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THERMAL CONDUCTIVITY OF SUPERCONDUCTORS

Irving N. Greenberg

Army Electronics Command
Fort Monmouth, New Jersey

December 1969

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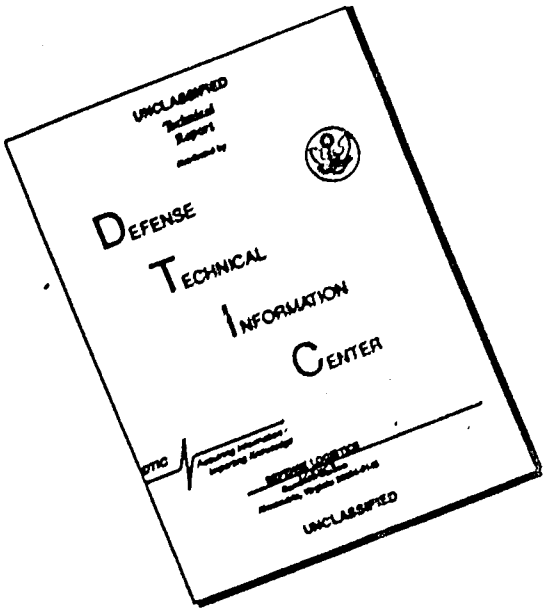

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Research and Development Technical Report
ECOM-3200

THERMAL CONDUCTIVITY OF SUPERCONDUCTORS

by

Irving N. Greenberg

December 1969

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THERMAL CONDUCTIVITY OF SUPERCONDUCTORS

Irving N. Greenberg

Institute for Exploratory Research

DECEMBER 1969

DA Task No. 1T0 61102 B11A 01 26

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THERMAL CONDUCTIVITY OF SUPERCONDUCTORS

INTRODUCTION

The discovery of electrical superconductivity in 1911 triggered experiments designed to determine whether the phenomenon occurs in heat transport. The first results[1] showed that instead of thermal superconductivity, the heat conduction in the superconducting state was lower than in the normal state. Since, in metals, in the normal state, the conductivity is composed of the electronic component plus the lattice component, it may be written as

$$\varkappa_n = \varkappa_{e\ell,n} + \varkappa_{ph,n} \quad . \tag{1}$$

In the superconductive state, we may write

$$\varkappa_s = \varkappa_{e\ell,s} + \varkappa_{ph,s} \quad . \tag{2}$$

Here the subscript n stands for the normal state, s for the superconducting state, $e\ell$ for the electronic contribution to the thermal conductivity, and ph the lattice contribution. Since the "superelectrons" which carry the resistanceless current in a superconductor cannot be expected to carry the thermal current, $\varkappa_{e\ell,s}$ would be expected to be smaller than $\varkappa_{e\ell,n}$.[2] Likewise, since the superelectrons move without friction against the lattice, they presumably do not contribute to the scattering of the lattice waves, hence $\varkappa_{ph,s}$ might be expected to be larger than $\varkappa_{ph,n}$.[3] Therefore, since the heat is carried only by that fraction of the electrons which are still normal and by the lattice component, $\varkappa_s$ would be expected to be smaller than $\varkappa_n$, because the lattice contribution is small in both states. Qualitatively, this explains the results.

A complete understanding of the thermal conductivity in superconductors can only be achieved as a consequence of a detailed microscopic theory of superconductivity. The thermodynamic and electrodynamic behavior of superconductors has led to a working hypothesis which has been remarkably successful in a rough interpretation of the observed effects, although, in its crude form, it cannot have any physical significance. This is the two-fluid model in which the electron fluid is regarded as a completely interpenetrating mixture of a normal and a superconductive constituent.

The Two-Fluid Model

The two-fluid model does not explain the phenomena of superconductivity but is a convenient scheme for their description. It assumes[4] that a fraction (1-X) of the Fermi surface is modified; the electrons on the surface condense into a lower state. It also assumes that the electrons in those modified regions cannot be thermally excited, though the fraction of the Fermi surface thus affected is a function of temperature and increases with decreasing temperature. The superconductive regions can be oriented so as to yield a supercurrent. It has been shown experimentally that the decrease in total entropy is a result of the growth of the superconductive concentration and that, in fact, the entropy of this constituent is zero at all temperatures

below the critical temperature T_c. Since the superconductive regions contribute zero to the entropy, there being no thermal excitation, the Thomson coefficient for supercurrents is zero, and the entropy is less than it would be in the normal state. Similarly, the electronic thermal conductivity is reduced, since only the normal fraction of the Fermi surface contributes toward it. Such conclusions led to the postulate that there is an energy gap in the electron spectrum of the metal[5] which is roughly coincident with the Fermi energy. The Bardeen, Cooper, Schrieffer (BCS) theory[6] and some experimental data[7] seem to favor such a model. On the other hand, the lattice component of thermal conductivity is enhanced, since the lattice waves can only be scattered by the electrons on the normal fraction of the Fermi surface. Another explanation is that in the superconducting state the lattice thermal conductivity is increased relative to that in the normal state because the energy gap in the electronic spectrum leads to an increase in the relaxation time for phonons. The energy gap confers on the metal an aspect which is not too different from that of a dielectric crystal.[8] Owing to the small size of the gap, this behavior can not be seen except at very low temperatures. This feature of superconductivity (dielectric-like behavior) becomes very convincing in the heat conduction. However, because of the smallness of the lattice term, the electronic contribution (though rapidly falling) will dominate the thermal conductivity just below T_c.

Assume[4,9] that the modification of the superconducting fraction of the Fermi surface has associated with it a latent heat; thus the Helmboltz free energy, usually of the form

$$F = -1/2\ \gamma T^2, \tag{3}$$

is now modified to

$$F = -1/2\ \chi^{\eta}\ \gamma T^2 - (1 - \chi)\beta\ . \tag{4}$$

The first term is the contribution from the normal region, the second term is the contribution from the superconducting region, γ and β are constants characteristic of their respective regions. The latter term is due to the latent heat since there is no continuum of states available for thermal excitation. The condition

$$(\partial F/\partial \chi)_T = 0 \tag{5}$$

gives χ as a function of T. It is not possible to assume simply $\eta = 1$, as it would be in the absence of interaction between the n- and s- regions, since this would not generally satisfy(5). If one takes $\eta = 1/2$, the observed thermodynamic properties are approximately reproduced, i.e.

$$\chi = (\gamma T^2/4\beta)^2 = (T/T_c)^4, \tag{6}$$

where T_c is the transition temperature, for which $\chi = 1$. The specific

heat per unit volume is

$$C = - T\,(d^2F/dT^2) = 3\gamma(T^3/T_c^3). \tag{7}$$

but the specific heat due to the thermal excitation of the electrons in the normal region is

$$C_n = - T(d^2F/dT^2)_x = \gamma(T^3/T_c^3), \tag{8}$$

The difference $C - C_n$ is ascribed to the change of energy as electrons change their phase, i.e. from being in an s-region to being in an n-region.

The thermal conductivity of normal metals can be written

$$\kappa = 1/3\ C\ v\ \ell \tag{9}$$

where

$$C = \gamma T \tag{10}$$

is the electronic specific heat, v is the velocity of electrons of Fermi energy (assumed isotropic) and

$$\ell = v\tau \tag{11}$$

is the effective electron mean-free-path. The two-fluid model has been applied[10] to the thermal conductivity: the electronic thermal conductivity in the superconducting state differs from that in the normal state because C and possibly ℓ are altered. For C we should now use C_n, because we are concerned with the transport of energy by electrons which remain normal when passing along a temperature gradient, rather than with a change of energy due to a change of phase. Thus,

$$\kappa_{e\ell,s}/\kappa_{e\ell,n} = (T/T_c)^2(\ell_s/\ell_n). \tag{12}$$

It should be noted that if we had used the C defined by (7) instead of C_n defined by (8) to calculate $\kappa_{e\ell,s}$, there would have been a discontinuity at the transition temperature in the curve of $\kappa_{e\ell}$ vs T, similar to that observed for the specific heat, because $\ell_s(T_c)$ must equal $\ell_n(T_c)$.

The behavior of ℓ_s requires some assumption; ℓ_s could differ from ℓ_n because, when an electron is scattered from a state in the n-region, there are fewer final states available to it, since the states in the s-region are modified. The ratio ℓ_s/ℓ_n should depend on the mechanism of scattering. It was suggested[10] that for scattering by static imperfections

$$\ell_s = 2\ \ell_n/(1 + \chi) \tag{13}$$

so that $\ell_s > \ell_o$. This form would be appropriate if scattering were isotropic and if a fraction $\chi/2$ of the possible final states were blocked by electrons in the s-states. Thus, if the thermal resistance is mainly due to static imperfections, the fractional change of the conductivity, on passing from the normal to the superconducting state is

$$f = W_{o,n}/W_{o,s} = \varkappa_{o,s}/\varkappa_{o,n} = 2(T/T_c)^2/i + (T/T_c)^4. \tag{14}$$

Consider now the case where the thermal resistance is mainly due to lattice waves: at low temperatures an electron, interacting with a phonon, does not change its "horizontal" position on the Fermi surface (from a position or region of large concentration to that of a lower one) by a large amount (see reference 11 p.9 and Fig. 1). It thus appears that an electron in the n-region will, in the majority of cases, remain in the n-region after an interaction, so that $\ell_s = \ell_n$. Hence the change in the ideal (intrinsic) thermal resistance

$$g = W_{i,n}/W_{i,s} = \varkappa_{i,s}/\varkappa_{i,n} = (T/T_c)^2. \tag{15}$$

It would hardly be expected that (14) and (15) would give the temperature dependence of the ratios f and g exactly, although one would expect these equations to give at least a qualitative description of their variation. We shall see later that this is so for (14) but not for (15).

The two-fluid model, in the explicit form given above, reproduces the thermodynamic properties only at temperatures above about $T_c/2$; at lower temperatures, the specific heat decreases exponentially with decreasing temperature, and in view of (9) one would expect $\varkappa_{e\ell,s}$ to behave similarly. It should be noted that at T_c, the superconductive heat conductivity $\varkappa_s$ breaks away from $\varkappa_n$. The change may be sudden or gradual, Fig. 1, but no discontinuity in $\varkappa$ is observed at T_c even though this effect has been carefully investigated.[3] However, at T_c there is a discontinuity in the specific heat, Fig. 2.[12] This jump is of magnitude

$$C_{e\ell,s} = 1.43\gamma\, T_c \tag{16}$$

[compare with equation (10)]. Measurement of γ provides direct information about $N(E_F)$, the density of states at the Fermi level. At lower temperatures the energy gap $\Delta(T)$ tends to dominate the specific heat, but a simple formula like

$$C_{e\ell,s} \approx \exp(-\Delta(T)/T) \tag{17}$$

is not adequate, until Δ reaches its limiting value Δ_o, which is expressed

$$\Delta_o \approx 1.76\, \underline{k}\, T_c \tag{18}$$

where Δ_o is the value of the energy gap at $T = 0$ and $\underline{k}$ is the Boltzmann constant.

The Ratio $\varkappa_s/\varkappa_n$

Since the electrons in the superconductive region of the Fermi surface cannot be thermally excited into a continuum of states, it follows that lattice waves can be scattered only by the electrons of the normal region, and not by those of the superconductive regions of the Fermi surface. Thus,

$$W_{E,s}/W_{E,n} = \chi = (T/T_c)^4 \tag{19}$$

where W_E is the thermal resistance due to the conduction electrons, and if $\varkappa_{ph}$ is limited by the interaction with conduction electrons

$$\varkappa_{ph,s}/\varkappa_{ph,n} = 1/\chi \ . \tag{20}$$

However, the lattice resistance due to phonon-phonon interactions should be unchanged by the transition from the normal to the superconducting state. It can thus be seen that $\varkappa_{e\ell,s} < \varkappa_{e\ell,n}$, but $\varkappa_{ph,s} > \varkappa_{ph,n}$, so that, depending on the circumstances, $\varkappa_s$ may be either smaller or larger than $\varkappa_n$.

The ratio of electronic thermal conductivities in the superconducting and normal states $\varkappa_{e\ell,s}/\varkappa_{e\ell,n}$ has been difficult for superconductive theory to explain. When impurity scattering is dominant, the BCS theory[8] predicts[13] that this ratio should be a universal function of T/T_c, independent of the particular element measured. The expression is complicated but it is a very similar function to, and its values are close to, those of the Heisenberg-Koppe formula[10,14]

$$\varkappa_{e\ell,s}/\varkappa_{e\ell,n} = 2(T/T_c)^2/1 + (T/T_c)^4 \text{ [cf equation (14)]}. \tag{21}$$

Both expressions agree with experiment, and they have zero slope at $T = T_c$. The temperature dependence of $\varkappa_s/\varkappa_n$ is shown in Fig. 3. However, a radically different behavior is observed in metals like lead, mercury, and indium, where T_c occurs in the phonon scattering region of Fig. 4a.[15] In these elements previous workers have found that $\varkappa_{e\ell,s}/\varkappa_{e\ell,n}$ falls from T_c as rapidly as (T/T_c).[16] The BCS prediction for this region is completely at variance with the observations.[13]

As can be seen from Fig. 3, $\varkappa_s$ should become extremely small at sufficiently low temperatures. However, only the electronic component of thermal conductivity has been considered in these calculations.[8] This is by far the dominant mechanism for a pure metal in the normal state. But, it should be remembered that this is only the case because phonon conduction in metals is inhibited owing to the extremely effective scattering of phonons by the free electrons.[11,17,18] The removal, on cooling, of a progressively increasing fraction of the electron fluid from the thermal distribution in the superconductive state not only decreases the heat conduction by electrons but also decreases the scattering of phonons by them. Accordingly, phonon conduction in the metal will become the dominant process at sufficiently low temperatures. Its behavior, then, will be closely analogous to that of a dielectric crystal.

Thus, at some temperature below T_c, $\varkappa_s/\varkappa_n$ must become larger than the function of Fig. 3. So far, no theoretical attempt has been made to determine this temperature; however, experimental data suggest that it will be below 0.4 T_c in the case of a pure metal. At sufficiently low temperatures, phonon mean-free-paths are limited by the size of the crystal[19,20] and by its surface roughness,[20,21] resulting in a mean-free-path independent of temperature. Also, below the Debye temperature, θ_D, phonon velocities are roughly constant and the lattice specific heat varies as T^3. Thus, the thermal conductivity should become proportional to T^3, in the case of good single crystals, the factor of proportionality depending on the diameter[19] of the specimen since the only relevant process will be scatter of phonons on the walls of the specimen. Thus a size effect in the heat conductivity of a superconductor is expected. Moreover, $\varkappa_s$, which is chiefly limited by scatter of electrons on point-imperfections at higher values of T/T_c must become less sensitive to these at lower temperatures, since their scattering cross section is small for phonons. Instead, $\varkappa_s$ must be strongly influenced by extended lattice faults.

The relative importance of conduction by phonons will be shifted to higher reduced temperatures as the impurity content of the specimen rises. For very impure specimens which have a low electronic conduction in the normal state, one can expect values of $\varkappa_s$ which approach or even exceed those of $\varkappa_n$. The explanation of the inversion of the $\varkappa_s/\varkappa_n$ ratio in the case of alloys is thus provided by a combination of depressed electron and enhanced phonon conduction. The correctness of this model is borne out, at least qualitatively, by experiments.[22] Even so, it must be regarded as surprising that, in some cases, for example in a lead alloy with 10% bismuth, a rapid rise of $\varkappa_s$ occurs already at T_c.

The opposite case is given by a pure metal with an intrinsically high electrical conductivity, such as aluminum, in which the residual heat conduction due to the normal electrons will remain the dominant factor in $\varkappa_s$ even at the lowest temperatures in spite of an enhanced phonon conductivity. In such cases one should expect a close adherence to the semi-empirical formula (f-function), particularly when, as in aluminum, T_c is well below the maximum in the thermal conductivity.

The Electronic Thermal Conductivity of Superconductors with Strong Electron-Phonon Coupling

Experiments on the strong elemental superconductors lead and mercury indicate that the electronic thermal conductivity of these materials differs markedly from that of typical weak superconductors like tin or indium. For lead and mercury[3,23] the ratio, $\varkappa_s/\varkappa_n$, of the thermal conductivity in the superconducting and normal states when plotted against the reduced temperature T/T_c shows a steep positive slope of about 5 near $T = T_c$. For tin[24] and indium,[25] on the other hand, the experiments yield a smaller slope of about 1.6.

A theory of the electronic thermal conductivity of superconductors, based on the quasiparticle approximation and the Boltzmann equation approach of Bardeen, Rickayzen, and Tewordt,[13] has been carried through previously.[26]

The results obtained are in substantial agreement with the data on tin and indium. The lack of agreement of this theory and the data on lead is not surprising since, as shown in the work of Schrieffer et al,[27] the strong electron-phonon coupling causes the quasiparticle picture to be quite meaningless over much of the energy spectrum.

It therefore seemed reasonable to apply Schrieffer's theory, which was used in explaining tunneling characteristics, to discuss the electronic thermal conductivity of strong superconductors without recourse to the quasiparticle approximation.[28] The starting point for this theory is the Kubo formula in which the thermal conductivity is expressed in terms of the correlation function of two heat current operators.[29] This is first examined in the Hartree-Fock approximation in the Nambu[30] space. It is shown that in the Eliashberg[31] approximation of neglecting the momentum dependence of the electronic self-energy, the calculation of the thermal conductivity is reduced to a quadrature, involving however the complex energy gap and renormalization functions which are solutions of the Eliashberg gap equations at finite temperatures. These expressions are too complicated to be reproduced here but the reader is referred to the original paper (reference 28) for more details. The problem was also considered in the ladder approximation in the Nambu space. A generalized Boltzmann equation was derived which includes corrections to the Hartree-Fock approximation corresponding to the replacement of the scattering by the transport cross-section. This treatment shows that the standard Boltzmann equation for superconducting quasi-particles is obtained in the weak-coupling limit.

The thermal conductivity of pure superconducting lead has been considered to be anomalous for many years.[32] The experimental results are summarized in Fig. 5. As was mentioned above, the curve of κ_s/κ_n vs T/T_c for typical weak-coupling superconductors tin and indium has a small limiting slope of about 1.5. In the case of the strong-coupling superconductors, lead and mercury, the decrease in the thermal conductivity is steeper, i.e. the limiting slope for lead is about 9.[33]

The strong-coupling superconductors are characterized by large electron-phonon matrix elements, and by peaks at low energies in the density of phonon states in which the electrons are coupled. These distinguishing characteristics have unambiguously been shown to be responsible for the anomalously large values in lead and mercury of the ratio of the energy gap at 0 °K to the critical temperature, and for the anomalous thermodynamic properties of these metals.[34] It has often been speculated that the smaller thermal conductivity of these strong-coupling superconductors is another consequence of their unusual electron-phonon interactions. It was not clear, heretofore, how this explains the great reduction in thermal conductivity.

