciable normal magnetothermal resistivity effects in the largest fields used. This may be attributed to a rather short electronic mean free path even in the fairly pure indium sample, since previous work[5] indicates that quite long

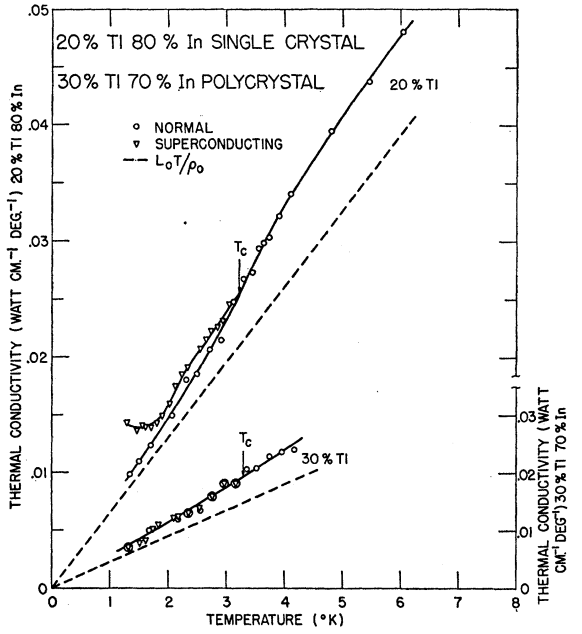

FIG. 4. Thermal conductivity of indium +20 and 30 percent thallium *versus* temperature (different ordinates for the two samples).

electronic mean free paths, such as exist in high purity metals, are required for normal magnetothermal resistivity effects to be observable at the relatively low fields used in the present experiment.

The thermal conductivity of the pure indium sample is plotted against temperature in Fig. 2, where T_c is the zero field superconducting transition temperature from magnetic measurements. Since the thermal conductivity when the specimen is in the normal state, K_n, is proportional to temperature with a slope of $1/\beta$ in almost exact agreement with the Wiedemann-Franz estimate L_0/ρ_0 (see Table II), we conclude from Eq. (1) that conduction by electrons with scattering by impurities is the principal mechanism of heat transport in this moderately pure sample.

The temperature variation of the thermal conduc-

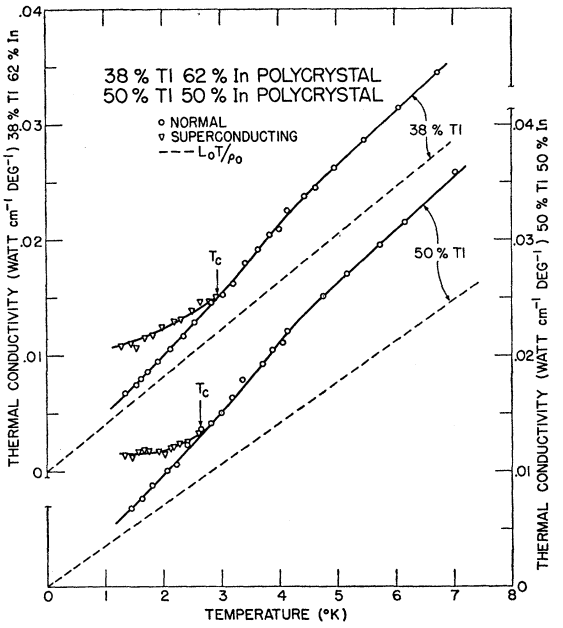

FIG. 5. Thermal conductivity of indium +38 and 50 percent thallium *versus* temperature (different ordinates for the two samples).

tivity of the six alloys is shown in detail in Figs. 3–5 inclusive. In Fig. 6 the smooth curves for these specimens are compared with each other and with curves obtained by Hulm[21] for a single crystal of indium containing 10 percent thallium. Values of K_n taken from the smooth curves for all our specimens are listed in Table III. As is expected theoretically for electronic

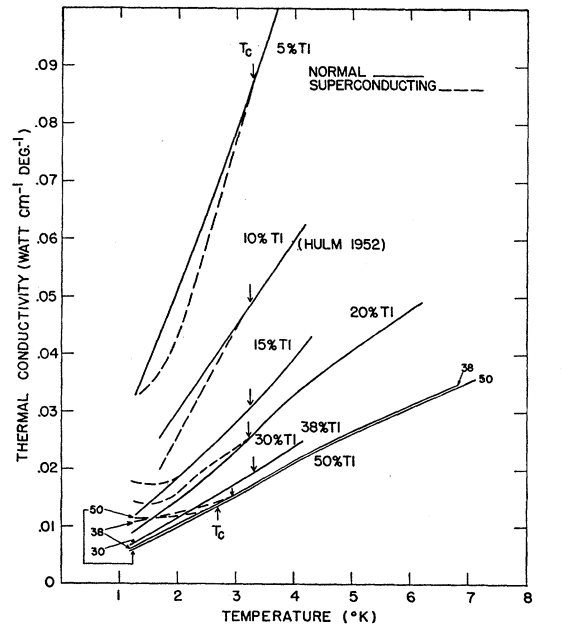

FIG. 6. Comparison of thermal conductivity *versus* temperature curves for seven alloy specimens (including Hulm's curve for indium +10 percent thallium).

TABLE III. Smoothed values of the normal state thermal conductivity at selected temperatures in the liquid helium range.

T °K	In watt-cm^{-1} deg^{-1}	5% Tl	15% Tl	20% Tl	30% Tl	38% Tl	50% Tl
				milliwatt-cm^{-1} deg^{-1}			
1.30	0.86	33.3	12.0	9.5	7.3$_5$	6.4	6.1
1.40	0.93	35.8	12.9	10.2	7.9	6.9	6.6
1.60	1.06	41.0	14.8	11.7	9.0$_5$	7.9	7.6
1.80	1.20	46.1	16.6	13.1	10.2	8.9	8.6
2.00	1.33	51.5	18.4	14.7	11.4	9.9	9.6$_5$
2.20	1.46	57	20.3	16.3	12.6	11.0	10.7
2.40	1.60	62.$_5$	22.2	17.9	13.8	12.0	11.8
2.60	1.73	68	24.1	19.6	15.0	13.1	12.8
2.80	1.86	73.$_5$	26.0	21.4	16.2	14.1	13.9
3.00	2.00	79	28.1	23.3	17.5	15.2	15.1
3.20	2.13	84.$_5$	30.2	25.2	18.7	16.4	16.2
3.40	2.26	90	32.3	27.2	20.0	17.5	17.4
3.60	2.40	96	34.4	29.3	21.3	18.7	18.6
3.80	2.53	102	36.8	31.2	22.6	20.0	19.8
4.00	2.66	108	39.2	33.0	24.0	21.2	21.1
4.20	2.79	···	41.7	34.6	28.0	22.4	22.3

heat conduction and is fairly obvious from these figures and from Tables II and III, both the normal electrical and normal thermal conductivities of the alloys at a given temperature are lower than the corresponding quantities for pure indium at the same temperature and show a systematic decrease with increasing thallium content. However, the alloy data exhibit a feature which is not apparent in the pure indium curve, namely, that up to 4°K the normal thermal conductivity curve tends to turn upwards, away from the dotted line L_0T/ρ_0, as the temperature is increased. This behavior is undoubtedly due to the importance of lattice conduction in the alloy specimens owing to the rather low values of the electronic thermal conductivity. As already pointed out the first term in Eq. (3) is likely to be dominant at a few degrees Kelvin. Thus the total normal state thermal conductivity of our specimens may be expressed at least over part of the temperature range, as a sum of electronic and lattice terms of the form

$$K_n = T/\beta + T^2/A. \tag{7}$$

To check this prediction it is convenient to plot K_n/T *versus* T, and typical results of such a plot for three of our alloys are shown in Fig. 7. In each case, the experimental points below 4°K lie fairly close to a straight line, although the scatter is rather large for the 5 percent Tl specimen where the lattice conductivity is only a small part of the total conductivity. The intercept on the K_n/T axis, $1/\beta$, is compared in Fig. 7 and in Table II with the Wiedemann-Franz value of the coefficient of electronic thermal conductivity, L_0/ρ_0, calculated from the residual electrical resistivity. It will be seen that for the 5, 15, and 20 percent thallium specimens, all single crystals, $1/\beta$ and L_0/ρ_0 agree within 1 percent, which, together with the results already given for pure indium, provides a rather striking verification of the Wiedemann-Franz formula. The agreement is not so good for the 30, 38, and 50 percent thallium specimens, however, the difference amounting to nearly 30 percent in the sample of highest thallium content, for reasons which are at present obscure.

Experimental values of the coefficient $1/A$ were obtained for the six alloy specimens from straight line plots such as those shown in Fig. 7, and are listed in the sixth column of Table II. From the work of Makinson[3] the theoretical value of this coefficient may be expressed in the form

$$1/A = (4.93K_\infty)/(\Theta^2 N_a^2), \tag{8}$$

(see α, Sec. I). The observed values of $1/A$ and Eq. (8) have been used to compute the effective number of conduction electrons per atom for each alloy shown in the last column of Table II and in Fig. 8. In each case K_∞ was derived from the slope of the high temperature electrical resistivity[22] using the Wiedemann-Franz formula and substituting the pure-indium Θ value, 100°K. N_a appears to increase somewhat with increasing thallium content, but lies in the neighborhood of unity for all the specimens. On the basis of an extrapolation to zero thallium content, the effective number of conduction electrons per atom for indium[31] itself is about 0.75, which is of the same order of magnitude as N_a estimates obtained from specific heat measurements.[32]

Before leaving the normal state data, it should be noted that Makinson's theory indicates that the temperature range in which phonons are scattered chiefly

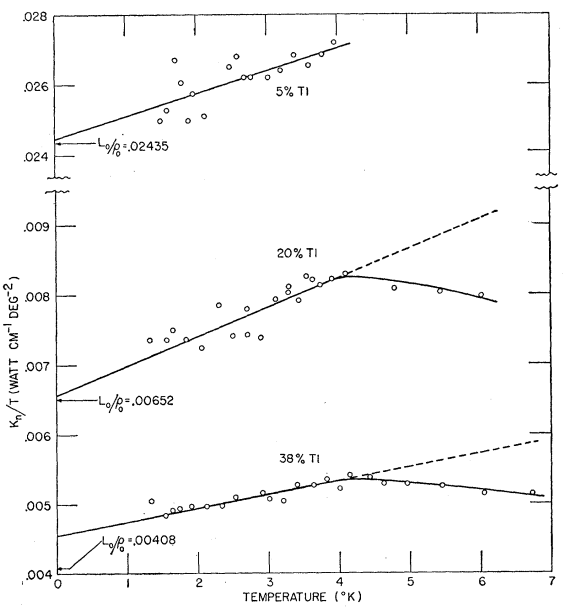

FIG. 7. Normal state thermal conductivity divided by the absolute temperature for three alloy specimens *versus* temperature.

[31] The electronic thermal conductivity of the pure metal is too high to permit a direct determination of $1/A$.