The calculation is based on the foregoing theory,[28] and the general theory is supplemented by a specific model[35] for the phonon spectrum and the electron-phonon coupling constants in lead. The phonon spectrum used is shown in Fig. 6. It is found that even near the critical temperature, long-lived, particle-like excitations exist for the energies important in thermal conduction. In this quasiparticle limit, the general formula obtained in reference 28 (equation 2.17) reduces to (neglecting the effect of scattering-in terms)

$$\kappa_s = A/T^2 \int_{\Delta_1(\Delta_1,T)}^{\infty} d\omega\, \omega[\omega^2 - \Delta_1(\omega,T)]^{\frac{1}{2}}/Z_1\Gamma_s(\omega,T), \tag{22}$$

where

$$A = N(0)\, V_F^2/24\pi\, \underline{k} \tag{23}$$

with N(0) the density of states at the Fermi surface for one spin, V_F the Fermi velocity, ω the angular frequency of the phonons, $\Delta_1(\omega,T)$ the real part of the Eliashberg gap function[28,31], Z the renormalization function, $\Gamma_s(\omega,T)$ the quasiparticle lifetime which is related to the parameters of the Eliashberg theory according to[28b,29]

$$\omega Z_1\Gamma(\omega) = 2Z_2(\omega^2 - \Delta_1^2) - 2\Delta_1\Delta_2 Z_1 , \tag{24}$$

$\underline{k}$ is Boltzmann's constant, and T the absolute temperature. Equation (22) has the same general form as is obtained from a phenomenological Boltzmann equation.[13,28a] But, there is an important difference because the virtual effects of phonons in causing the superconducting transition have not been approximated by a model potential, but have been treated in the same way as the real transitions which scatter quasiparticles. As a result, the large value of the energy gap (in units of $\underline{k}\, T_c$), is in principle and practice contained in (22).

In order to bring out the physical origins of the large limiting slope of the reduced thermal conductivity of lead (κ_s/κ_n vs T/T_c), it is helpful to have a formal expression for this slope. Such an expression follows at once from (22). The thermal conductivity in the normal state is obtained from this equation by setting Δ equal to zero. Forming the ratio κ_s/κ_n and taking the derivative at the critical temperature, one obtains

$$d/dt(\kappa_s/\kappa_n) = -1/2\beta_c^2(\partial\Delta_1^2/\partial t)\Big|_{t=1}$$

$$\int_0^{\infty} d\omega\, \bar{\Gamma}^{-1}(\omega,T_c)\, \mathrm{sech}^2\, 1/2\beta_c\omega \Big/ \int_0^{\infty} d\omega(\beta_c\omega)^2\, \bar{\Gamma}^{-1}(\omega,T_c)$$

$$\mathrm{sech}^2\, 1/2\beta_c\omega + \int_0^{\infty} d\omega\, \omega^2\, \bar{\Gamma}^{-1}(\omega,T_c)\, \mathrm{sech}^2\, 1/2\beta_c\omega \cdot \partial/\partial t$$

$$\ln[\bar{\Gamma}_n(\omega,T)/\bar{\Gamma}_s(\omega,T)]_{t=1} \Big/ \int_0^{\infty} d\omega\, \omega^2\, \bar{\Gamma}^{-1}(\omega,T_c)$$

$$\mathrm{sech}^2\, 1/2\beta_c\, \omega \tag{25}$$

where $\beta = 1/\underline{k}T$, $t = T/T_c$, $\bar{\Gamma} \equiv Z_1\Gamma$, and the temperature derivative of Δ_1^2 is taken outside the integration because it is essentially constant in the

relevant region of ω. The following three factors appear to be responsible for the large slope in lead as contrasted with weak-coupling materials:
1. The larger value of the ratio $2\Delta(0)/\underline{k}\,T_c$ (4.3 for lead as opposed to 3.5 for materials well described by the BCS theory) has as its corollary a larger value of the slope $-\partial/\partial t(\Delta_1/T)|_{t=1}$ (14.1 for lead, 9.4 for materials following BCS). The more rapid opening-up of the energy gap in lead means physically that the heat carrying quasiparticles are more rapidly frozen out. This is the most obvious cause of the reduced thermal conductivity, but, taken by itself, it does not suffice to explain the large effect. 2. The quasiparticle lifetime τ^{-1} decreases more rapidly with frequency in lead than in weak-coupling materials. This effect has its origin in the small density of low-frequency phonons in lead.* The ratio of integrals multiplying $\partial/\partial t(\Delta_1)^2$ in (25) is the larger the more rapidly τ^{-1} decreases with frequency. In loose physical terms one can say that in all materials, the advent of the energy gap suppresses the carriers that are most weakly damped, and are thus most efficient in carrying energy. This theory indicates that in lead this supression is particularly effective. For the ratio of integrals mentioned, a value of about 1.1 is found. For the model of Debye phonons and "jellium" matrix elements worked out by Tewordt,[26b] the ratio is about 0.5. 3. The ratio $\tau_n(\omega,T)/\tau_s(\omega,T)$ decreases for lead when T decreases below T_c so that the last ratio of integrals in (25) is positive. The sign of this term appears to be connected with the coherence factors which go into a calculation of the relaxation rate for a quasiparticle in a superconductor. In this model, the dominant relaxation process is one in which two quasiparticle excitations annihilate, emitting a phonon. This is labeled process 3 in Fig. 7. This gives a positive sign. The other two kinds of processes, labeled 1 and 2 in Fig. 7, scattering of quasiparticles with phonon emission and absorption, give the opposite sign. The value for this term [the last ratio of integrals in (25)] is calculated to be 3.5. Working backwards from the final slope obtained in reference 26b, it can be concluded that for the model used in this reference, the ratio is negative and approximately -0.9.

Although no one of the three factors discussed is large enough to account for the effect, taken together they change the slope 1.6 obtained in Tewordt's[26b] model to the large value 11. In Tewordt's model the virtual processes are accounted for by the BCS model and the real processes by a Debye spectrum of longitudinal phonons coupled to the electrons by "jellium" matrix elements.

The model, although containing the effects discussed above, has certain weaknesses. The absolute value of the thermal conductivity at the critical temperature has approximately the correct value. At lower temperatures, however, the complete absence of low-frequency phonons will result in the thermal conductivity in the normal state not approaching the T^{-2} increase of the Bloch theory, but instead, increasing exponentially. In spite of such weaknesses, the basic conclusions of this theory appear sound.

This theory is based on a previous theory[26a] which was motivated by a

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*Note in Fig. 6 that there are no longitudinal phonons below 7 meV and no phonons whatever below 2.15 meV(milli-electron volts).

feeling that the quasiparticle approximation, in the sense of lifetimes being small compared to excitation energies, might break down for thermal conductivity in lead. The present theory indicates that no such breakdown occurs. However, the virtual effects of high energy phonons are important for thermal conductivity. These are consistently treated by the previous theory[38] and not by a phenomenological Boltzmann equation. The results are in fair agreement with experiment.

The difference in behavior between the strong-coupling and the weak-coupling superconductors is clearly apparent from Fig. 1; the $\varkappa_s$ curve departing from $\varkappa_n$ abruptly in the case of lead and gradually in the case of tin. It can also be seen that the transition temperature T_c, for lead, is above the maximum in $\varkappa_n$ and for tin, it is below it. This means that the scatter of the normal electrons, at the onset of superconductivity, is mainly by phonons in lead and by impurities in tin. In both cases, however, $\varkappa_s$ is lower than $\varkappa_n$ for the whole range of superconductivity.

Thermal Conductivity in the Superconductive State

The usual procedure is to measure the thermal conductivity of superconductors both in the normal and the superconductive states. The former measurements are made in a magnetic field larger than that needed to quench superconductivity, and, if necessary, are reduced to zero field strength by extrapolation.[3]

Observations on the thermal conductivity in the superconducting state can be classified[4] into (a) cases where $\varkappa_{ph} < \varkappa_e$, and $W_i > W_o$, (b) cases where $\varkappa_{ph} < \varkappa_e$, and $W_o > W_i$, (c) cases where $\varkappa_{ph}$ is negligible in the normal state but appreciable in the superconducting state, and (d) cases where $\varkappa_{ph}$ is appreciable both in the normal and in the superconducting states. There are, of course, cases intermediate between any of the above classes, and their interpretation is correspondingly uncertain. W_o and W_i are the residual and ideal (intrinsic) thermal resistivities, respectively. Thus, as in the case of thermal conductivity in normal metals, the thermal conductivity of superconductors can be discussed in terms of the scattering of electrons by lattice waves, i.e. the ideal thermal resistance W_i, the elastic scattering of electrons by impurities, i.e. the residual thermal resistance, W_o, and the lattice component of thermal conductivity.

The Ideal Resistance in the Superconducting State

To realize the condition $W_i > W_o$ below T_c, the specimen must be very pure and the transition temperature reasonably high. This condition has, so far, been fulfilled only in lead and mercury. The thermal conductivity of lead is shown in Fig. 1b; Figs. 5 and 8 show $\varkappa_s/\varkappa_n$ vs T/T_c for both lead and mercury.

From the reasoning used to develop (15), $\varkappa_s$ should be independent of T just below T_c, until scattering by imperfections becomes important.[4] In general, $\varkappa_s$ should be of the form

$$1/\varkappa_s = W_s = W_{i,s} + W_{o,s} \tag{26}$$

where

$$W_{i,s} = W_{i,n}(T_c) \tag{27}$$

is independent of temperature and $W_{o,s}$ is related to $W_{o,n}$ by (14), while

$$W_{o,n} \propto T^{-1} \quad . \tag{28}$$

For this discussion, it is important to note that $W_{o,s}$ should increase monotonically with decreasing temperature, and so should W_s.

The observed behavior of $\varkappa_s$ does not conform to these predictions. Immediately below T_c,

$$\varkappa_s \propto T^{-} , \tag{29}$$

so that

$$g = (T/T_c)^{F} , \tag{30}$$

in contrast to (15). At lower temperatures $\varkappa_s$ does not decrease steadily with decreasing temperature, but increases again and then decreases at a temperature such that $W_{o,n}$ is comparable to $W_{i,n}$.[4]

There are at least three interpretations of the observed behavior of $\varkappa_s$.[4] The one considered most likely by Klemens[4] is that $W_{i,s}$ is approximately described by (15), but for some unknown reasons which are presumably outside the scope of the two-fluid treatment, (15) does not describe g immediately below T_c. Just below T_c, the actual g-function is smaller than (15), but not by a very large amount [the observed values of $\varkappa_s$ are not less than $3/4\ \varkappa(T_c)$ at the minimum]; at lower temperatures $\varkappa_s$ increases again to its theoretical value $\varkappa(T_c)$, then, at still lower temperatures, decreases monotonically, due to $W_{o,s}$.

Then there is the interpretation that (30) holds over a wide range of temperatures, but that the ideal and imperfection resistances do not combine additively as in (26), so that W_s is not a monotonic function, even though $W_{o,s}$ and $W_{i,s}$ are. This viewpoint raises two questions: (1) Why should $W_{o,s}$ be so much smaller than $W_{i,n}$? and (2) Why should (26) break down so violently at intermediate temperatures that W_s decreases with decreasing temperatures, even though both $W_{i,s}$ and $W_{o,s}$ increase?

The third interpretation ascribes the maximum in $\varkappa_s$ to an enhanced lattice thermal conductivity in the superconductive state, but the difficulty is that a rather large amount of lattice conductivity is needed, i.e. $\varkappa_{ph}$ (4 °K) $\approx$ 1 watt/cm-deg.[15] By direct evaluation of a theoretical formula[34], an estimate for lead was obtained which implies that $\varkappa_{ph}$ (4 °K) $\gtrsim 10^{-2}$ watt/cm-deg. Also, measurements[35] on lead showed that $\varkappa_s$ was limited only by boundary scattering at the lowest temperatures. An upper limit of, say 5%, can be put on the resistance of all other phonon mechanisms at 1 °K. If this 5% were all due to the scattering of phonons by electrons, and the assumption[4]

made that the ratio of this scattering in the superconducting and normal states is $(T/T_c)^4$ [cf equation (19)], the measurements would require that $\varkappa_{ph,n}$ (4 °K) be at least 10^{-2} watt/cm-deg., or extra resistance would be visible at 1 °K as a deviation from the pure T^3 behavior observed. Hence, since $\varkappa_{ph,s}$ has been observed, at lowest temperatures, to be limited by boundary scattering, this gives an upper limit to $\varkappa_{ph,s}$ at higher temperatures which is too low to account for the peak in the $\varkappa_s$ curve at about 3 °K.

Some experimental evidence[36] has been reported which seems to support the second interpretation. Measurements on high purity tin and thallium, Figs. 9 and 10 show, first, a behavior of the electronic thermal conductivity at the transition from the normal to the superconducting state which is similar to that found in lead and mercury,[2,3] and second, an anisotropy of

$$\alpha_o = \alpha_{T \to 0\ ^oK}, \tag{31}$$

which, in the case of thallium does not exceed ~ 10%, but for tin, α along the [001] axis is 1.4 times greater than α along the [110] axis, see Table I.

At sufficiently low temperatures, the electronic thermal conductivity in the normal state can be expressed

$$T/\varkappa_n = \rho_o/L + T\,W_i\,(T) \quad . \tag{32}$$

Here the first term is determined by the scattering of electrons by lattice defects and the specimen boundaries (ρ_o is the residual electrical resistivity and L is the Lorenz number) and the second by scattering by lattice vibrations (phonons). According to Makinson[37]

$$TW_i\,(T) = \alpha T^3 \quad . \tag{33}$$

There is also a change in the quantity

$$\alpha' = d[T\,W_i(T)]/dt^3 \quad , \tag{34}$$

which on the simplest theory[37] should be a constant. The change in $T\,W_i(T)$ (or in α'), see Fig. 11, lies outside all possible experimental errors and, can, evidently only be explained by a lack of additivity in the scattering of electrons.[36] Table I shows the ratio, at $T = T_c$, of the scattering by lattice imperfections to the scattering by phonons, which is determined by the value of $\rho_o/L \propto T^3$. It can be seen from the table that for the purest specimens measured, the conductivity at temperatures near T_c is limited by scattering of electrons by phonons.

The data of Fig. 12 and Table I show that for a relative increase in phonon scattering (a reduction in $\rho_o/L \propto T_c^3$), $\varkappa_s/\varkappa_n$ decreases near T_c.

$\varkappa_s/\varkappa_n$ is then close for specimens of thallium and tin* with the same ratios $\rho_o/L \propto T_c^3$ (specimens Tl-8, Sn-1 and Sn-2). For the thallium and tin, therefore, as was found earlier[1,2] in the experiments on mercury and lead, the reduction in the electronic thermal conductivity at the transition from the normal to the superconducting state is sharper when the electrons are scattered by phonons than when the scattering is by lattice defects.

A qualitative explanation of the different form of the dependence of $\varkappa_s/\varkappa_n$ on T/T_c for scattering by imperfections and by phonons is: In the former case, the electron mean free-path is the same in both the normal and superconducting states of the metal. In the latter case it is rather the mean collision time, τ, between electrons and phonons which should stay constant, assuming an unchanged interaction between them. As a result of the change in the electron energy spectrum in the superconducting state, this leads to a reduction in the electron mean-free-path and therefore in the value of $\varkappa_s/\varkappa_n$. A calculation of the heat conductivity for the case τ = constant leads to the following result

$$\varkappa_s \sim \tau/T \int_0^\infty \epsilon^2 \frac{\partial n}{\partial \epsilon}\left(\frac{\partial \epsilon}{\partial \xi}\right)^2 d\xi \sim \tau/T \int_0^\infty [\Delta^2 \cosh 2\varpi/\exp\{\Delta T^{-1} \cosh \varpi\} + 1]d\varpi \quad (35)$$

$$\varkappa_s/\varkappa_n = 3/2\pi^2 \int_0^\infty \chi^2 \operatorname{sech}^2\left(1/2\sqrt{\chi^2 + (\Delta/T)^2}\right)d\chi, \quad (36)$$

where $\epsilon = \sqrt{\xi^2 + \Delta^2}$ is the excitation energy in the superconductor, $n = (e^{\epsilon/T} + 1)^{-1}$, and Δ is the superconducting energy gap, assumed to be of value 1.7 T_c. The curve R of Fig. 12 is calculated from (35) and (36). It can be seen that (35) and (36) only describe the variation of $\varkappa_s/\varkappa_n$ with T/T_c qualitatively. This may possibly be due to the electron-phonon interaction being different in the normal and superconducting states (by electrons, is meant the so-called normal electrons of the superconductor). Another possibility is that the different dependences of the $\varkappa_s/\varkappa_n$ on T/T_c for thallium, tin, mercury and lead (Fig. 12) are produced by the differences in Δ/T_c for these metals.[41]

The Residual Resistance in the Superconducting State

In the case of tin, indium, tantalum, thallium, vanadium, and nioblum, the normal state electronic thermal conductivity, for those specimens which have been studied, is determined at T_c and below by imperfection scattering, and the same applies to the various alloys and to impure specimens of lead and mercury. These specimens can be used to test (14) for $\varkappa_{e,s}$, except where $\varkappa_{ph,s}$ is appreciable and complicates the picture. As long as lattice

*There appears to be some anisotropy in $\varkappa_s/\varkappa_n$ vs T/T_c in tin. The change of $\varkappa_s/\varkappa_n$ with T/T_c for specimens along the [110] axis follows a steeper law than for specimens along the [001] axis. This is similar in form to the anisotropy in ultrasonic absorption near T_c.[40]

conduction is unimportant, the ratio $\varkappa_s/\varkappa_n$ should agree with (14); if $\varkappa_s/\varkappa_n$ is larger than expected, the difference is ascribed to $\varkappa_{ph,s}$, though it is usually not possible to prove that this is so.

$\varkappa_s$ has been measured for tin down to about $T_c/3$.[3,42] Fig. 13 shows values of $\varkappa_s/\varkappa_n$;[3] the specimens are numbered in increasing order of W_o. Note that the curves for Sn2 and Sn3 are practically coincident, even though their values of W_o differ by a factor of about 2. The high values of $\varkappa_s/\varkappa_n$ are ascribed to $\varkappa_{ph,s}$. Since these specimens have appreciable lattice conduction even in the normal state, this seems a plausible interpretation.

Similar results were obtained for indium.[3,43] However, in all cases it is found that the observed f-function decreases more rapidly with temperature just below T_c than the function (14) (semiempirical function). It could be that this departure from the conclusions of the two-fluid theory just below T_c is related to the similar departure already noted for the g-function. Sladek, on the other hand, suggested the following form for $\varkappa_{el,s}/\varkappa_{el,n}$:

$$f = 3(T/T_c)^2/2 + (T/T_c)^4 \quad , \tag{37}$$

which he based on an assumption about ℓ_s which seems no more artificial than (13).[4]

Substantially similar results for $\varkappa_{o,s}$ have been obtained for tantalum[3], tin, indium, thallium, tantalum and vanadium;[44] the case of niobium was complicated by frozen-in magnetic flux.

Not much data are available on $\varkappa_{el,s}/\varkappa_{el,n}$ below about $T_c/2$, partly because not many measurements have been made at sufficiently low temperatures and partly because of the increasing importance of $\varkappa_{ph,s}$ as the temperature is decreased.

Measurements of $\varkappa_s$ below about 1 °K have been made.[35,45-47] For tin and tantalum indications have been found[45] that $\varkappa_s/\varkappa_n$ decreased faster with temperature than it should according to equations (12) and (14). This was confirmed by the extensive work on tin[46], where an exponential decrease with temperature was found in $\varkappa_s$ for two pure specimens, changing at lower temperatures to a T^3 dependence. The latter variation is ascribed to lattice conduction, while at higher temperatures $\varkappa_{el,s}$ is important (it is $\varkappa_{el,s}$ which varies exponentially).[48] A specimen of lead which had previously been measured at helium temperatures[49] was measured down to 0.4 °K.[35] Below 1 °K it was found that $\varkappa_s \propto T^3$ (presumably lattice conduction), but just at the upper limit of the measured temperature range, indications were found of a faster variation, which is confirmed if one joins up these measurements with those at higher temperatures. Probably this is a case of $\varkappa_{el,s}$ decreasing exponentially with temperature. Measurements of tin, indium, thallium, aluminum, tantalum, and niobium from 0.4 ° to 1° K disclosed an exponential variation of $\varkappa_s$ in the case of thallium; in the other cases, the effect appeared to be masked by lattice conduction.