[32] J. R. Clement and E. H. Quinnell, Phys. Rev. **79**, 1028 (1950).

by electrons must be succeeded, at high enough temperatures, by a range in which impurity scattering is dominant. In order to check this possibility, the normal state curves for the 20, 38, and 50 percent thallium samples were determined somewhat above 4.2°K, as shown in Figs. 4, 5, and 6. It was found that the rapid rise of lattice thermal conductivity for these samples below about 4°K was followed at higher temperatures by a region of nearly constant or even slightly decreasing lattice thermal conductivity. This behavior is illustrated more clearly by the plots of K_n/T *versus* T for the 20 and 38 percent thallium specimens in Fig. 7, where above 4°K, the experimental points lie below the dotted line extrapolated from low temperatures. It was also observed that in the liquid hydrogen region, which could not be conveniently included in Figs. 2–7, the thermal conductivity of the 15 and 38 percent thallium samples was approximately equal to T/β, the value expected for electronic heat conduction alone. There can be little doubt, therefore, that in qualitative agreement with Makinson's theory the lattice thermal conductivity of the present alloys passes through a maximum between liquid helium and liquid hydrogen temperatures. However our results above 4°K are not extensive enough to warrant a detailed comparison with the theory.

B. The Superconducting State

Experimental values of K_s, the thermal conductivity of each of the seven specimens in the "virgin" superconducting state, are plotted against temperature in Figs. 2–5, while the smoothed superconducting curves for the alloy specimens and a 10 percent thallium specimen investigated by Hulm[21] are shown together for comparison in Fig. 6. Values of K_s taken from the smooth superconducting state curves for our seven specimens are listed in Table IV. With increasing thallium content two striking changes are observed, first a systematic decrease in the magnitude of K_s similar to that previously noted for K_n, and second a gradual change in the *relative* positions of the superconducting state and normal state curves. Whereas the superconducting state curve lies below the normal state curve for the 0, 5, and 10 percent thallium specimens, it lies above the normal state curve for 15 and higher thallium percentages, except for the 30 percent specimen where the two curves are practically coincident. The observation that K_s exceeds K_n at high concentrations is in agreement with the results of de Haas and Bremmer[19] for the lead-thallium and lead-indium systems and those of Mendelssohn and Olsen[20] for lead-bismuth alloys, and seems to be a general feature of the behavior of binary alloys.

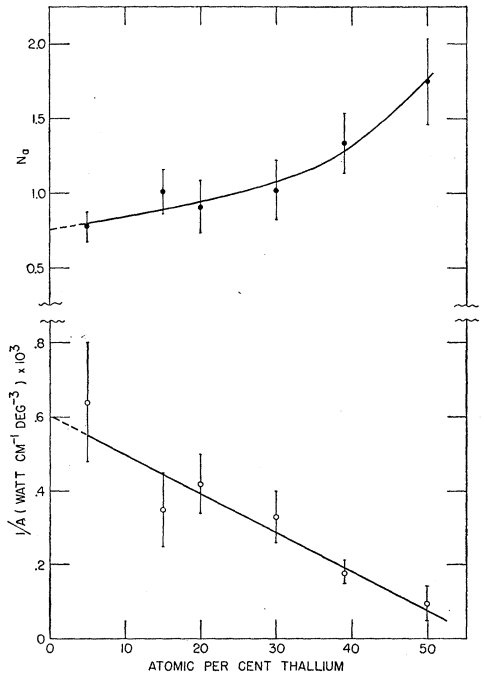

FIG. 8. Effective number of conduction electrons per atom, N_a, and the lattice conductivity coefficient $1/A$ *versus* thallium content.

TABLE IV. Smoothed values of the superconducting state thermal conductivity at selected temperatures below T_c

T °K	In watt-cm^{-1} deg^{-1}	5% Tl	15% Tl	20% Tl	30% Tl	38% Tl	50% Tl
				milliwatt-cm^{-1} deg^{-1}			
1.30	0.225	32.7	17.6	14.2	7.3_5	10.9	11.5
1.40	0.255	33.5	17.4	14.0	7.9	11.1	11.5
1.60	0.353	35.5	17.3	13.9	9.0_5	11.4	11.5
1.80	0.480	38.6	17.6	14.5	10.2	11.9	11.6
2.00	0.65	43	18.5	15.8	11.4	12.3	11.8
2.20	0.84_5	49	20.3	17.8	12.6	12.8	12.1
2.40	1.05	56	22.2	19.6	13.8	13.4	12.6
2.60	1.27	63	24.1	21.0	15.0	14.0	13.2
2.80	1.48	70	26.0	22.4	16.2	14.6	···
3.00	1.74	77	28.1	23.9	17.5	···	···
3.20	2.00	84	30.2	25.3	18.7	···	···

In seeking a detailed interpretation of the present results, we consider first the behavior of pure indium. Here, as already noted, heat transport by electrons with scattering by impurities dominates when the specimen is in the normal state. The superconducting state curve may thus be expected to have a functional form resembling that of the second term on the right-hand side of Eq. (2), or in other words the ratio K_s/K_n should be representable by a characteristic function of the type of $f(t)$ for impurity scattering of electrons. In Fig. 9, experimental values of the ratio K_{es}/K_{en} obtained from the pure indium smooth curves[33] in Fig. 2 are compared with Hulm's earlier data for a slightly purer indium sample. It is striking that the

[33] Because of the low values of K_s at the lowest temperatures used, lattice conductivity (estimated from the alloy results) probably amounted to as much as 3 percent of the total thermal conductivity of the superconducting metal. The K_{es} data used in Fig. 9 were obtained by subtracting estimated K_{gs} values from the observed K_s. Only the points below about $0.6t$ were affected by this correction.

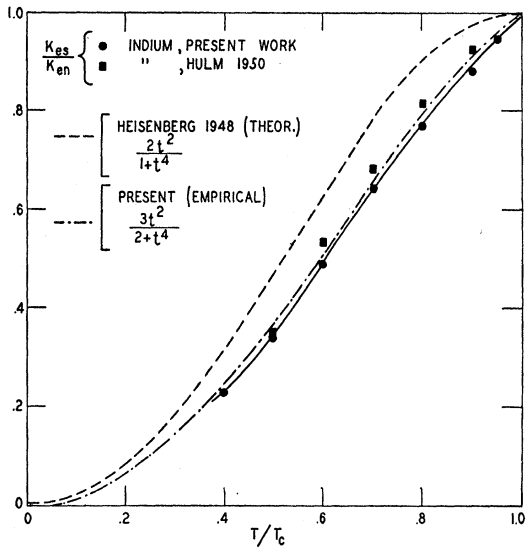

FIG. 9. K_{es}/K_{en} for indium *versus* reduced temperature compared with Heisenberg's function $2t^2/(1+t^4)$ and the empirical function $3t^2/(1+t^4)$.

observed ratio values for the two indium samples are almost coincident. However, the experimental points lie markedly to the right of the function $2t^2/(1+t^4)$ obtained theoretically by Heisenberg.[13,34] By trial and error it was found that the indium data could be quite well represented by the empirical function $3t^2/(2+t^4)$, shown by the chain curve in Fig. 9. The data seem to point to a positive temperature gradient of K_{es}/K_{en} at the transition temperature, in contrast to the zero value predicted by Heisenberg.

In discussing our alloy data it will be assumed that both the electronic and the lattice heat conduction processes effective in the normal state are present in modified form in the superconducting state. After combining Eqs. (2), (4), and (7) and omitting the irrelevant terms, we obtain a total thermal conductivity for the superconducting state of the form

$$K_s=[Tf(t)]/\beta+[T^2h(t)]/A, \qquad (9)$$

where the first term on the right is due to transport by electrons with scattering by impurities and the second due to transport by phonons with scattering by electrons. Assuming that $f(t)$ has the same form as for pure indium and substituting the observed values of K_s and the parameters β and A (see Table II) in Eq. (9), we may obtain the function $h(t)$ for each specimen. Smooth curves of $h(t)$ *versus* t obtained in this fashion for the six alloy samples are compared with various negative powers of t in Figs. 10 and 11. In all cases $h(t)$ exceeds unity in agreement with the hypothesis that electrons in the "superconducting phase" do not scatter phonons.

The results for all six specimens are qualitatively similar in that the curves have the same general shape and do not follow a simple power law owing to a very steep rise of $h(t)$ just below the transition temperature. Quantitatively, however, it will be seen that whereas the lower concentration, single crystal curves lie between t^{-3} and t^{-4} at lower temperatures, the high concentration, polycrystalline curves rise more steeply with decreasing temperature. These effects seem to be outside the limits of experimental error and would appear to invalidate the hypothesis that $h(t)$ is the same characteristic function of temperature for all alloy specimens. It is not clear whether the marked difference between Figs. 10 and 11 is due to the change of composition or to the difference in crystal grain size, although it seems unlikely that the large grains of the polycrystals (~2-mm diameter) would appreciably affect the lattice thermal conductivity. Our results agree fairly well with rough estimates of $h(t)$ obtained by Hulm[21] for indium containing 10 percent thallium (t^{-5}) and by Olsen[35] for lead containing 10 percent bismuth (t^{-6}).

C. Isothermal Magnetic Field Transitions

To supplement the measurements for the pure normal and pure superconducting states already

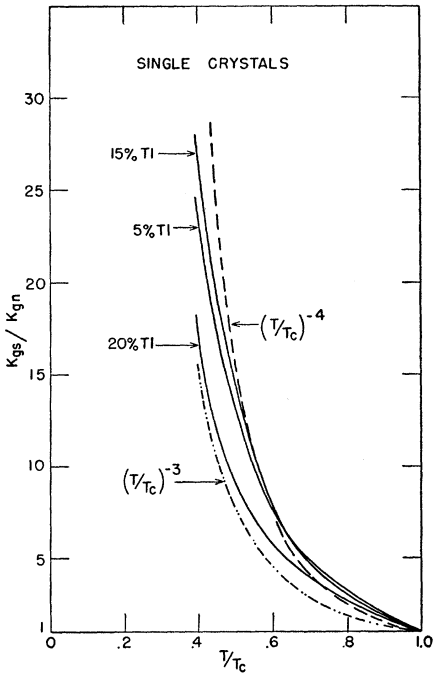

FIG. 10. K_{gs}/K_{gn} for indium-thallium single crystals *versus* reduced temperature compared with the functions t^{-3} and t^{-4}.

[34] The function $2t^2/(1+t^4)$ is only an approximation to Heisenberg's exact ratio function, $f(t)$, based upon Koppe's detailed calculation of the population of normal electrons in the superconductor [H. Koppe, Ann. Physik (6) **1**, 405 (1947)]. $f(t)$ coincides almost exactly with $2t^2/(1+t^4)$ down to $0.5T_c$, but decreases in an exponential manner as the absolute zero is approached.

[35] J. L. Olsen, Proc. Phys. Soc. (London) **A65**, 518 (1952).

described, the thermal conductivity of each specimen was studied as a function of magnetic field at several different temperatures below the superconducting transition point. Since the magnetic history of a specimen is particularly important in the case of alloys, which are subject to large trapped flux effects, each magnetic transition was begun with a virgin superconducting specimen, that is, a specimen cooled from above the transition temperature in zero magnetic field. The thermal conductivity was measured in both increasing and decreasing magnetic field so that the influence of the trapped flux could itself be investigated.

Typical results in the form of curves of thermal resistivity *versus* longitudinal magnetic field for pure indium and for two representative alloy samples are shown in Figs. 12–14, inclusive. When the critical field is known accurately from induction measurements,[22] the abscissa is the reduced field H/H_c. In order to facilitate comparison with the present results, Stout and Guttman's induction and resistivity data are also plotted in reduced form in Fig. 13. Their data were obtained after the samples had been exposed to a field sufficient to destroy superconductivity.