Presumably, the exponential behavior of $\kappa_{e,s}$ at low temperatures is related to a similar variation in the specific heat. In some cases, indications of such a variation of the specific heat of superconductors well below the transition temperature have been observed. It appears likely, therefore, that the Gorter-Casimir two-fluid theory breaks down at very low temperatures.

The Lattice Component of Thermal Conductivity in the Superconducting State

In superconductors one should expect heat to be carried by phonons rather than by electrons at low temperatures, where the concentration of normal electrons must become vanishingly small. This phonon conduction will be enhanced by the reduction of the scattering which the phonons experience by encounters with normal electrons. Evidence for this effect can be obtained either by observing the temperature dependence of κ_s at sufficiently low temperatures, or by introducing agents into the specimens which will scatter phonons selectively. Both types of experiments have been carried out, and have shown beyond doubt that a superconductive metal exhibits behavior identical with that of a dielectric crystal, as far as thermal conductivity is concerned, when sufficiently near to absolute zero. Even if κ_{ph} is too small to be observed in the normal state, in the superconductive state W_E decreases very rapidly with temperature, so that at very low temperatures $\kappa_{ph,s}$ is only limited by the scattering of phonons by static imperfections or boundaries. Thus, experiments below 1 °K usually give clear indications of lattice conduction.

In the dimensional equation,

$$\kappa = A\,C\,\ell\,v, \tag{38}$$

where C is the specific heat per unit volume of the heat carriers, v is their velocity and ℓ is their mean-free-path; A is a constant which is usually equal to 1/3, v is temperature-independent and C is proportional to T^3.[9] Hence κ will vary with T^3 since ℓ is constant. As was pointed out by Casimir[19], scatter of phonons only occurs at the geometric surface of the specimen in a perfect dielectric crystal at low enough temperatures. This means that ℓ is constant and is determined by the specimen dimensions. Thus the magnitude of κ is dependent on size alone. This type of behavior has indeed been observed[20] in dielectric crystals, the heat conductivity being proportional to T^3 and of the predicted magnitude.

Clear evidence for a similar behavior in superconductors has been found in measurements of thermal conductivity in lead[21], particularly κ_s down below 1 °K. It was pointed out[22] that phonons and electrons each have one scattering mechanism for which theory and experiment agree, and one for which there is much confusion. The heat conduction by phonons at the lowest temperatures is expected to be limited by boundary scattering and to vary as T^3. This is well substantiated experimentally; Fig. 14 shows results for lead and thallium. Similar results have been obtained for tin, indium, and niobium. However, when one extrapolates this to higher temperatures and attempts to obtain that part of the phonon conductivity which is limited by electronic scattering, confusion arises because the electronic scatterers are themselves carriers of heat. As a result, estimates of this part of the phonon conductivity

are very unreliable and disagreement with theoretical predictions not surprising; similarly with electronic conductivity limited by phonon scattering.

Although the curve of Fig. 14 shows a definite variation of κ_s with T^3, the numerical value of κ_s was found to be rather smaller, in this case, than would be expected on the basis of Casimir's treatment which, for a cylindrical specimen, predicts $\ell \cong d$ (d is the specimen diameter). Similar deviations are found in other cases. At the lowest temperatures, κ_s has been found to vary as T^3 in lead[35], tin and indium[47], and tin.[46,61] It was found that generally the group at Oxford[35,47,60] deduced values for W_B which were five to ten times higher than values expected from the external dimensions of their specimens, while the group at Cambridge[46,61] found values of W_B in rough agreement with the external dimensions.[4] Two possible explanations have been given[4] for the findings of the Oxford group: (1) their specimens contained considerably more grain boundaries and (2) κ_{ph} is reduced by frozen-in magnetic flux.

A study of the effect of strain on κ_s shows clearly that even a very small degree of cold work, such as is produced by a slight vibration of the cryostat, can raise the numerical value of κ_s substantially. This difficulty was not fully understood in most of the researches quoted in the foregoing. More careful work[53] has shown that, at least in the case of tin, values for κ_s can be obtained which are sufficiently close to the value predicted by Casimir to make scattering by the specimen boundaries the dominant process.

Even so, however, the tendency of κ_s to fall short of the predicted value deserves attention.[8] The situation can be represented, conveniently, by introducing several thermal resistances which are characterized by different mean-free-paths, and which are combined additively. Thus, denoting the mean-free-path derived from observation as ℓ_o, we write[8]

$$1/\ell_o = (1/d) + (1/\ell_b) \tag{39}$$

in which ℓ_b is a mean-free-path characteristic of an additional resistance in the bulk material. The circumstance that, as yet, no metal specimen has been found in which this additional internal resistance is zero, whereas it is of considerable magnitude in most, may be due to the fact that the metals are much more plastic than the dielectric crystals investigated. This is a field where further research is indicated, particularly because the features associated with the internal scattering appear to be complex. Although the temperature dependence of κ_s is cubic in many cases, both higher and lower powers of T have been observed.[5] Moreover, it has been found that even at the lowest temperatures, a single crystal of the given material will exhibit a thermal conductivity proportional to T^2, even though a polycrystalline sample may show a T^3 dependence. This suggests that the internal scattering centers, which are most probably dislocations, may have a more profound effect than the crystal boundaries.

In the case of impure tin specimens[46] κ varies more slowly than T^3 except at the lower end of the temperature range. At higher temperatures $\kappa_{ph} \propto T^2$. Goodman[46] presumed the dominant scattering mechanism in the T^2 region to be scattering by the free electrons. Klemens[4] pointed out that this was unlikely, since from (19), W_{E_s} should vary as T^2, not as T^{-2}. However, it has been shown[4] that dislocations can play an important part in determining κ_{ph}, even

in normal metals where W_E is not quenched. It seems quite possible, therefore, that in the T^2 region $\varkappa_{ph,s}$ is limited mainly by dislocations. This interpretation can also be applied to a tantalum specimen[53] where $\varkappa_{ph,s}$ was found to vary as T^3 below 1 °K.

A more convincing proof of the phonon nature of $\varkappa_s$ at low temperatures is provided by work in which selected scattering mechanisms are introduced into the specimen.[9] Observation of the different effects of changes on $\varkappa_s$ and $\varkappa_n$ allows a more unambiguous assessment of the nature of the energy transport in each case. Assuming that the heat is entirely carried by phonons in the superconductor, at low enough temperatures, we may expect the following behavior of $\varkappa_s$ and $\varkappa_n$ in the same specimen:
(1) $\varkappa_s$ should be insensitive to point imperfections, i.e., to the amount or nature of the impurity, whereas $\varkappa_n$ should be much reduced by small amounts of impurity and should be sensitive to its nature. (2) $\varkappa_s$ should be reduced by large-scale imperfections, e.g., grain boundaries, such as are introduced by plastic deformation and recrystallization, whereas $\varkappa_n$ should not be greatly influenced by them. Providing that the specimen is pure enough, dislocations should reduce both $\varkappa_s$ and $\varkappa_n$. In many cases, however, $\varkappa_n$ is so small already because of impurities, that the only observable effect is the reduction in $\varkappa_s$. (3) $\varkappa_s$ should be reduced when the specimen diameter becomes small compared to the phonon mean-free-path in the bulk material, whereas $\varkappa_n$ should not.

Experiments designed to test these predictions have been performed on lead.[54] The results unequivocally show the phonon nature of the heat transport. Fig. 15a shows $\varkappa_s$ and $\varkappa_n$ for two single crystals, one of pure lead and one of an alloy containing 0.7% bismuth.[9] The conductivities in the normal state at 1 °K differ by a factor of 100 and (even in the superconducting state at 4 °K) there is still a large difference. The conductivity at this temperature evidently is still mainly electronic, but the two $\varkappa_s$ curves merge below 2 °K. Very similar numerical values of $\varkappa_s$ were obtained at 1 °K with specimens of lead containing the same amount of tin or thallium. On the other hand, measurements on a lead specimen containing 0.6% thallium (PbTl 0.6%) before and after severe strain due to bending showed $\varkappa_s$ reduced to 1/6 its original value, whereas $\varkappa_n$ was completely unchanged, Fig. 15b.[8] Probably, the dislocations, introduced into the sample by the strain, are very effective scatterers of phonons, but the electronic conductivity is unaffected by them because of the thallium impurity.

The effect of sample size on $\varkappa_s$ is more difficult to demonstrate clearly. Simply to compare measurements made on a thick rod and a thin wire of the same material can not be conclusive since it is almost impossible to avoid straining the latter. Thus, it would be difficult to distinguish with certainty between reduction in $\varkappa_s$ due to limitation of the phonon mean-free-path resulting from geometrical boundaries or from dislocations. However, an experiment has been performed[54] on a lead foil 0.07 mm thick which was stabilized mechanically by being rolled into a scroll. Since the phonon mean-free-path of the material was of the order of 0.5 mm, a size effect should have been noticeable in the foil. Indeed the heat conduction of the foil at 1 °K was found to be five times smaller than that of a bulk specimen of the same material, whereas $\varkappa_n$ is essentially the same in both cases. Moreover, the temperature dependence of $\varkappa_s$ for the scroll approaches T^2, which is to be expected for boundary scattering.

Metals, such as the transition metals, which have low intrinsic electrical conductivity should exhibit the most pronounced effect of enhanced phonon conduction. The most striking example of this kind has, indeed, been observed in tantalum[55] which was measured down to 0.2 °K. The result of these investigations indicates that $\varkappa_s/\varkappa_n$ is even larger than one in the neighborhood of 1 °K. If the data are plotted in a form which permits comparison with the semiempirical function (f-function), see Fig. 16, it can be seen that the latter represents the data remarkably well down to about 0.4 T_c. Below this temperature, there is an enormous rise in the phonon conduction which at 0.2 T_c assumes a value about a hundred times larger than the electronic contribution. Data on niobium, included in Fig. 16, and on vanadium present a similar pattern. The results for tantalum have been used to separate the phonon contribution $\varkappa_{ph,s}$ from the electronic part $\varkappa_{el,s}$.[56] This analysis shows that at a temperature $T_c/4$, the phonon conductivity is still increasing with decreasing temperature even though the ratio $\varkappa_{ph,s}/\varkappa_{el,s}$ approaches 10^2, indicating the strong scatter of phonons by the normal conduction electrons. Comparing the numbers clearly indicates that the maximum in $\varkappa_s$ will be less pronounced or will disappear for metals with better intrinsic electronic conductivity.

Aluminum is a typical example of the latter behavior.[56,57] Here the data agree well with the semiempirical function (f-function) over the entire range, including the lowest temperatures. Fig. 17 shows the observations[56] of $\varkappa_s$ plotted for pure aluminum and an alloy with 1.7 atomic % copper. The pure metal follows the B.C.S. function with an energy gap slightly smaller than that predicted by the theory. At temperatures below $T_c/3$, however, the alloy shows a deviation to higher values, indicative of a phonon component.

The thermal conductivity has been measured on two indium-lead alloy samples containing 4.05 and 7.31 atomic % lead, respectively, down to 0.4 °K.[58] The results were interpreted in the light of the Bardeen, Rickayzen, and Tewordt (BRT)[13] theory. This theory assumes that the dominant electron scattering is due to impurities and the dominant phonon scattering is caused by electrons. The normal-state data were fitted with

$$\varkappa_n = AT + BT^3 \tag{40}$$

where the first term represents $\varkappa_{el,n}$ and the second, $\varkappa_{ph,n}$. This determined the two parameters A and B. It was found that the phonon contribution was very small in both the normal and the superconducting cases. Similarly the superconducting data were expressed by

$$\varkappa_s = ATR_{el} + \varkappa_{ph,s} \; . \tag{41}$$

Here R_{el} is the BRT ratio of electronic thermal conductivity the two states, and $\varkappa_{ph,s}$ the lattice component, included the effects of boundary and point-defect scattering as well as the electronic scattering considered by BRT. Hence, the additive resistance approximation

$$1/\varkappa_{ph,s} = 1/\varkappa_{BP} + 1/\varkappa_{BRT} \tag{42}$$

was used. Here

$$\kappa_{BRT} = BT^{-} R_{ph} \tag{43}$$

is the BRT value assuming phonon scattering by electrons alone. κ_{BP} is the phonon thermal conductivity limited by boundary and point-defect scattering according to Slack.[50] κ_{BP} involves two additional adjustable parameters, the mean-free-path due to boundary scattering L and a temperature T_{Ω} which is a measure of the point-defect scattering. In evaluating L, the velocity of sound was taken as $1.9 \times 10^{-}$ cm/sec. The accepted value of the energy gap for indium, $2\epsilon_o(0)/\underline{k}\, T_c = 3.7$ was used.

As shown in Figs. 18 and 19 the agreement between theory and experiment is quite good. The fit to the superconducting data obtained in this manner is particularly good at the lower temperatures. In this region boundary and point-defect scattering predominate. The slight disagreement near 1 °K is attributed to the limitations of the additive resistance approximation.[50] The small phonon contribution (the linearity of the normal-state data rules out the strong possibility of a larger phonon term) probably accounts for the poor fit at higher temperatures, where the BRT result predominates. However, it is quite apparent that κ_s is largely lattice conductivity over almost the entire range shown. The maximum or plateau region near 1 °K for the superconducting case is caused by the transition from the scattering of the phonons by electrons, W_E, to a combination of boundary and point-defect scattering, W_{BP}.[52]

One cannot obtain a value for $W_{E,s}$ from the very low temperature observations (except an upper limit, which is probably very much larger than $W_{E,s}$), because of the importance of phonon-phonon interactions, which are not influenced by the superconducting behavior. It is only possible to observe $W_{E,s}$ over a limited temperature range below T_c. It has been determined in this way for Sn96-Hg 4,[ ] lead-bismuth alloys[ ] which had been previously measured[ ], and for indium-thallium alloys.[ ]

A conflicting picture of the ratio $h = W_{E,n}/W_{E,s}$ results from these observations. Hulm[ ] suggested $h \approx (T_c/T)^{ }$, Olsen[ ] $h \approx (T_c/T)^{6}$, and Sladek[ ], whose measurements seem most suitable for the evaluation of h, did not obtain a simple power law, nor the same curve of h versus T/T_c for all his samples, but rather a series of curves for h, all in the vicinity of $h = (T_c/T)^{4}$, but too high just below T_c and tending to become too low at lower temperatures.

The interpretation contains uncertainties, hence W_{ph} could easily have components other than W_E (this is certainly so at lowest temperatures and may be so even if $W_{ph} \propto T^{-}$), which would tend to decrease h. The separation of κ_s into $\kappa_{ph,s}$ and $\kappa_{e,s}$ involves the assumption that the ratio $f = \kappa_{e,s}/\kappa_{e,n}$ is independent of alloy composition. Nevertheless there are probably real discrepancies from $h = (T_c/T)^{4}$, particularly just below T_c, just as there are discrepancies in $\kappa_{i,s}$ just below T_c.

It was mentioned above that the f-function (semiempirical formula) breaks down in those cases in which scattering of electrons in the normal state is not caused by impurities but by phonons. In fact, the observed values of κ_s/κ_n for a metal-like lead, which has a low characteristic temperature and a relatively high transition temperature (7.2 °K), do not follow the f-function for any temperature region. It can be seen from Fig. 1

however, that $\varkappa_s$ exhibits a maximum at 0.5 T_c which is similar to those shown by tantalum and niobium at much lower reduced temperatures. The question therefore arises whether the maximum in $\varkappa_s$ of lead is different in nature from the enhanced phonon conduction found in the $\varkappa_s$ of the transition metals. Fortunately, the sensitivity of the phonon conduction to dislocations allows this problem to be decided experimentally.[65] When the pure single crystal of lead of Fig. 1 was strained at helium temperature, it was observed that $\varkappa_s$ was indeed reduced. However, this reduction occurred only at temperatures well below the maximum in $\varkappa_s$, i.e., in the reduced temperature region found in tantalum and niobium.[3] The maximum in lead was quite unaffected, whereas it was drastically reduced in the transition metals by similar treatment.

A clearer picture of the behavior in the case of lead can be obtained from the curves in Fig. 20.[a] This shows that at temperatures above $\sim 0.4\ T_c$ the experimental values are lower than those given by the f-function (semiempirical function), whereas they are higher below that temperature. Introducing dislocations into the specimen by strain does not affect the higher temperature region of $\varkappa_s$ at all. However, $\varkappa_s$ now follows the semiempirical function remarkably well below $\sim 0.4\ T_c$. Thus, it seems that the failure to obey the f-function arises from two quite different reasons. At high temperatures, where the predominant process is the scatter of electrons by phonons, the theoretical understanding is not yet sufficient, whereas phonon conduction becomes predominant below 0.4 T_c. Once phonon conduction is drastically reduced by scattering on dislocations, the semiempirical formula holds quite well. Hence the maximum in $\varkappa_s$ in lead is entirely electronic in nature and is clearly connected with the maximum in $\varkappa_n$.[8]

Klemens[4] points out that the interpretation[3,4] of the thermal conductivity of lead-bismuth alloys contains difficulties. Fig. 21 shows plots of $\varkappa_n$ and $\varkappa_s$ versus T for these alloys. It is easily seen that if the increase of $\varkappa_s$ for the alloys 0.2% Bi and 0.5% Bi over the values of $\varkappa_s$ for alloys of low bismuth content is to be explained in terms of enhanced lattice conduction, then $\varkappa_{ph,s}$ for these two alloys is higher than $\varkappa_{ph,s}$ for the alloys 0.1% Bi and 0.02% Bi, and possibly even higher than $\varkappa_{ph,s}$ for pure lead. Of course, it is possible to explain this by assuming some imperfections to be present in the more dilute alloys and not in the more concentrated alloys, though this disagrees with the usual observations.

Thermal Conductivity in the Intermediate State

A superconducting pure element, in the shape of a long cylinder, undergoes a sharp transition from the superconductive to the normal state upon the application of a longitudinal magnetic field. In other cases the transition is gradual; increasing the magnetic field causes a gradual increase of flux in the specimen, until all the material is in the normal state. Upon removing the field, the material does not return to the original superconductive state, but some magnetic flux remains frozen in.

The intermediate state of the material is not homogeneous, rather it consists of a mixture of normal and superconducting regions in the material, the former having high flux density (above the critical field) and the latter, zero flux. Since the lines of flux are continuous, the structure of the intermediate state is dominantly one of filaments or layers, alternately normal and superconducting, lying in the direction of the field.

A number of measurements have been made of the thermal conductivity of superconductors in the intermediate state, with the specimens as long cylinders. With longitudinal fields there will usually not be a marked mixing of the two states, except in the case of alloys, when the normal state inclusions will be mainly filaments running the length of the specimen. With transverse fields, however, the specimen will readily break up into a mixture of two states, and the normal state inclusions would then be, predominantly, layers perpendicular to the cylinder axis, and thus to the direction of heat flow. The thickness of the individual regions may be of the order of 0.01 cm.