The full curve (a) showing the first increase in field for a virgin superconducting sample is in all cases different from the dotted curve (b) showing the return to the nonvirgin zero-field state. For pure indium, as expected, the thermal resistivity decreased sharply from the pure superconducting state value W_s to the pure normal state value W_n as the critical field was surpassed. A correspondingly sharp rise occurred with

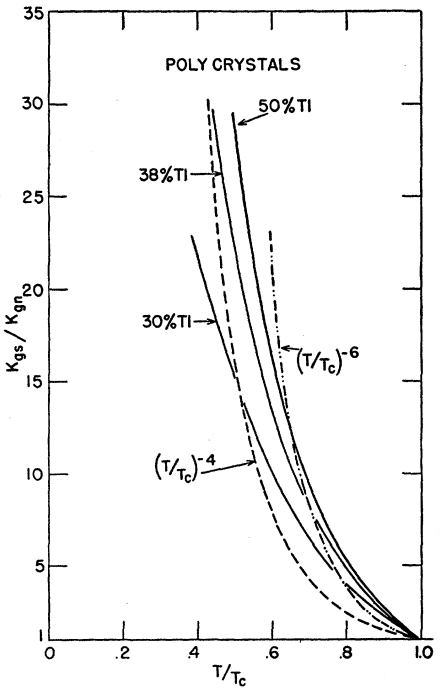

FIG. 11. K_{gs}/K_{gn} for indium-thallium polycrystals *versus* reduced temperature compared with the functions t^{-4} and t^{-6}.

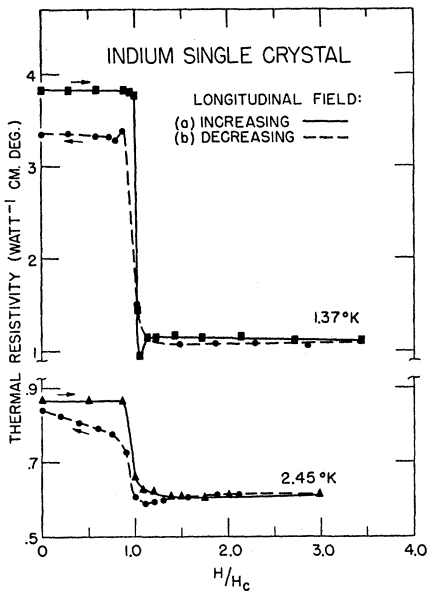

FIG. 12. Thermal resistivity of indium *versus* reduced longitudinal magnetic field at two temperatures below T_c.

decreasing field, but the thermal resistivity reached a slightly different value, W_s', presumably due to the trapping of a certain amount of normal material. If x_n is the volume fraction of this normal material, and if we assume, for reasons given later, that the superconducting and normal regions provide parallel heat paths, then the final thermal conductivity should have the value

$$1/W_s' = (1-x_n)K_s + x_n K_n. \tag{10}$$

In Table V, typical observed values of W_s' are compared with values estimated from Eq. (10) by using K_s and K_n data from Tables III and IV and x_n values obtained from Stout and Guttman's induction measurements.[22] The measured and calculated values of W_s' are in quite good agreement both for pure indium, and for indium containing 5 and 50 percent of thallium. There is, however, a discrepancy for intermediate concentrations of thallium.

The alloy transition curves are typified by the upper, 1.45°K, curves for the 20 percent thallium specimen in Fig. 13. On first increasing the magnetic field, the thermal resistivity rose quite sharply at the critical field value, as anticipated, but then unexpectedly continued to rise beyond W_n, passed through a maximum, and dropped down to the normal state value only at a field well above critical. Maxima of this type were observed for all specimens containing 15 percent or more thallium and became more pronounced as the temperature was decreased.

From Fig. 13, it may be seen that each thermal resistivity maximum occurs at field strengths where the electrical resistivity remains zero but the magnetic induction has started to rise. It may be inferred from

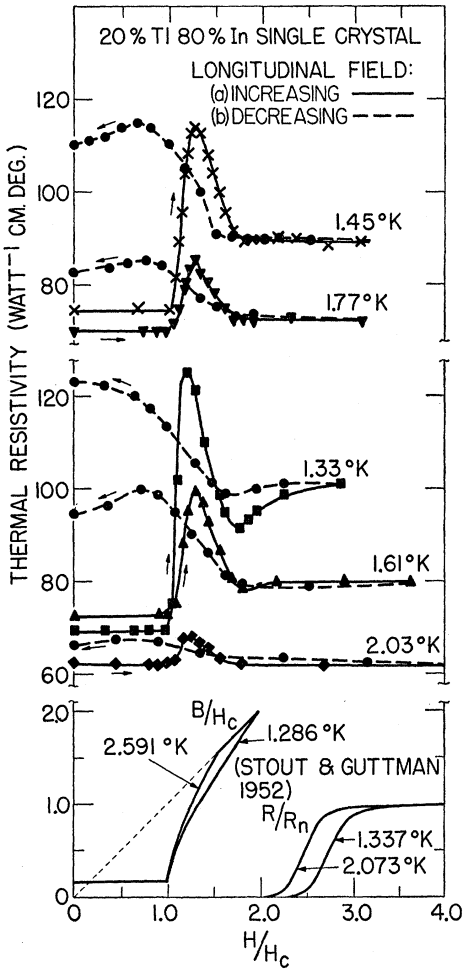

FIG. 13. Thermal resistivity of indium +20 percent thallium *versus* reduced longitudinal magnetic field at various temperatures compared with reduced magnetic induction and reduced electrical resistance data of Stout and Guttman.[22]

the last two properties that part of the specimen remains superconducting at fields well above critical. Indeed, since the electrical resistivity is zero until the last vestige of field penetration has taken place, the superconducting regions are probably thin filaments or plates parallel to the longitudinal axis of the specimen. The existence of a "mixed state" of this type has long been known for superconducting alloys, but is still not satisfactorily explained.[36] According to the present work, the thermal resistivity of a specimen in this state may greatly exceed that observed for either the pure normal or the pure superconducting states. Such behavior cannot be explained using a simple mixture formula of the type Eq. (10), whatever arrangement of superconducting and normal regions is assumed. It seems likely that the boundaries between these regions produce an increased thermal resistivity by limiting the mean free paths of the heat carriers. In order to decide which carriers are affected in this manner the electron and phonon mean free paths for a typical alloy specimen in the pure normal and pure superconducting states are given in Table VI.