With a cylindrical specimen in a longitudinal field, with normal and superconducting filaments along the direction of heat flow, the overall thermal conductivity would be expected to be given by the average.[2]

$$\varkappa = \chi_n \varkappa_n + (1 - \chi_n)\varkappa_s \tag{44}$$

where χ_n is the fraction of normal material and can be deduced from flux measurements. Similarly, for transverse fields, the thermal resistance averages are given by

$$W = \chi_n W_n + (1 - \chi_n) W_s \quad . \tag{45}$$

As a consequence of either (44) or (45), the thermal conductivity in the intermediate state (either with subcritical fields or with frozen-in (trapped) flux) should be intermediate between the normal conductivity $\varkappa_n$ and $\varkappa_s$ as measured in the virgin superconducting state. Within the bounds of this restriction, hysteresis effects are possible.

Such behavior was indeed observed in many early measurements in transverse fields[2,66] and in longitudinal fields.[3] Later measurements showed variations of $\varkappa$ with magnetic field strength, however, which could not be reconciled with either (44) or (45). In the case of some lead-bismuth alloys and of niobium, it has been found[22] that the thermal resistance passed through a maximum value, on applying a field, which was higher than the resistance in either the normal or the superconductive state, Fig. 22. Also, on removal of the field, $\varkappa$ did not return to the original value $\varkappa_s$, but to a value again lower than either $\varkappa_s$ or $\varkappa_n$ (a hysteresis effect). These anomalies seem more likely to occur the lower the temperature and the larger the impurity content, but this is not a general rule. This effect has been ascribed[22] to a heat flow mechanism which occurs in the superconductive state in addition to electronic conduction; in the intermediate state this mechanism would be inhibited. A two-fluid circulation was suggested for this additional mechanism.[22] A more likely explanation seems to be lattice conduction.[4]

Further instances of anomalies in transverse fields were found later for pure lead[35,67], pure tin and indium (but not for tin containing 0.134% Bi)[68], and for mercury.[69,70]

The anomalously high thermal resistance in the intermediate state has been attributed to various scattering mechanisms acting at the boundaries of the filaments. The situation has been greatly clarified by a systematic

investigation of the alloy series SnIn.[72] The induced magnetic moment and the dependence of the electrical and thermal resistance on the magnetic field strength were measured on these specimens. A typical set of results for an almost perfect single crystal containing 2.8% indium is given in Fig. 23 for two temperatures. Whereas the fraction of frozen-in flux is largely temperature independent, the maximum in the thermal resistance is pronounced at 2.03 °K and practically nonexistent at 2.65 °K. From this it can be deduced that the structure of the intermediate state is much the same at different temperatures and that the relevant scattering mechanisms may be different. More detailed analysis does indeed suggest that the filament boundaries scatter both electrons and phonons but that the temperature dependence is different for the two mechanisms.

Theory of the Thermal Conductivity of Superconducting Alloys with Paramagnetic Impurities

The prediction of "gapless" superconductivity in paramagnetic alloys[73] and the confirmation of this prediction[73] are significant recent developments.[74] Although the theory is based on an approximate treatment of a simple model and more detailed experiments are needed, the prediction is unambiguous and the confirmation convincing. The assumption is that the static magnetic impurities are randomly distributed and that their spins are uncorrelated. The theory makes it clear that the key feature of the superconducting state is the condensation phenomenon. A gap in the single particle excitation spectrum is evidently not a necessary requirement for either the infinite conductivity or the perfect diamagnetism of the condensed state. The experimental investigation of this phenomenon of superconductivity without an energy gap promises to improve our understanding both of superconductivity and of the effects of magnetic impurities in metals in general.

Based upon this theory, the electronic thermal conductivity $\varkappa_s$ of a weakly coupled, isotropic superconductor, doped with a small concentration of paramagnetic impurities, is calculated, starting from a Kubo formula, by considering the electron-impurity interaction in the ladder approximation.

A considerable simplification of the final expression occurs if it is assumed that the total single particle lifetime is much smaller than the exchange lifetime τ_s. With this assumption, an expression is obtained for $\varkappa_s/\varkappa_n$ of the form

$$\varkappa_s/\varkappa_n = (3/2\pi^2)\beta^3 \int_0^\infty d\omega\, \omega^2 \operatorname{sech}^2(\tfrac{1}{2}\beta\omega)\, h(\omega/\Delta,\alpha) \tag{46}$$

$$\alpha \equiv (\tau_s\Delta)^{-1} \quad . \tag{47}$$

Δ is the average order parameter, and

$$\beta \equiv (1/\underline{k}T) \quad , \tag{48}$$

k is the Boltzmann constant, and T absolute temperature. The units are chosen so that $\hbar = 1$. For non-magnetic impurities, the usual result is found that

$$h(\omega/\Delta < 1) = 0 \tag{49}$$

and

$$h(\omega/\Delta > 1) = 1 \quad , \tag{50}$$

the average order parameter $\Delta(T,\tau_s)$ being the energy gap in this case. For a paramagnetic alloy, the lower limit of integration is the physical energy gap $\omega_o(\Delta,\alpha)$ and not the average order parameter $\Delta(T,\tau_s)$. Moreover, the function $h(\omega)$ increases smoothly toward unity for $\omega > \omega_o$.

The ratio κ_s/κ_n is evaluated numerically as a function of the reduced temperature $(T/T_c) \equiv t$ for different impurity concentrations, including non-magnetic impurities. The results are shown in Fig. 24.

Abrikosov and Gor'kov have shown that the energy gap function $\omega_o(T)$ is quite different than the Gor'kov order parameter $\Delta(T)$ in such alloys. It is found that κ_s/κ_n is less than unity in the "gapless" region $\Delta\tau_s < 1$. This theory predicts that even in the gapless region the thermal conductivity in the superconducting state is lower than that in the normal state, because although the energy spectrum has no gap, it is still distorted. In addition, the onset of gaplessness does not lead to an abrupt change in the thermal conductivity. Long before the gap actually vanishes, the BCS singularity in the density of states is smoothed out by the impurity scattering. Finally, it is found that κ_s/κ_n as a function of t, has a characteristic concentration dependence. For $t \gtrsim 0.9$, κ_s/κ_n decreases for small n_i while for $t \lesssim 0.75$, it increases with n_i (n_i is the paramagnetic impurity concentration).

For non-magnetic impurities in systems with weak electron-phonon interactions (to which this theory is restricted), a simple calculation of the thermal conductivity, using a Boltzmann equation, is possible. To justify the elaborate formalism used, it is pointed out that in the gapless region (always close to T_c), it is not possible to associate a narrow band of energies with a state of momentum near the Fermi momentum, i.e., the quasiparticle approximation breaks down. In addition, the effects of the paramagnetic impurities in renormalizing the energy spectrum are crucial. Both these effects would cause difficulties in conventional transport theory, but they are easily taken into account in the Kubo formulation.

The Thermal Conductivity as a Defect Detector in Superconductors

It has been demonstrated above that phonon conduction predominates in κ_s at low temperatures, that it is sensitive to strain, and independent of point imperfections. Clearly this can provide a distinction between these two different types of lattice defects. Investigations of this nature have the added advantage that, in the same specimen, the scattering of phonons and, by simply applying a magnetic field, that of electrons can be studied

without even warming the sample to room temperature. In most cases the magnetic fields required to destroy superconductivity are less than 1000 oersteds. The accompanying magneto-resistive effects in the normal state are small. Those which exist can usually be taken into account by running comparison experiments above T_c.[8]

Systematic experiments have been performed on the effect of strain and impurity.[68,75] The clearest results were obtained by Rowell[75], who subjected pure lead and a lead alloy to controlled bending at helium temperatures and measured the thermal conductivity in the normal and superconducting states before and after introducing the strain. Another feature was the study of annealing effects at different temperatures between that of liquid helium and room temperature. Order of magnitude agreement was obtained between the density of dislocations derived from the measurements of heat conductivity and those predicted on the basis of the strain introduced. More spectacular results than were obtained on lead are those on a niobium rod which was originally single crystal and which was subsequently stretched in steps until it ruptured. $\varkappa_n$ showed no effect except at the highest strain. Even after fracture $\varkappa_n$ changed only by a few per cent. On the other hand, the effect on $\varkappa_s$ is far-reaching. In its undisturbed condition, the niobium specimen showed a very pronounced maximum in $\varkappa_s$ at temperatures below $0.4\ T_c$. With successive stretching, this maximum was largely removed. Point imperfections, which scatter electrons, will reduce both $\varkappa_n$ and $\varkappa_s$ at high reduced temperatures, where the heat transport is still by electrons. The maximum in $\varkappa_s$ at low temperatures because of phonon conduction is unaffected. However, since $\varkappa_n$ is drastically reduced, $\varkappa_s$ may now exceed $\varkappa_n$ in this temperature region. At still lower temperatures, this relation is again reversed and $\varkappa_s/\varkappa_n$ becomes smaller than unity. Extended lattice defects, such as dislocations, introduced by strain, appear to have little or no effect on the electronic part of the conduction mechanism. Therefore, $\varkappa_n$, as well as the high temperature part of $\varkappa_s$, will not change materially. In the low temperature region, on the other hand, where heat is carried by phonons, $\varkappa_s$ is decreased. The phonons are scattered by the dislocations; with increasing strain the ratio $\varkappa_s/\varkappa_n$ becomes progressively smaller.[8]

This method can also be applied to the study of nuclear radiation damage. The thermal conductivity of a single crystal rod of niobium was measured first in the undamaged state then after neutron irradiation at room temperature. Both $\varkappa_n$ and $\varkappa_s$ are reduced by irradiation, Fig. 25. If it is assumed that both interstitials and vacancies have been produced by irradiation, it is believed[8] that, although the former may have migrated at the temperature of irradiation, the temperature was never high enough to cause migration of vacancies in niobium. Hence the decrease in $\varkappa_n$ is ascribed to the vacancies produced directly by the radiation and assume a more-complicated process to be responsible for the decrease in $\varkappa_s$. A calculation based on the condensation of interstitials due to irradiation yields an increase of about 10^9 dislocations/cm^2 in niobium. Using[76]

$$D = (h^2 v \gamma^2 b^2 / 28\ \underline{k}^2) N \qquad (51)$$

for a random array of dislocations, where h is Planck's constant, v the velocity of phonons, γ is Gruneisen's constant, b the magnitude of the

Burger's vector, k the Boltzmann constant, and N is the density of dislocations per unit area, to determine the change in κ with the number of dislocation lines, analysis of the observed change in κ_s yields 3×10^9 lines/cm^2, which is in surprisingly good agreement.

Conclusions

The thermal conductivity of superconductors is discussed from the viewpoint of the two-fluid model and the Bardeen-Cooper-Schrieffer theory. The significance of the ratio κ_s/κ_n is discussed and its dependence on T/T_c is shown to be a universal function independent of the particular element measured. The electronic thermal conductivity of superconductors with strong electron-phonon coupling differs markedly from typically weak superconductors like tin or indium. A theory is discussed to explain this phenomenon. The thermal conductivity in the superconductive state is discussed from the standpoint of: (a) the ideal resistance, (b) the residual resistance, (c) the lattice component, and (d) in the intermediate state. The existence of "gapless" superconductivity is shown in the theory of the thermal conductivity of superconducting alloys with paramagnetic impurities. Finally, the use of thermal conductivity to detect defects in superconductors is discussed.

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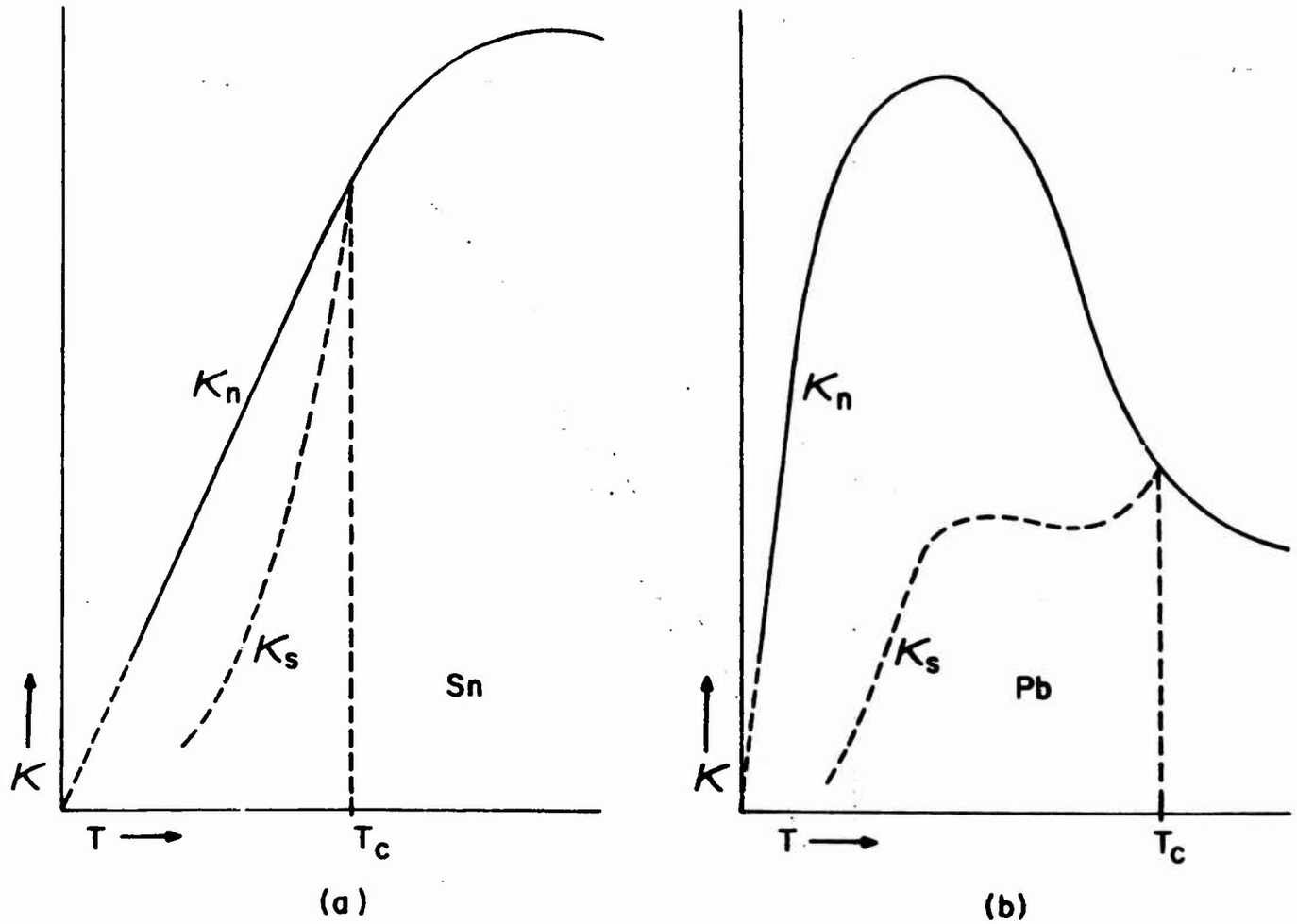

Fig. 1. The thermal conductivity of (a) tin and (b) lead in the normal and superconducting states.[8]

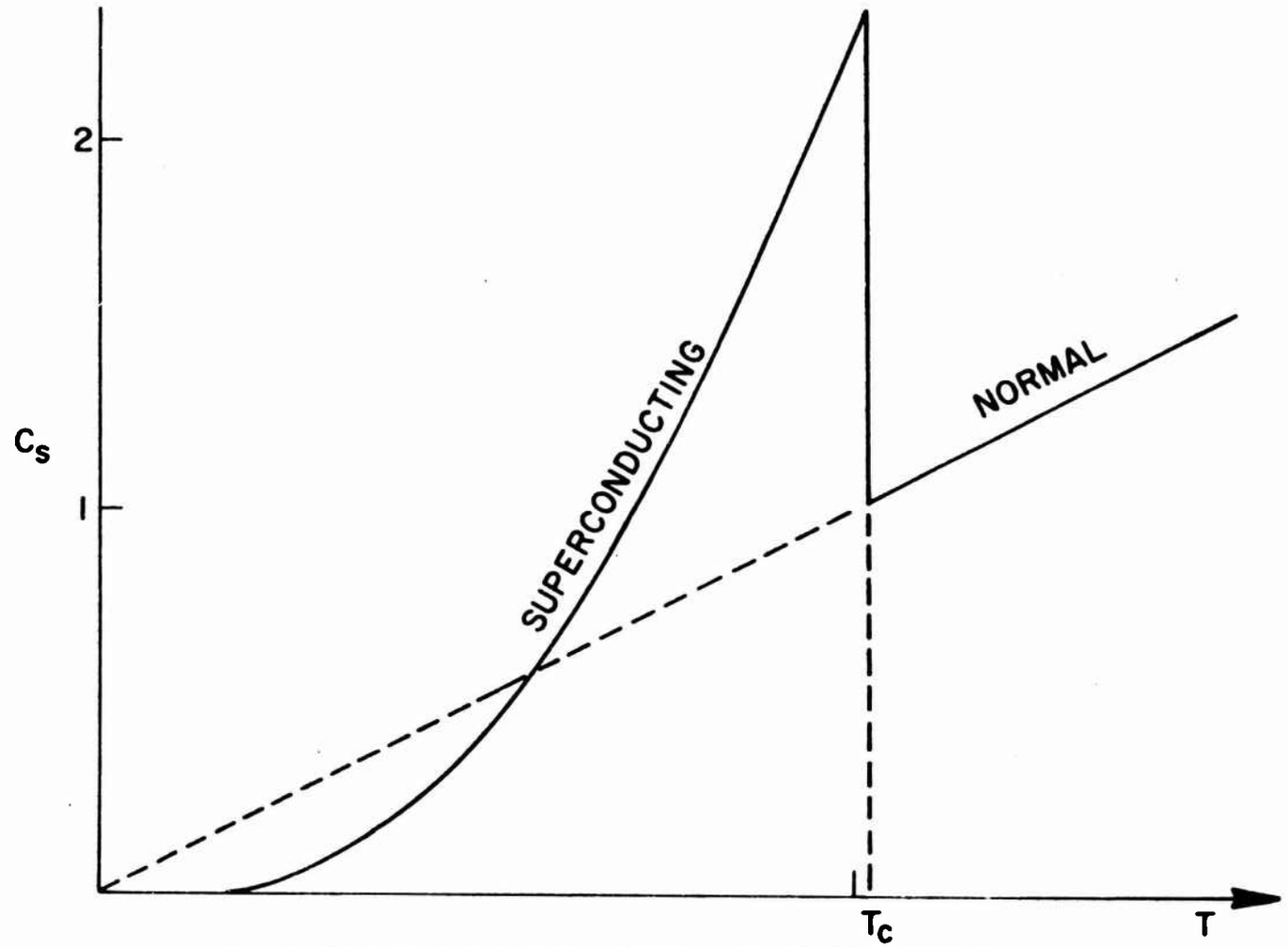

Fig. 2. Specific heat of superconductor, compared with electronic specific heat of normal metal.[12]

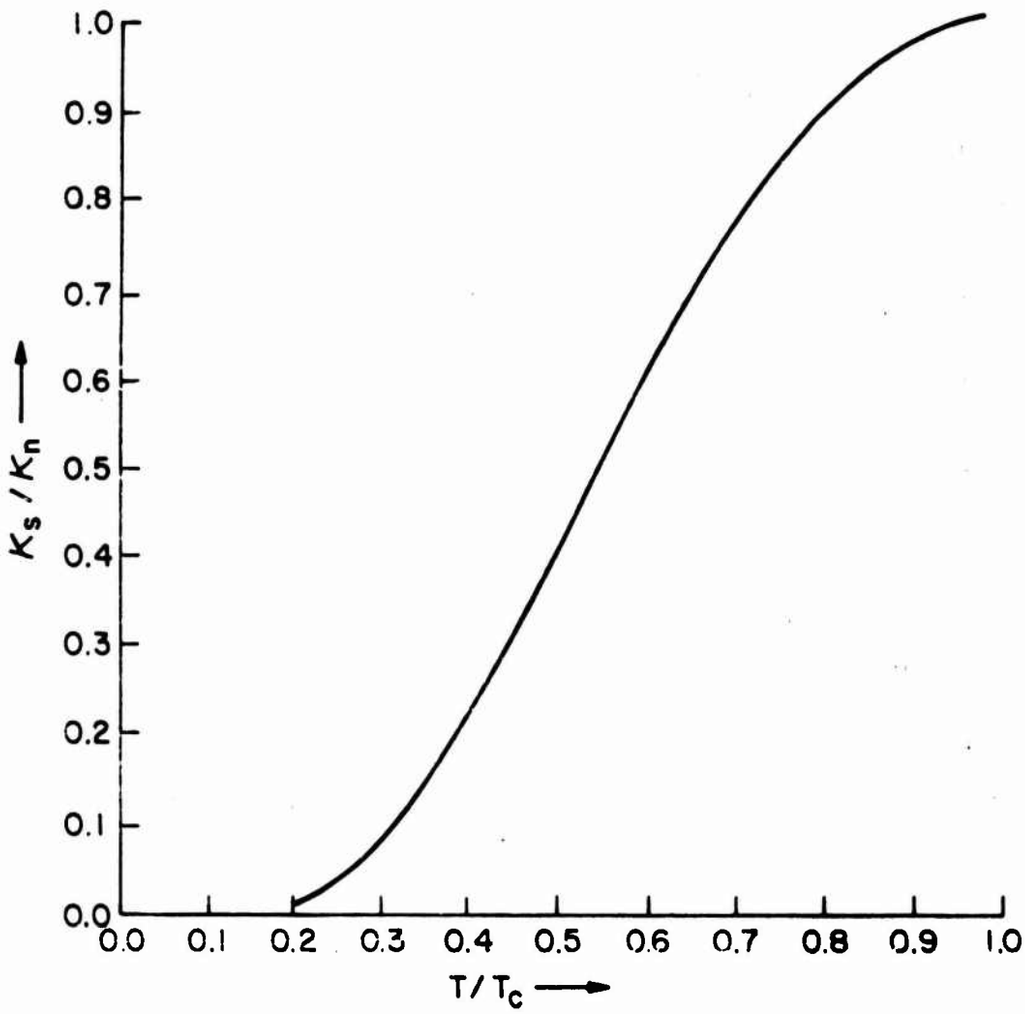

Fig. 3. The semiempirical function for κ_s/κ_n versus the reduced temperature.[8]

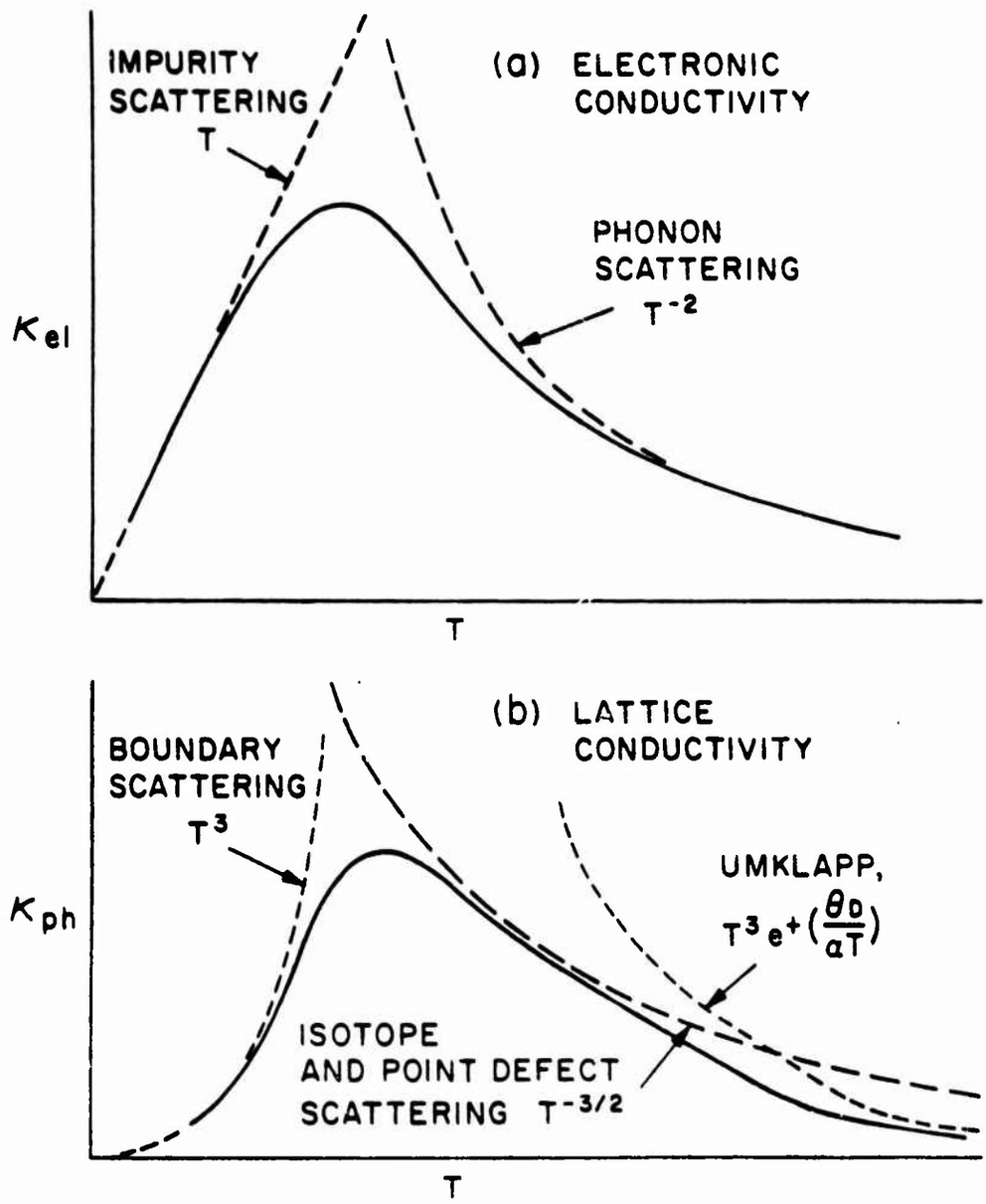

Fig. 4. Typical thermal conductivities (solid curves), and the effect of individual mechanisms (dotted curves).[15]

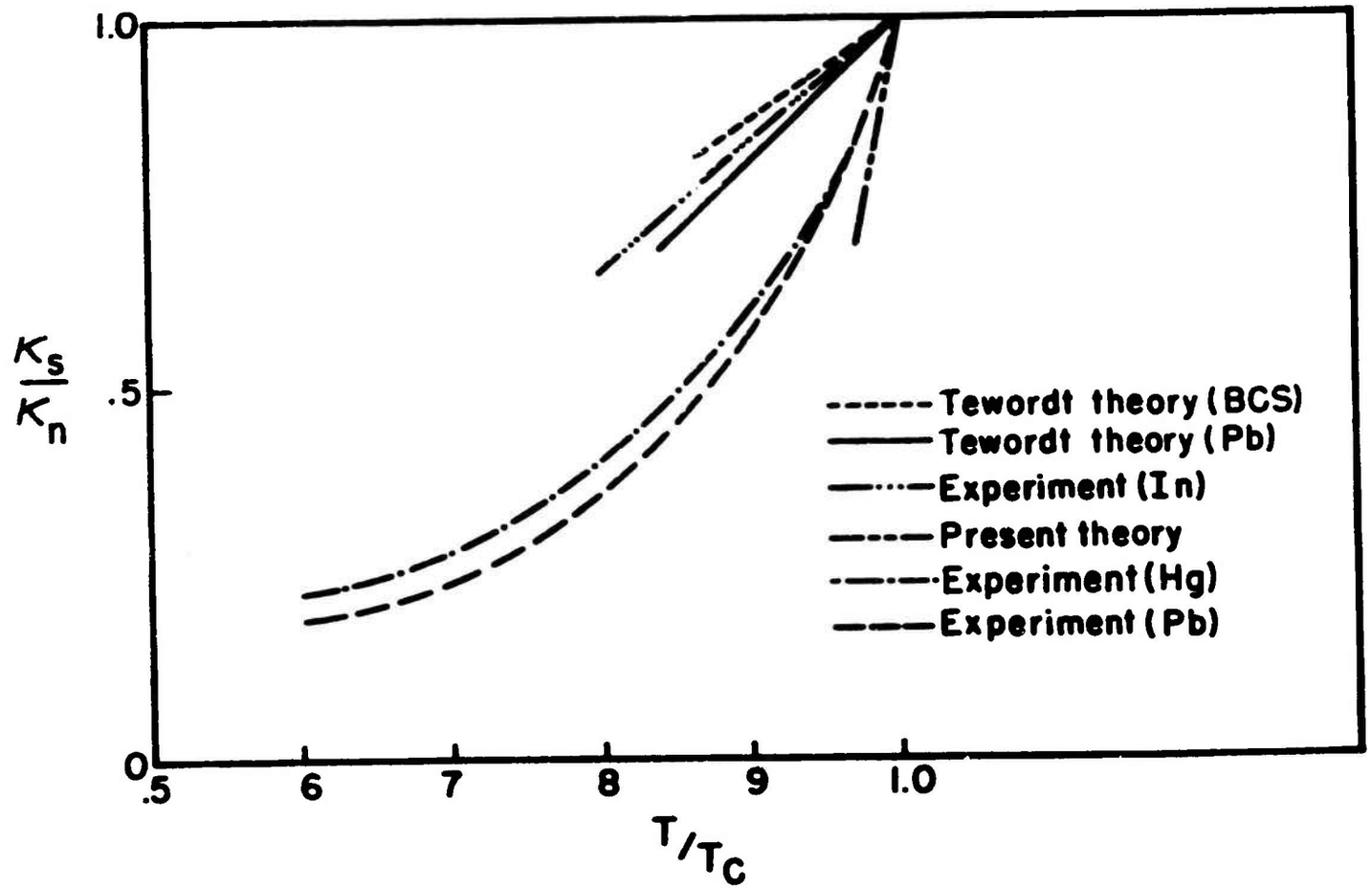

Fig. 5. κ_s/κ_n, ratio of the reduced thermal conductivity in the superconducting state to that in the normal state vs reduced temperature, T/T_c.[32]

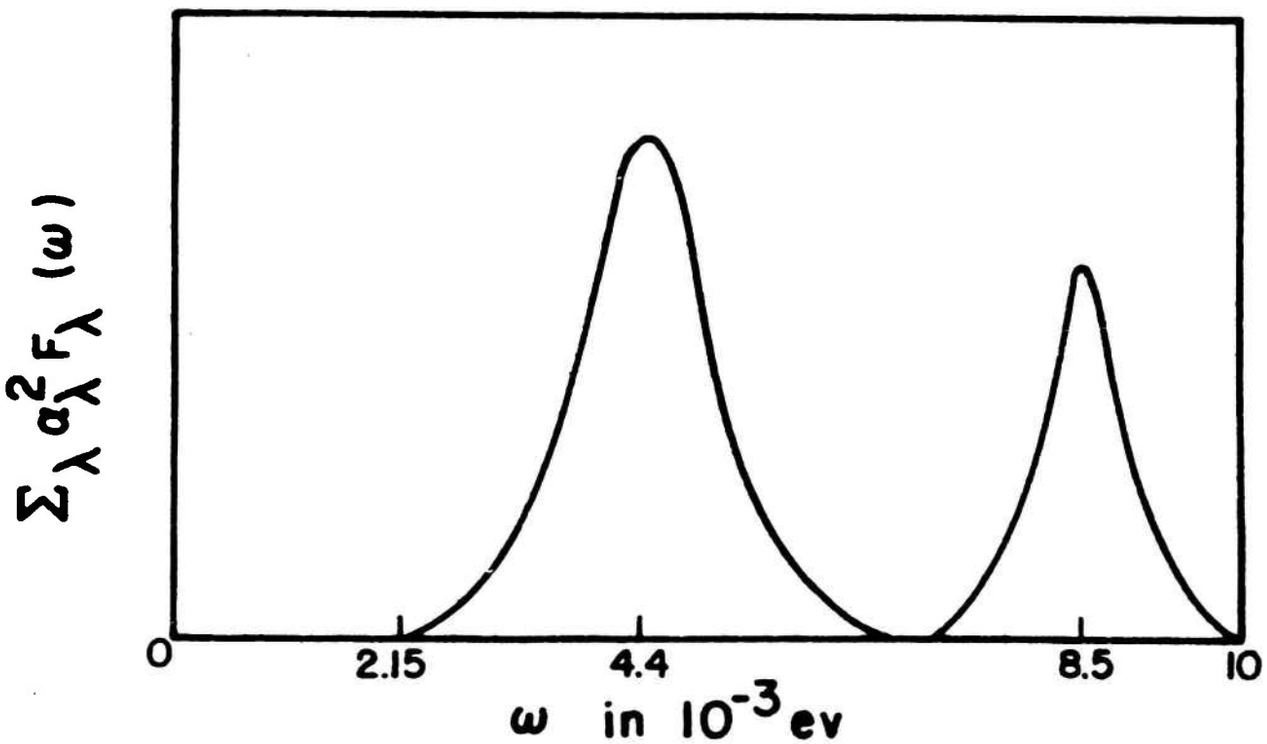

Fig. 6. Phonon spectrum for lead.[32]

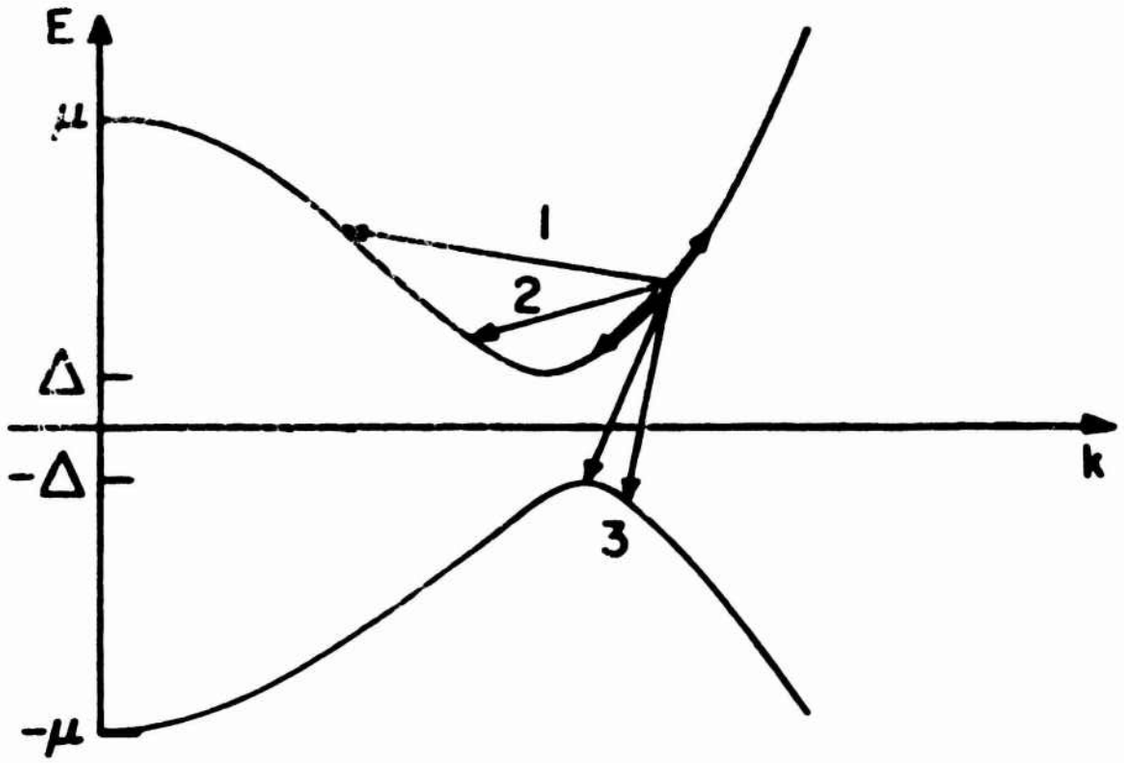

Fig. 7. Relaxation of quasiparticles by interaction with phonons. Processes 1 and 2 represent s ttering of a quasiparticle into another by phonon emission or absorption. 3 represents annihilation of quasiparticles to form a ground state pair.[3a]

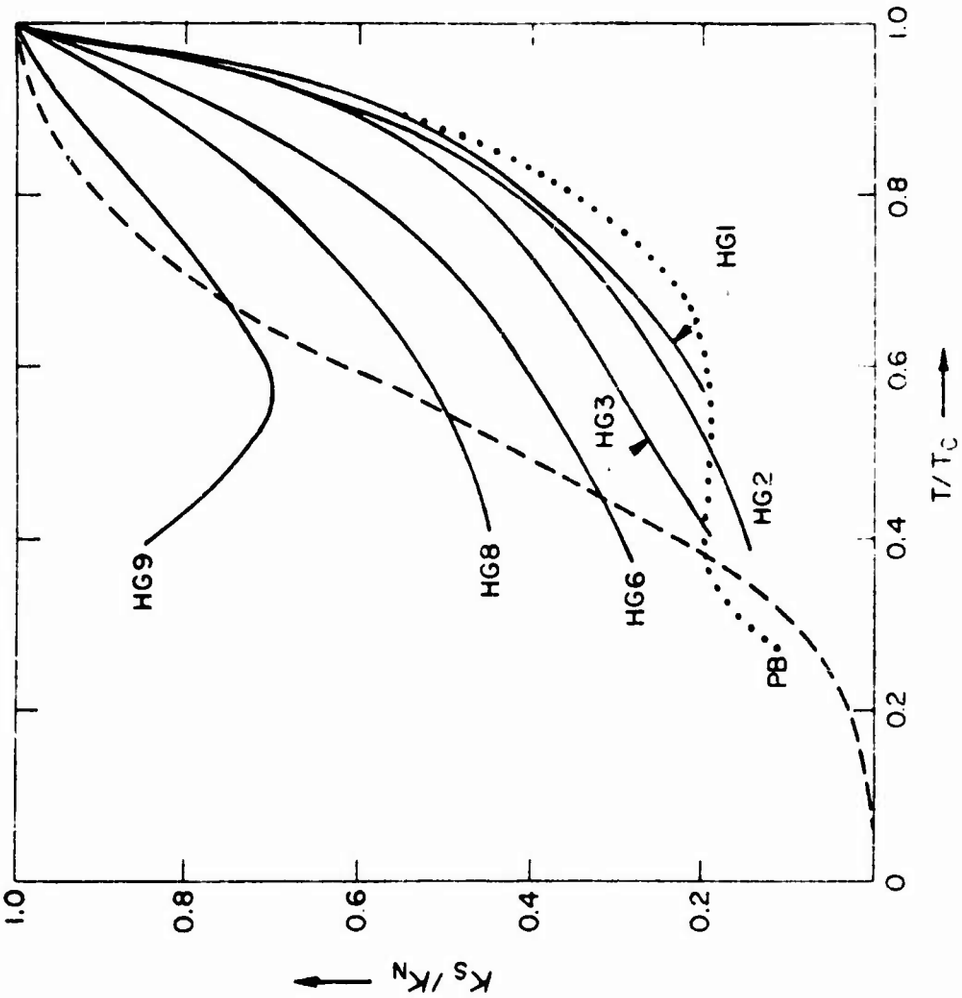

Fig. 8. κ_s/κ_n, ratio of the reduced thermal conductivity in the superconducting state to that in the normal state vs reduced temperature T/T_c of a number of mercury specimens, numbered in order of increasing residual resistivity, as well as a lead specimen (dotted curve). The dashed curve is the f-function [Equation (14)].