From Table VI, we note that the electronic mean free path for the 20 percent thallium specimen at 1.4°K, where the additional thermal resistivity was most pronounced, is not only much smaller than the phonon mean free path but is also less than the superconducting penetration depth ($\sim 10^{-5}$ cm). Since the superconducting filament or plate size is unlikely to be less than this penetration depth, the mean free path of the electrons is probably too small to be disturbed by the boundaries. However, the phonon mean free path is not only larger than the penetration depth, but is also much longer in superconducting material than in normal material. Thus, those phonons which start their paths in a superconducting region within a distance 10^{-3} cm from a normal boundary and cross the boundary will be scattered almost immediately in the normal matter owing to the smaller mean free path (7×10^{-5} cm). This gives rise to a superconducting layer of thickness about 10^{-3} cm next to the boundary where the effective lattice thermal conductivity is less than K_{gs}, the bulk lattice thermal conductivity of superconducting material. The effective lattice thermal conductivity will of course decrease continuously as the boundary is approached. By the same argument, we may expect the existence next to the boundary of a normal layer of thickness about 7×10^{-5} cm with an effective lattice conductivity greater than K_{gn}, the bulk lattice thermal conductivity of normal material. Since the thickness of the anomalous superconducting layer is much greater than that of the anomalous normal layer, a net reduction in the average thermal conductivity must result.

Although a rigorous calculation of the decrease in thermal conductivity due to boundaries is beyond the scope of the present work, it is clear that the observed decrease may only be explained using this model provided that the superconducting regions have an average thickness comparable with the mean free

TABLE V. The thermal resistivity in the virgin superconducting state, W_s, and after completion of a magnetic cycle, W_s', at two temperatures for most of our indium-thallium specimens.

Nominal composition atomic % Tl	T°K	W_s watt^{-1} cm-deg	W_s'(obs) watt^{-1} cm-deg	W_s'(calc) watt^{-1} cm-deg
0	1.37	3.84	3.35	3.1
	2.45	0.87	0.84	0.84
5	1.37	30.2	29.8	29.8
	1.73	28.1	27.3	27.1
15	1.37	57.4	100	60.8
	1.84	56.4	68.5	56.8
20	1.36	71.2	123	75.2
	1.77	68.8	83.0	70.2
38	1.34	91.3	132	108
	1.76	85.4	102	95.3
50	1.42	87.0	132	139
	1.76	86.1	104	110

[36] See reference 1, p. 37, for details.

path of phonons in the bulk superconductor, L_{gs}, which lies between 10^{-4} and 10^{-3} cm for the various alloy samples. Such thicknesses do not seem to be unreasonable, and the fact that the decrease in the thermal conductivity is more pronounced at lower temperatures is also consistent with the increase in L_{gs} due to the decrease in population of "normal phase" electrons.

Hitherto we have not discussed the return curves (b) for the high-concentration alloys (Figs. 13 and 14). These curves and Table V indicate that when the field was reduced to zero, the final thermal resistivity for most of the alloys was considerably greater than that estimated from Eq. (10) for a mixture of superconducting and trapped normal regions in parallel. However, it is interesting that this discrepancy in thermal resistivity is greatest for the 15 and 20 percent Tl specimens, and decreases for higher thallium contents, even though the percentage of trapped flux increases (see reference 22). If, as seems probable, the anomalously high W_s' values are due to boundary effects of the type suggested above for the mixed state, it appears that the increase in percentage of trapped flux with increasing thallium content is accompanied by an appreciable increase in thickness of the superconducting and the normal regions.

So far, we have considered only the effect of magnetic fields applied parallel to the cylindrical axis of the specimens. However, for most of our samples the thermal conductivity was also measured as a function of transverse magnetic fields at several temperatures below the superconducting transition point. In all cases, there was great similarity between the transverse and longitudinal transition curves at the same temperatures, as shown, for example, by representative curves for the 20 percent thallium specimen in Fig. 15. Although a sharp rise in thermal resistivity is observed at $H=\frac{1}{2}H_c$ in the transverse case, instead of at $H=H_c$ as in the longitudinal case, it will be seen that the heights of the thermal resistivity maxima and the final thermal resistivity values W_s' are practically the same in both cases.

Little is known regarding the structure of the intermediate state in high-concentration alloys, and it is not clear whether the destruction of superconductivity occurs by splitting of the specimen into laminae perpendicular to the cylindrical axis, as in the case of pure metals,[37] or by splitting into plates parallel to the cylindrical axis as is observed for the mixed state, or indeed whether both processes are involved. The similarity of the thermal resistivity maxima in transverse fields to those in longitudinal fields, as reported above, seems to suggest that quite small laminae (10^{-3} to 10^{-4} cm thick) occur parallel to the cylinder axis in transverse fields greater than critical. There may also be somewhat thicker laminae ($\sim 10^{-2}$ cm) perpendicular to the cylinder axis at fields between $\frac{1}{2}H_c$ and H_c, as is observed for pure metals,[38] since such laminae would be unlikely to influence the thermal resistivity of our alloys.