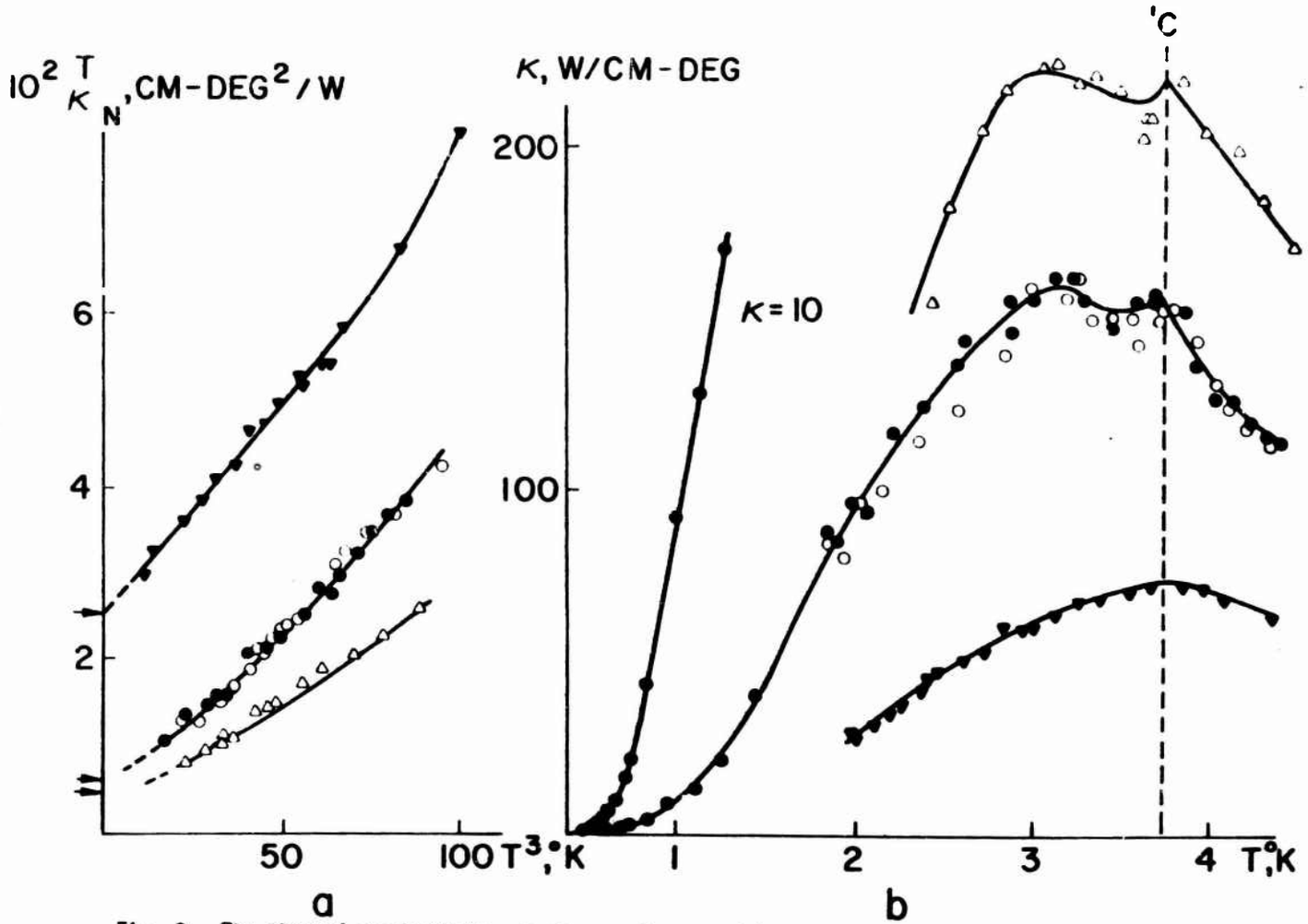

Fig. 9. The thermal conductivity of tin specimens: (a) normal state, (b) superconducting state, ○Sn-1, ●Sn-2, ▼Sn-3, △Sn-4. The arrows show the values of ρ_0/L_0T.[36]

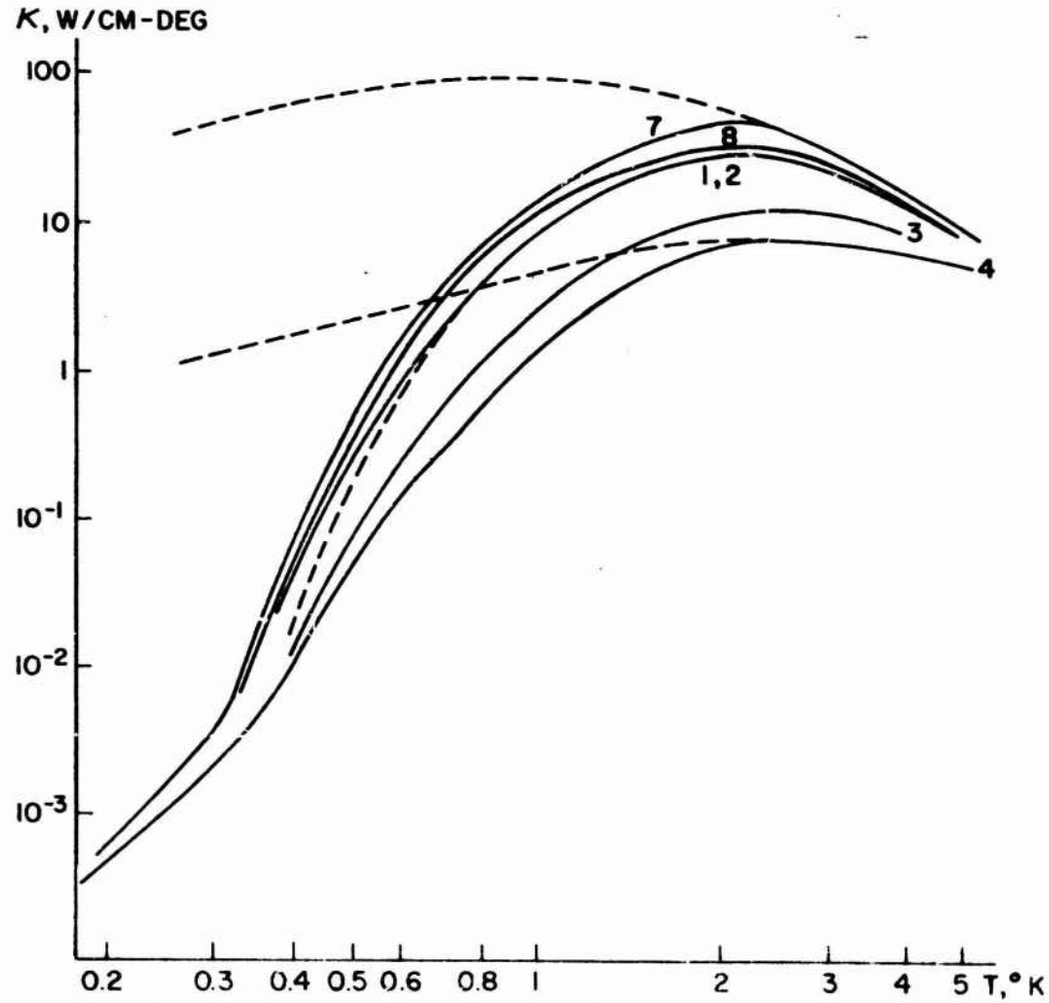

Fig. 10. The thermal conductivity of thallium specimens. The numbers of the corresponding specimens are shown on the curves. The dashed curves show the thermal conductivity in the normal state.[36]

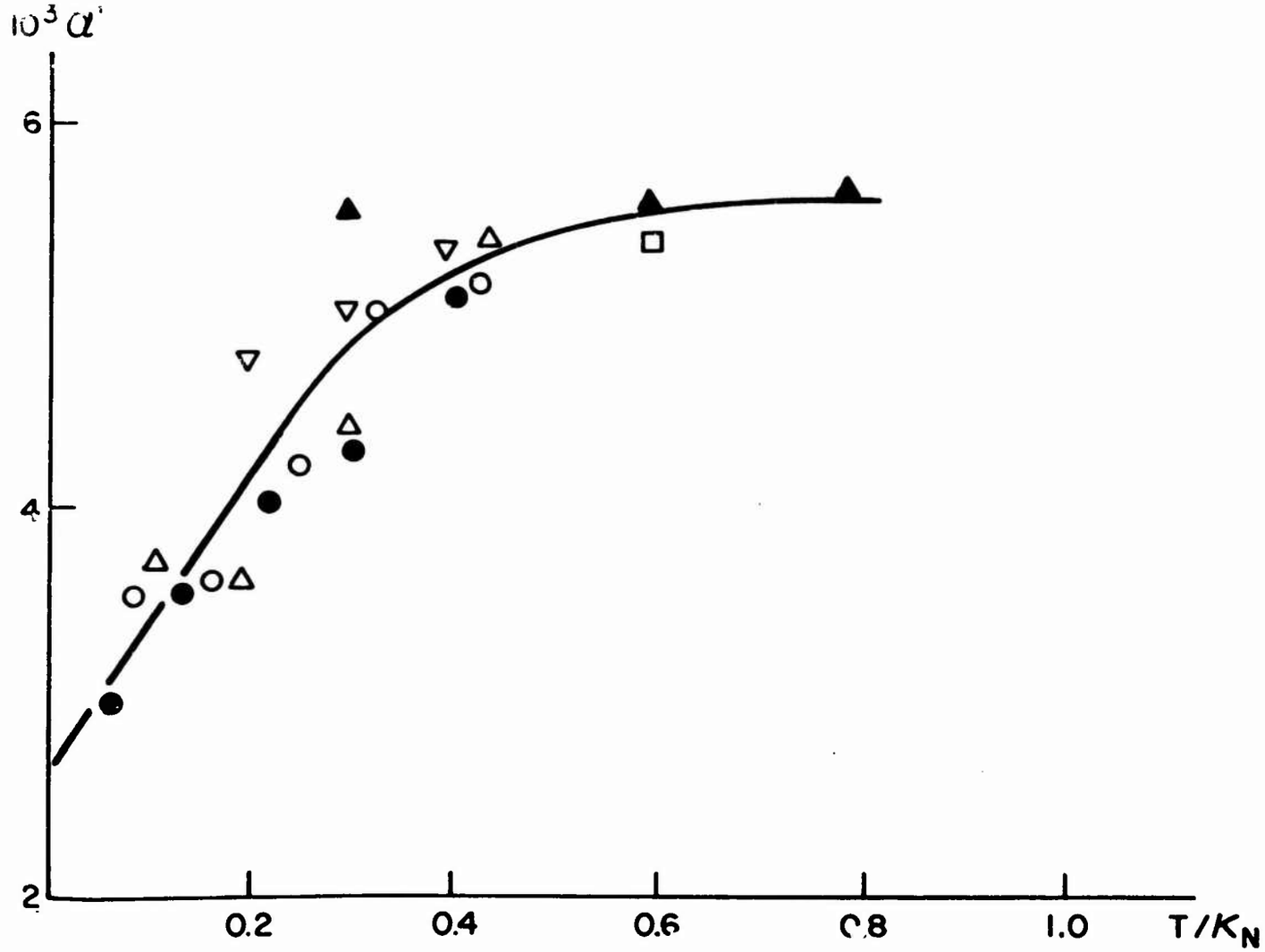

Fig. 11. The variation of α' with T/x_n for thallium specimens.[36]

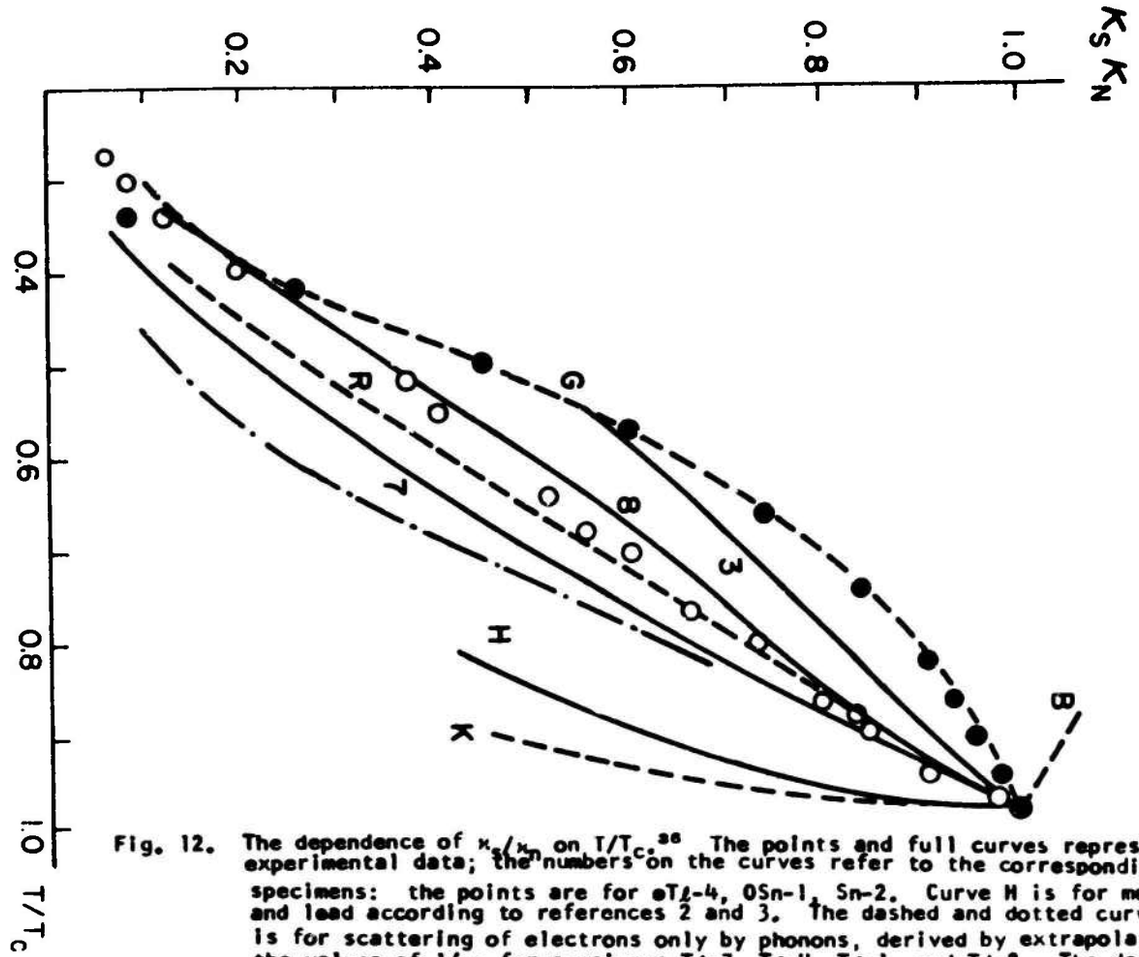

Fig. 12. The dependence of κ_s/κ_n on T/T_c.[36] The points and full curves represent experimental data; the numbers on the curves refer to the corresponding specimens: the points are for eTℓ-4, OSn-1, Sn-2. Curve H is for mercury and lead according to references 2 and 3. The dashed and dotted curve is for scattering of electrons only by phonons, derived by extrapolating the values of $1/\kappa_s$ for specimens Tℓ-7, Tℓ-8, Tℓ-1, and Tℓ-2. The dashed curves are theoretical: curve G is for the case of scattering of electrons by lattice defects[38], curves B, K, and R are for the case of scattering by phonons.[13 36 39]

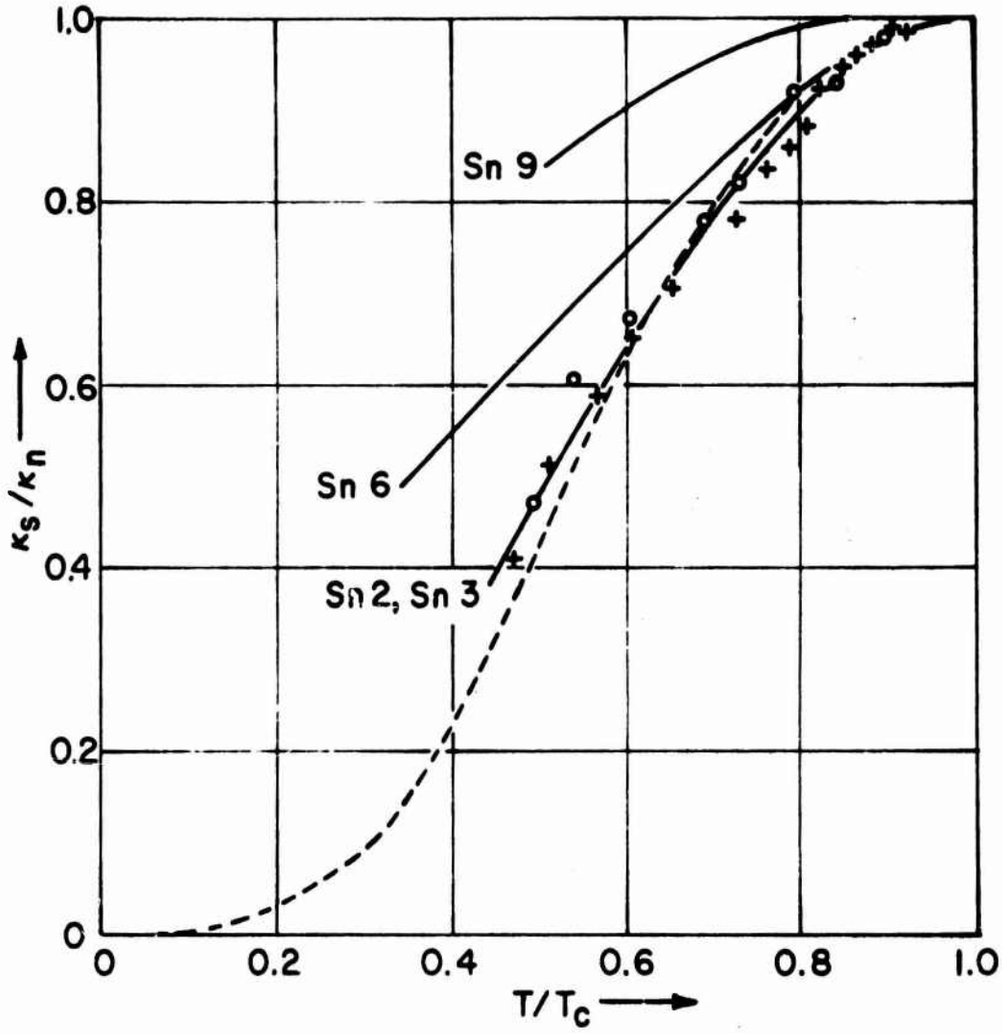

Fig. 13. κ_s/κ_n plotted against T/T_c for tin specimens, according to Hulm[3]; points O, Sn2 and +, Sn3 typical scatter; dashed line is Heisenberg-Koppe[10, 14] f-function (14).[4]