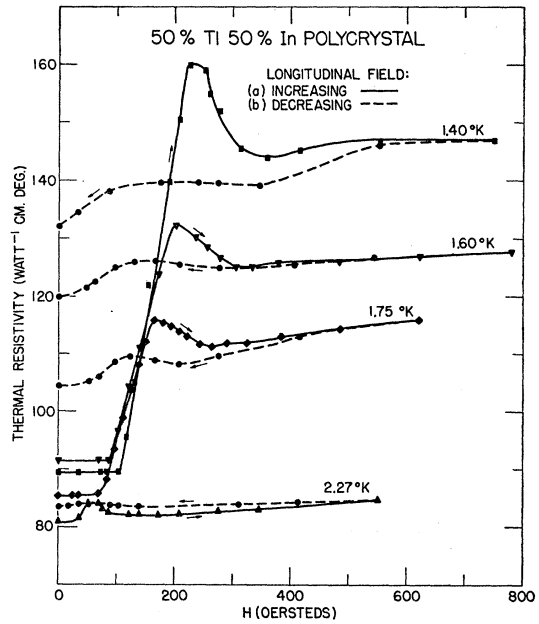

FIG. 14. Thermal resistivity of indium +50 percent thallium *versus* longitudinal magnetic field.

TABLE VI. Electron and phonon mean free paths in the In+20% Tl specimen at 1.4°K, estimated from thermal conductivity data.[a]

	Superconducting state	Normal state
Electrons	3×10^{-6} cm	2×10^{-6} cm
Phonons	1×10^{-3} cm	7×10^{-5} cm

[a] The kinetic theory formula $K=\frac{1}{3}CL\nu$, where C, L, and ν are the heat capacity, mean free path, and velocity of the heat carriers, respectively, was used.

[37] Reference 1, Chap. V.

IV. CONCLUSION

A. Normal State Behavior

For the seven specimens examined in the present work, the normal state thermal conductivity between 1.3°K and 4.2°K apparently consisted of an electronic term K_{en} proportional to the absolute temperature, due to scattering of electrons by impurities, and a lattice term K_{gn} proportional to T^2, due to scattering of lattice waves by electrons. Comparison of K_{en} with electrical resistivity data provided quantitative verification of the Wiedemann-Franz law for the single-crystal specimens, although not for the polycrystalline, high thallium content alloys. Since the electronic mean free path is much smaller than the grain size in the latter specimens and the theoretical derivation of the Wiedemann-Franz law does not appear to restrict its application to dilute systems, there is no apparent

[38] A. G. Meshkovsky and A. I. Shalnikov, J. Phys. (U.S.S.R.) **11**, 1 (1947).

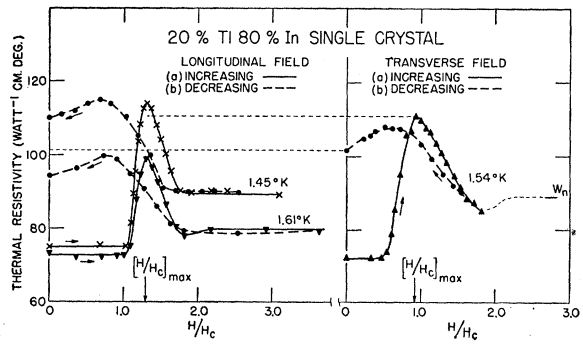

FIG. 15. Comparison of thermal resistivity in longitudinal and transverse magnetic fields for indium +20 percent thallium. $[H/H_c]_{max}$ indicates the field at which the thermal resistivity is a maximum.

reason for the departure from this law exhibited by the high-concentration alloys.

Our lattice thermal conductivity results for indium-thallium alloys yielded values for N_a, the number of conduction electrons per atom, close to unity. We have obtained similar values of N_a from analysis of lattice thermal conductivity data on copper-nickel alloys.[16,18] These values are reasonable in view of known electronic properties for the two alloy systems,[32,39–42] suggesting that Makinson's theory[3] of heat conduction by phonons with scattering by electrons is quantitatively correct. This is in contrast with the case of heat conduction by electrons with scattering by phonons where the agreement is only qualitative (see Sec. I).

Scattering of phonons by impurities became evident just above 4°K in the indium-thallium specimens whereas in copper-nickel alloys[16,18] of about the same concentrations, the lattice thermal conductivity is proportional to T^2 up to 20°K, indicating that impurity scattering is only important at higher temperatures. Thus, it seems that a given amount of thallium in indium is more effective in scattering phonons than the same amount of nickel in copper. Impurity scattering arises from the disturbance of the solvent lattice by the solute atoms, which is due to the mass difference between solute and solvent atoms and partly to the difference between the solvent-solute and solvent-solvent atom interaction energies. The relative importance of these two contributions is not known definitely for the alloy systems under consideration, but it is significant that the mass difference is much greater in the indium-thallium system than in the copper-nickel system and thus is probably responsible for the enhanced scattering of phonons by impurities in the former case.

[39] W. H. Keesom and B. Kurrelmeyer, Physica **7**, 1003 (1940).
[40] A. I. Schindler and E. M. Pugh, Phys. Rev. **89**, 295 (1953).
[41] C. Sadron, Ann. phys. **17**, 371 (1932).
[42] H. Krutter, Phys. Rev. **48**, 664 (1935).

B. Superconducting State Behavior

A significant difference was observed between the electronic thermal conductivity ratio function $f(t)$ for pure indium and that for pure tin. This may be due to the fact that the change in the electronic energy level density accompanying the onset of superconductivity is slightly different for different metals. Such a hypothesis may be justified as follows. According to Heisenberg, the thermal conductivity ratio is given by

$$K_s/K_n = C_s L_s / C_n L_n \qquad (11)$$

(see Sec. I) where C and L are the heat capacity and mean free path of electrons, respectively. Since for both tin and indium C_s/C_n is approximately equal to t^2, it is probably the mean free path ratio L_s/L_n which changes from one metal to the other. Heisenberg suggested that when a metal is superconducting the probability of "normal phase" electrons with energies less than the Fermi energy being scattered is the same as that when the metal is normal, but the probability of "normal phase" electrons in excited states being scattered is reduced by a factor t^4. This results in a mean value $2/(1+t^4)$ for the ratio of the mean free paths. However, if it is assumed that, due to their smaller density, the excited states are only half as important for scattering as the states below the Fermi energy, the mean free path ratio becomes $3/(2+t^4)$. This is combination with Eq. (11) gives the empirical ratio function actually observed for indium. It is possible that the differences in the extent of deviation of critical magnetic fields for different metals[43] from a parabolic law are also due to small modifications of the electron energy level densities such as suggested above.

The superconducting state behavior of the six alloy specimens is consistent with the presence of an electronic thermal conductivity term similar in form to that for pure indium, but greatly reduced in magnitude due to the increased impurity scattering, and a lattice thermal conductivity term much greater than that in the normal alloy due to the reduced scattering of phonons by the smaller population of normal electrons. Since according to the two-fluid model of superconductivity the effective number of normal electrons when the metal is superconducting is usually assumed to be t^4 times the corresponding number for the normal state, it might be expected that the ratio of lattice conductivities, K_{gs}/K_{gn}, would not only be a characteristic function of the reduced temperature $h(t)$ as suggested by Hulm,[5] but would also be simply related to the population factor t^4. However, since the experimental values of K_{gs}/K_{gn} (Figs. 10 and 11) do not lie on a single characteristic curve regardless of concentration, we must conclude either that the above picture is too naive or that our analysis of the results is inadequate, perhaps owing to the presence of other

[43] E. Maxwell and O. S. Lutes, National Bureau of Standards Report No. 3146, 1954 (unpublished).

terms in the lattice conductivity besides that due to scattering of phonons by electrons. The fact that the experimental ratio curves do seem to cluster around the simple power law t^{-4} suggests that the estimated population factor of normal electrons is a dominating influence upon $h(t)$.

It should be pointed out that our analysis of the superconducting state data has ignored the possibility of an appreciable component of thermal conductivity of the type suggested by Ginsburg[44] and Mendelssohn and Olsen[20] which is due to circulation of electrons in a manner analogous to the atomic circulation process responsible for the high thermal conductivity of liquid helium II. However, this term has been estimated[45,46] to be less than 10^{-7} watt-cm^{-1} deg^{-1}, which is four orders of magnitude lower than the lowest thermal conductivity encountered in our experiments.

C. Behavior in Magnetic Fields

It is not surprising that the large percentage of normal material which may be trapped in a superconducting alloy after a magnetic field cycle influences the thermal conductivity of the sample. However, when the observed thermal conductivity is lower than that of both the pure superconducting or pure normal state, as in many of our samples, it seems reasonable to conclude that an additional thermal resistivity is caused by the boundaries between superconducting and normal regions. This additional thermal resistivity also manifests itself when superconducting regions persist above the critical field. In this case, a maximum in thermal resistivity may be observed with both increasing and decreasing magnetic field.

The additional thermal resistivity may be interpreted as a lattice effect, if it is accepted that the phonon mean free path in the pure superconducting state is much longer than that in the pure normal state, and it is assumed that the thicknesses of both superconducting and normal regions lie somewhere between these two mean free path values. In the indium-thallium system, the regions are required to be between 10^{-4} and 10^{-3} cm thick in order to produce the observed extra thermal resistivity.

We first observed the additional thermal resistivity for cylindrical specimens in a longitudinal magnetic field, although we later found similar effects for the same specimens in transverse fields. It seems fairly definite that in the former case the boundaries between superconducting and normal regions are predominantly parallel to the cylindrical axis of the specimen and thus are parallel to the direction of heat flow. Our experiments seem to be the first ones in which parallel boundaries of this type give rise to an extra thermal resistivity. However, previous investigators have reported an increased thermal resistivity for cylindrical specimens in transverse fields, both for pure metals[47–50] and also in some cases for dilute alloys.[20,35,51] For pure metals these increases occur in the intermediate state, $\frac{1}{2}<H/H_c<1$, and can be explained qualitatively[50] by assuming that the mean free path of electrons is modified in the neighborhood of the boundaries between superconducting and normal laminae, which lie perpendicular to the cylindrical axis of the specimen. In any case, the thickness of the laminae[38] ($\sim 10^{-2}$ cm) seems to be too large compared to the phonon mean free path, at least above 1°K, to allow the effect to be interpreted as a lattice mechanism. In the previous alloy experiments, however, the situation is not so clear-cut because of the smearing out of the transitions beyond $H=H_c$ in some cases and the fact that the additional thermal resistivity is larger than would be expected for an electronic mechanism of the above type. One is forced to conclude that an additional lattice thermal resistivity may also be operative in these experiments, although the relation of the boundary directions to the heat flow directions remains obscure.

V. ACKNOWLEDGMENTS

The author is indebted to all the members of the Low Temperature Laboratory of the Institute for the Study of Metals for making this research possible. He wishes, in particular, to thank Professor J. K. Hulm for suggesting this problem and for his constant advice, aid, and encouragement, and Professor J. W. Stout and Professor L. Guttman for supplying the specimens.

[44] V. L. Ginsburg, J. Phys. (U.S.S.R.) **8**, 148 (1944).
[45] P. G. Klemens, Proc. Phys. Soc. (London) **A66**, 576 (1953).
[46] P. M. Marcus, Proc. Schnectady Cryogenics Conference, 1952 (unpublished), p. 100.
[47] R. T. Webber and D. A. Spohr, Phys. Rev. **84**, 384 (1951).
[48] D. P. Detwiler and H. A. Fairbank, Phys. Rev. **88**, 1049 (1952).
[49] J. L. Olsen and C. A. Renton, Phil. Mag. **43**, 946 (1952).
[50] J. K. Hulm, Phys. Rev. **90**, 1116 (1953).
[51] K. Mendelssohn and J. L. Olsen, Phys. Rev. **80**, 859 (1950).