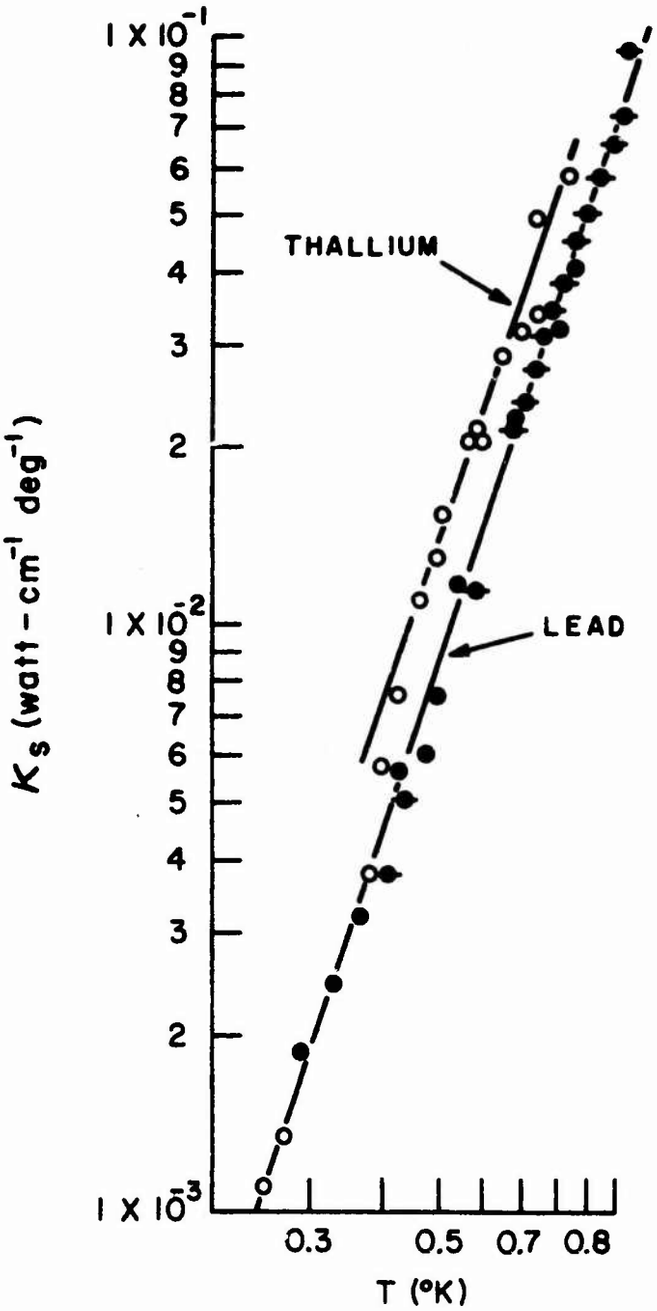

Fig. 14. A logarithmic plot showing the proportionality of κ_s at low temperatures with T^3 for lead and thallium.[8]

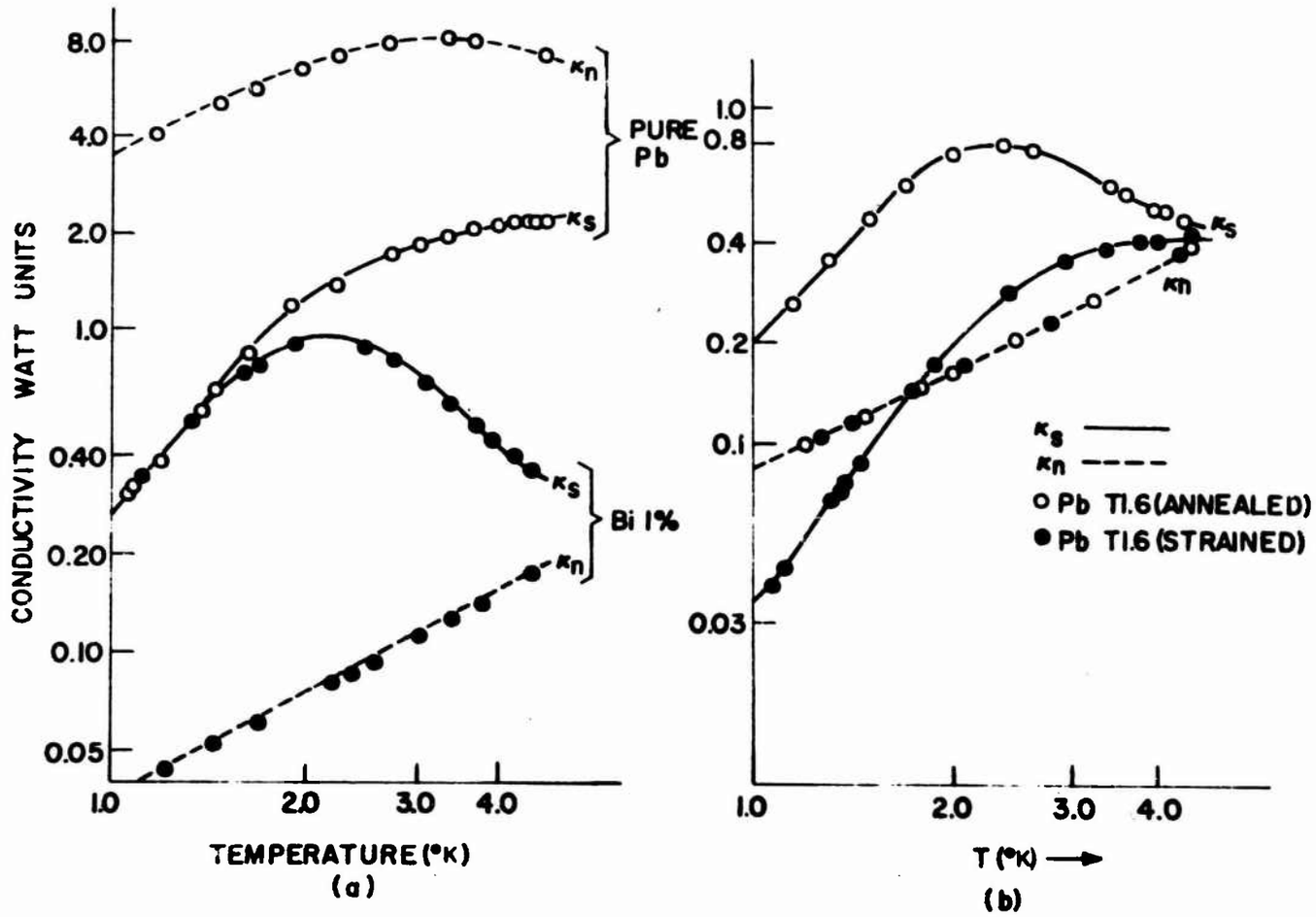

Fig. 15. The effect of (a) impurity and (b) strain on κ_s and κ_n in pure lead and in lead alloys. (b) Effect of strain on the conductivity of the specimen Pb T£0.6%.

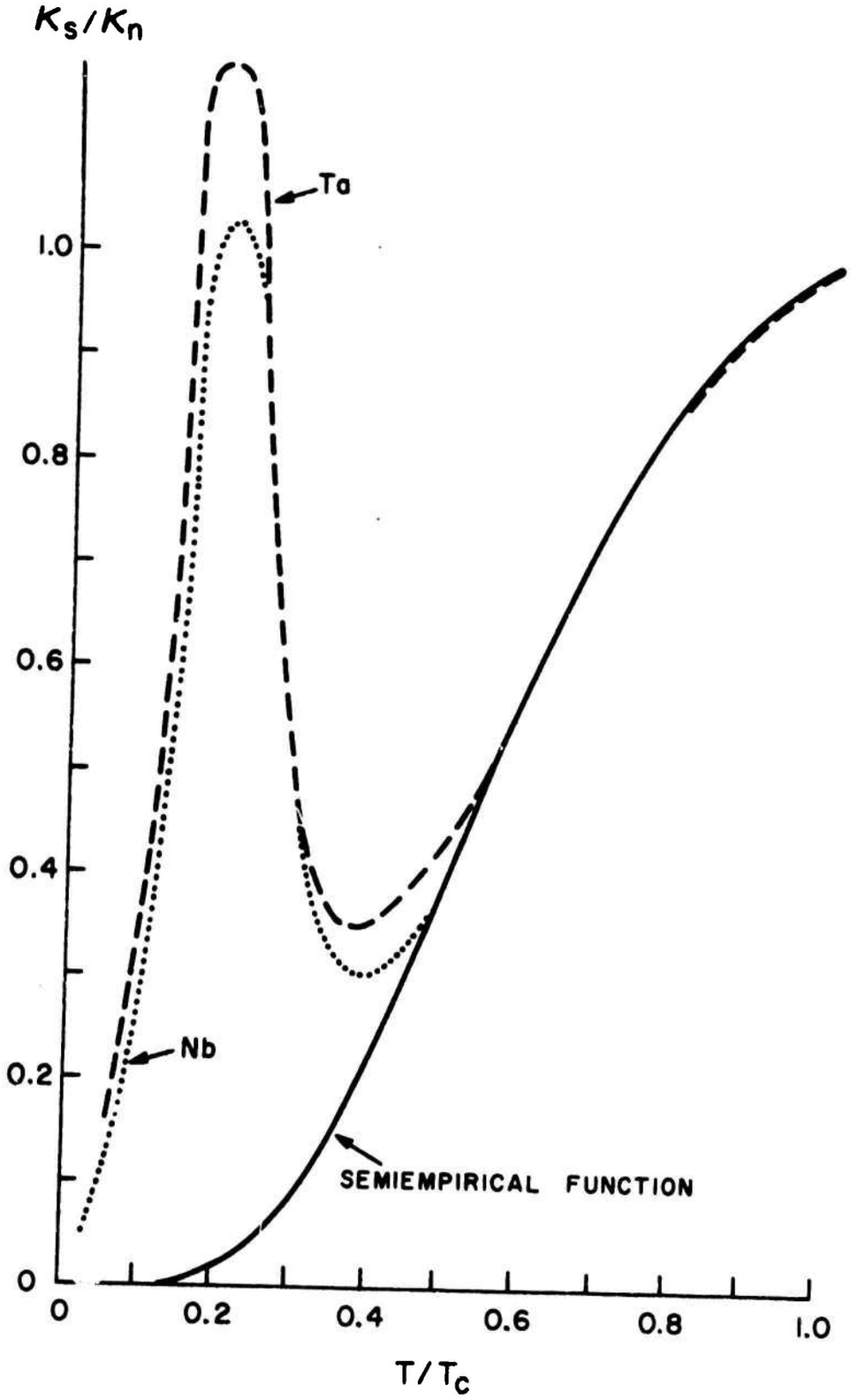

Fig. 16. κ_s/κ_n for tantalum and niobium single crystals.[8]

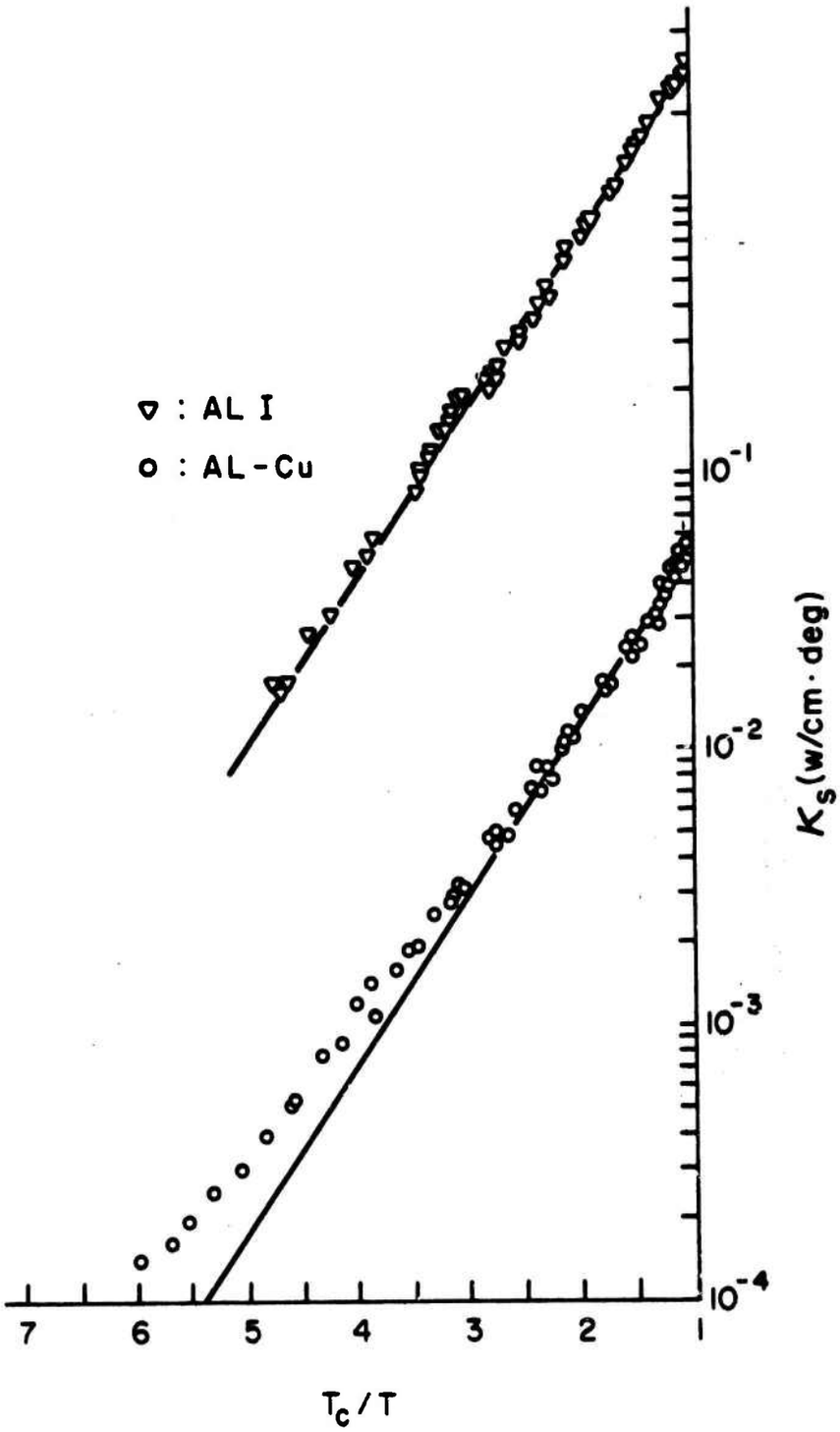

Fig. 17. κ_s for pure aluminum and an alloy with 1.7 atomic % copper.[8]

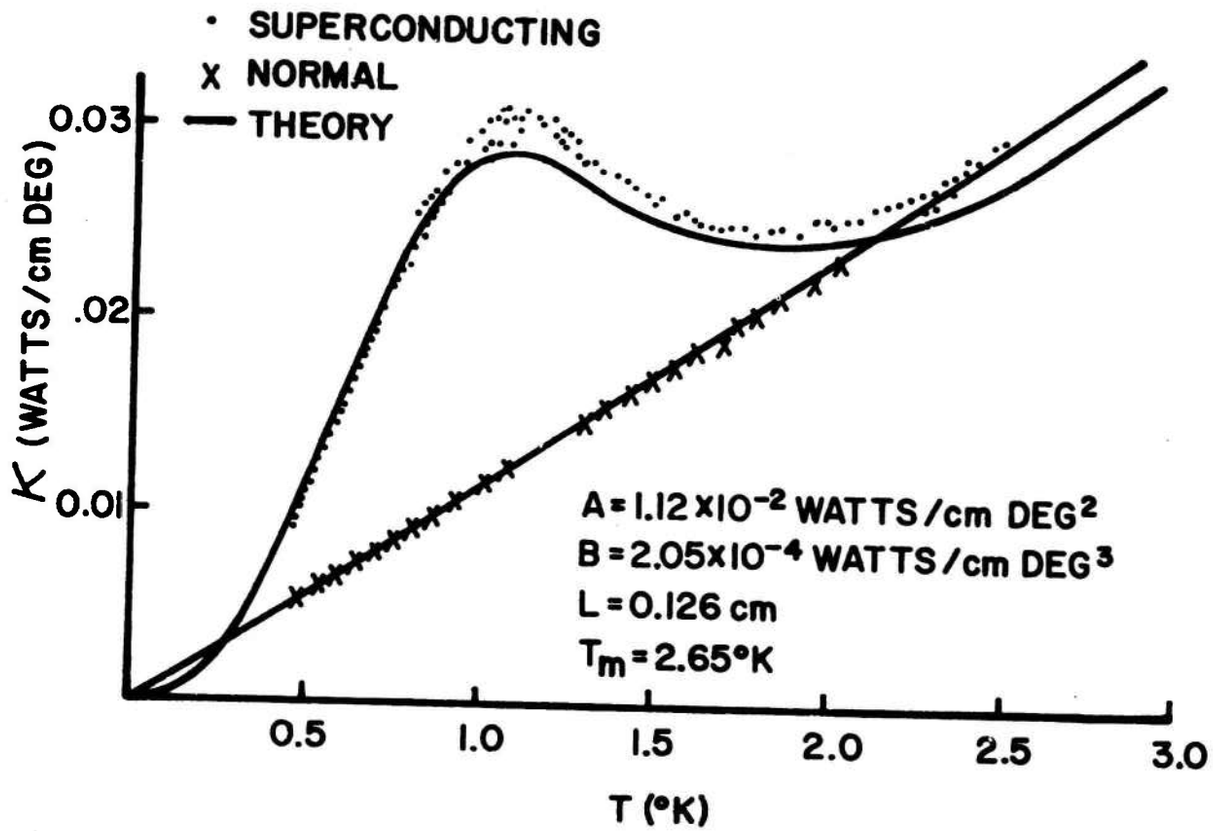

Fig. 18. Thermal conductivity versus temperature for In(4.05%Pb).[58]

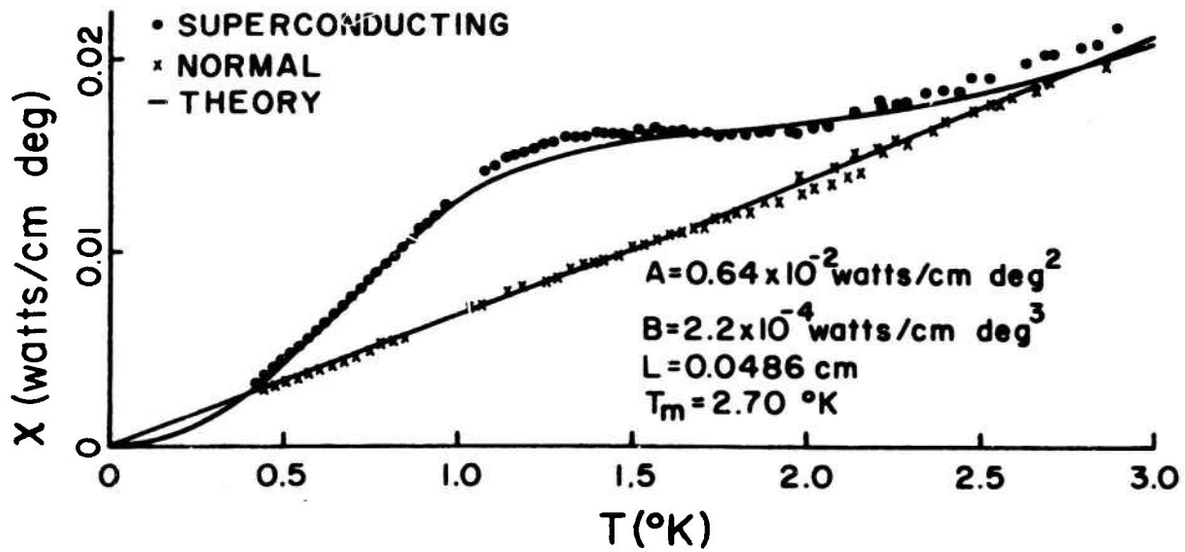

Fig. 19. Thermal conductivity versus temperature for In(7.31%Pb).[58]

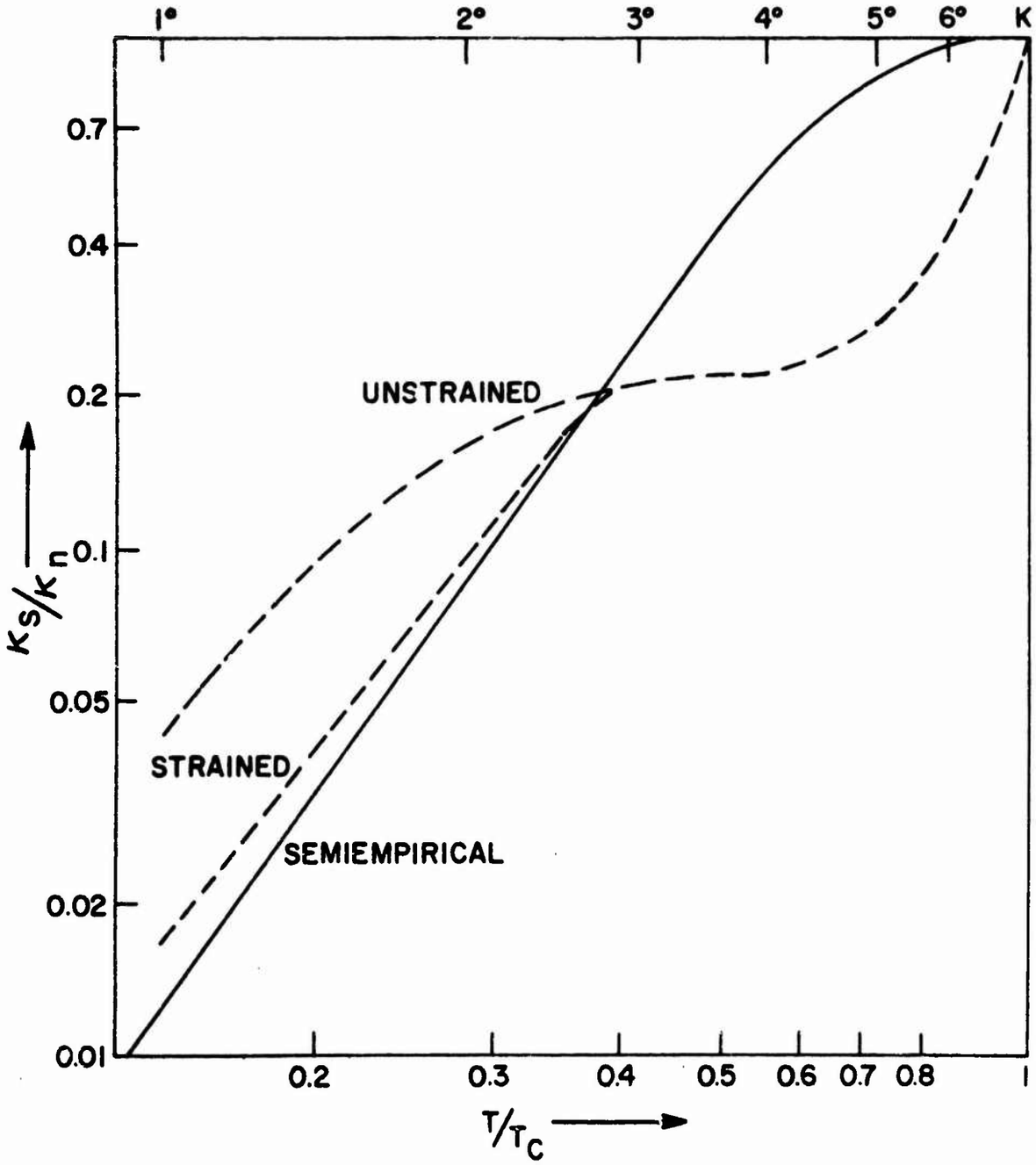

Fig. 20. The effect of strain on κ_s/κ_n versus T/T_c for lead.[8]

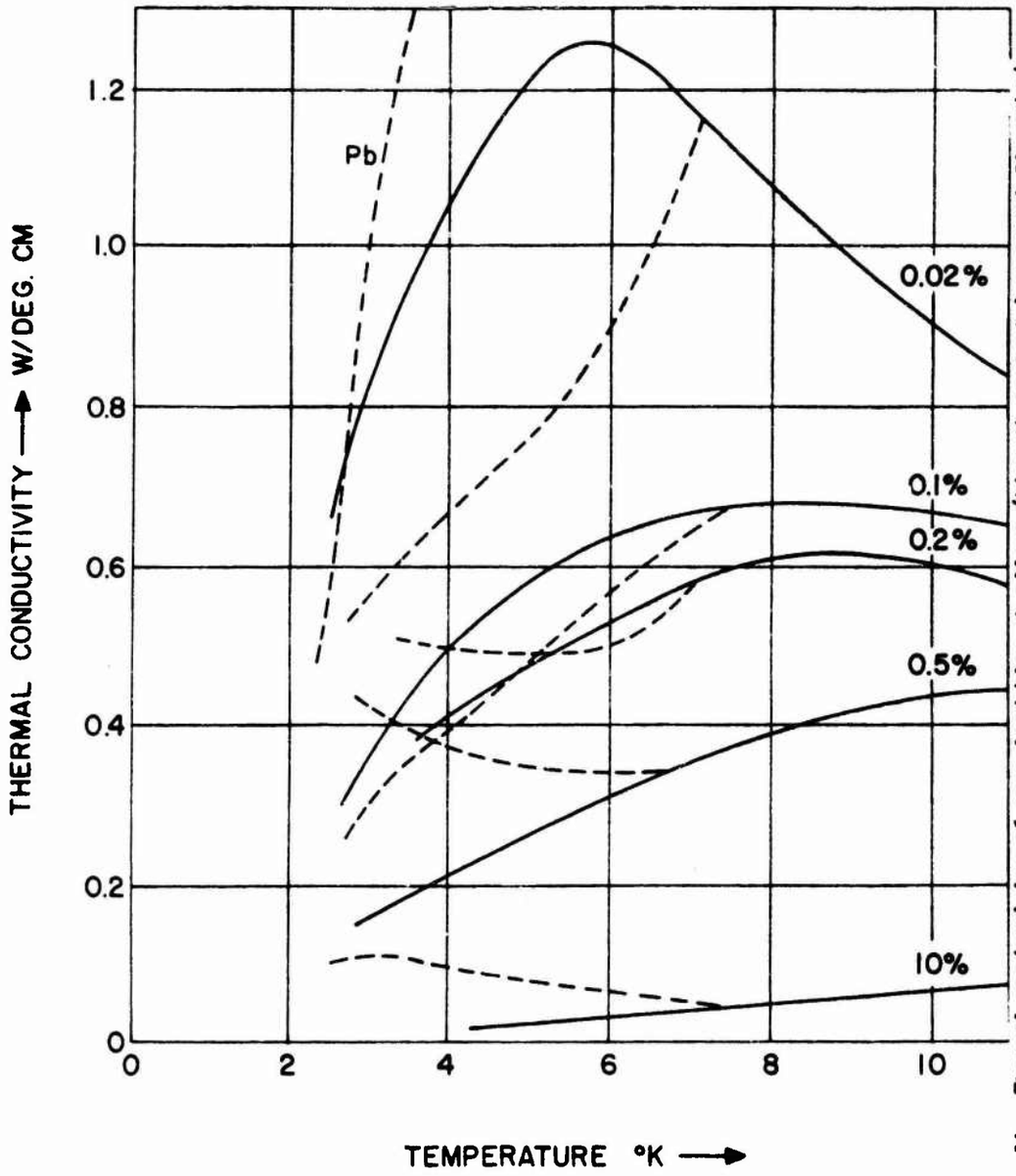

Fig. 21. Thermal conductivity of some lead-bismuth alloys (bismuth content in percent as marked on curves). Normal state, κ_s-solid line; superconductive state, κ_s-broken line.[4]

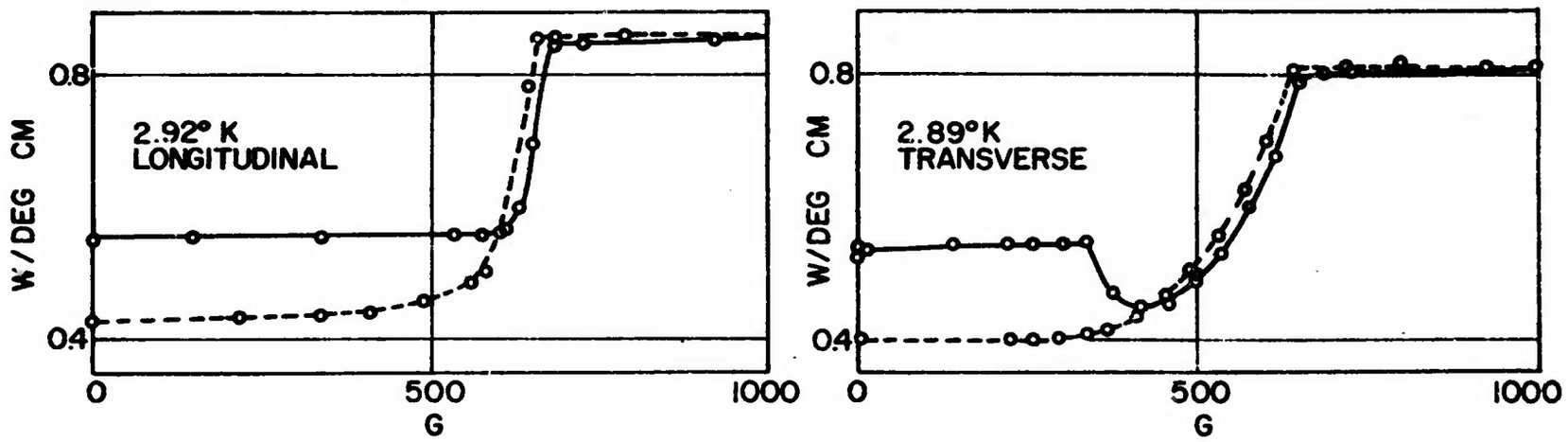

Fig. 22. Variation of the thermal conductivity of Pb-Bi 0.02% with longitudinal and transverse magnetic fields at about 2.9 °K. Solid line: field increasing; broken line: field decreasing.[4]

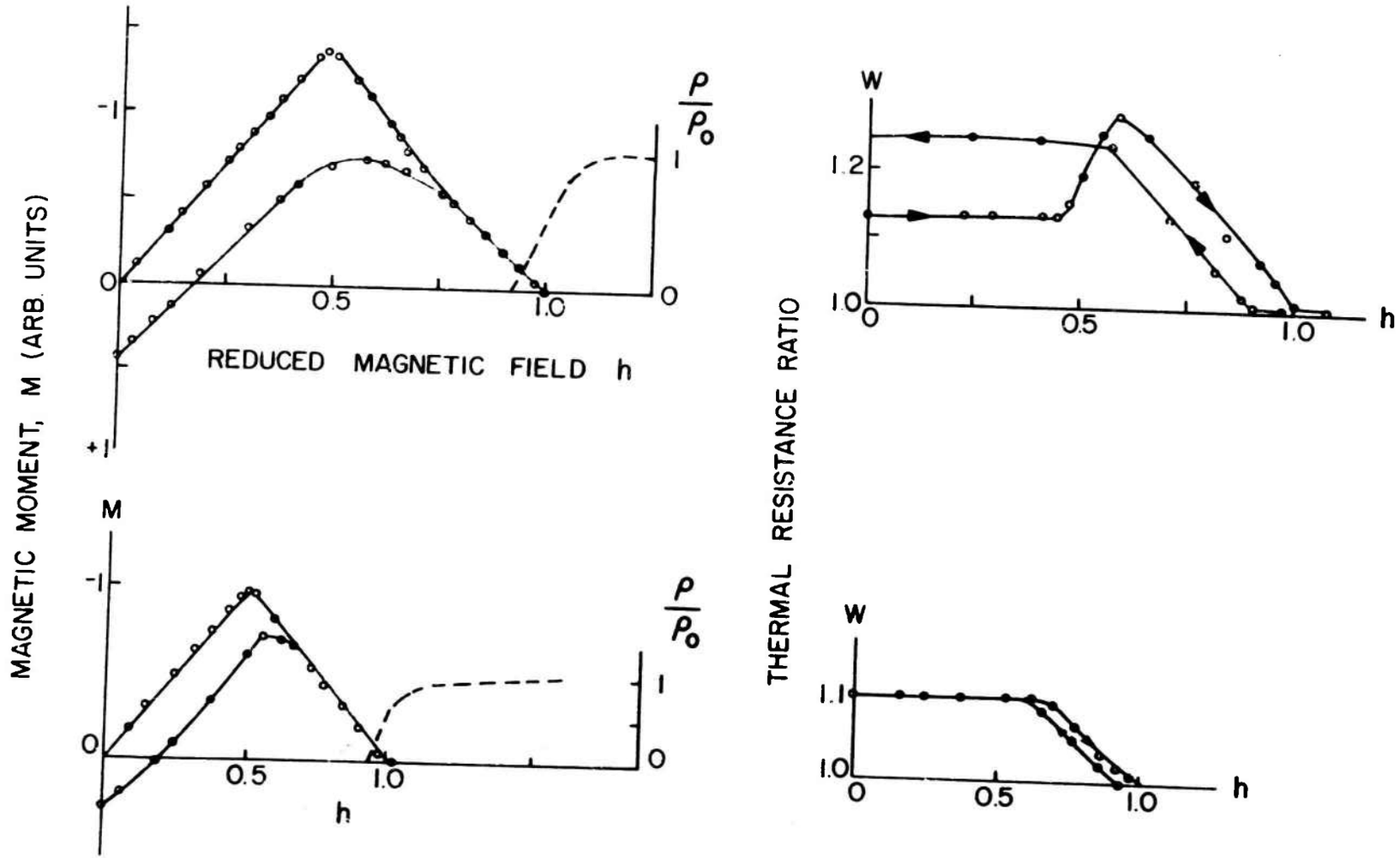

Fig. 23. Magnetic moment M, electrical resistance ratio ρ/ρ_0, and thermal resistivity ratio W of a tin cylinder with 2.8% indium during transverse destruction of superconductivity by a magnetic field. (a) 2.03 °K transverse field; (b) 2.65 °K transverse field.[8]

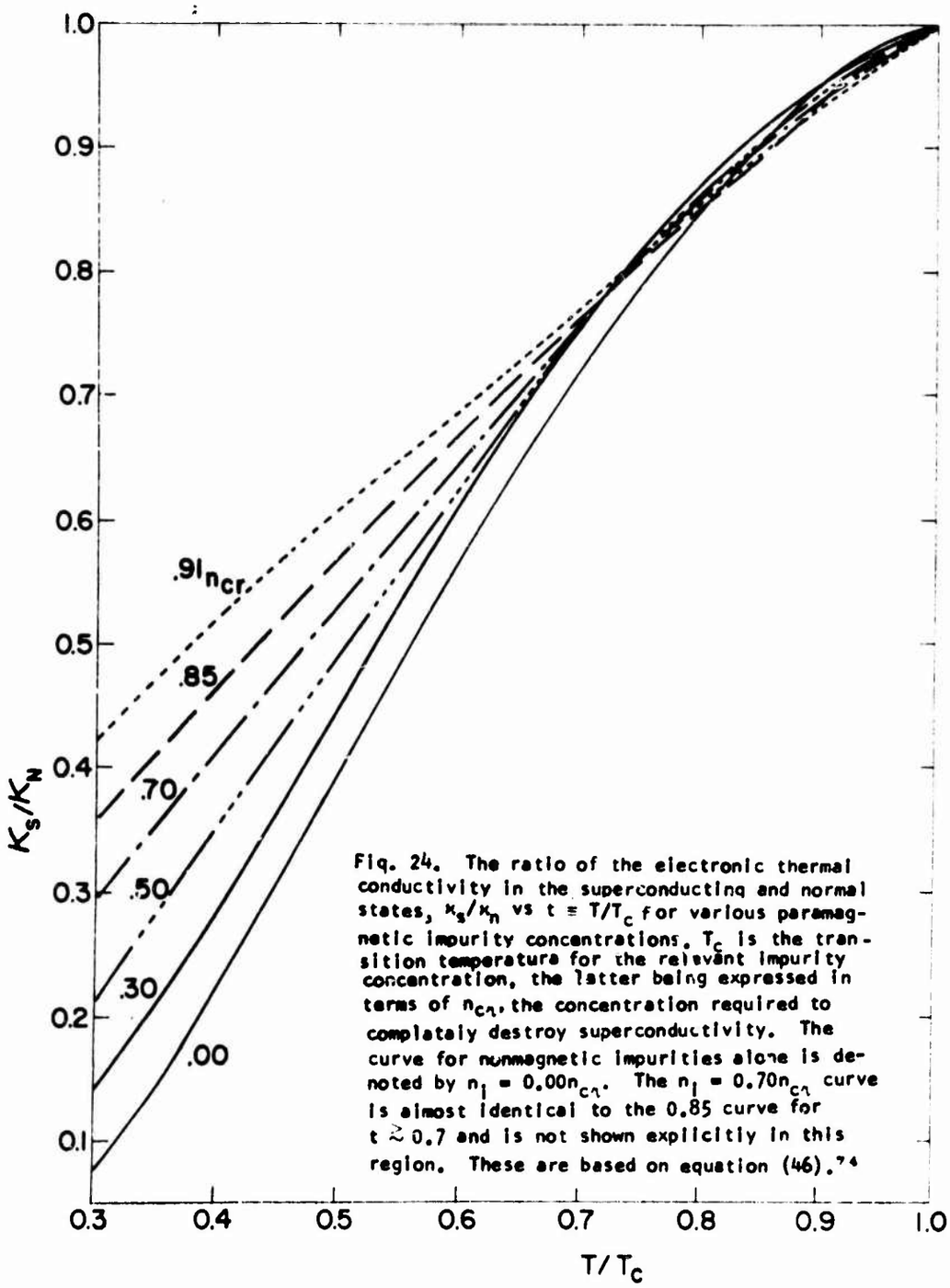

Fig. 24. The ratio of the electronic thermal conductivity in the superconducting and normal states, κ_s/κ_n vs $t \equiv T/T_c$ for various paramagnetic impurity concentrations. T_c is the transition temperature for the relevant impurity concentration, the latter being expressed in terms of n_{cr}, the concentration required to completely destroy superconductivity. The curve for nonmagnetic impurities alone is denoted by $n_I = 0.00n_{cr}$. The $n_I = 0.70n_{cr}$ curve is almost identical to the 0.85 curve for $t \gtrsim 0.7$ and is not shown explicitly in this region. These are based on equation (46).[74]

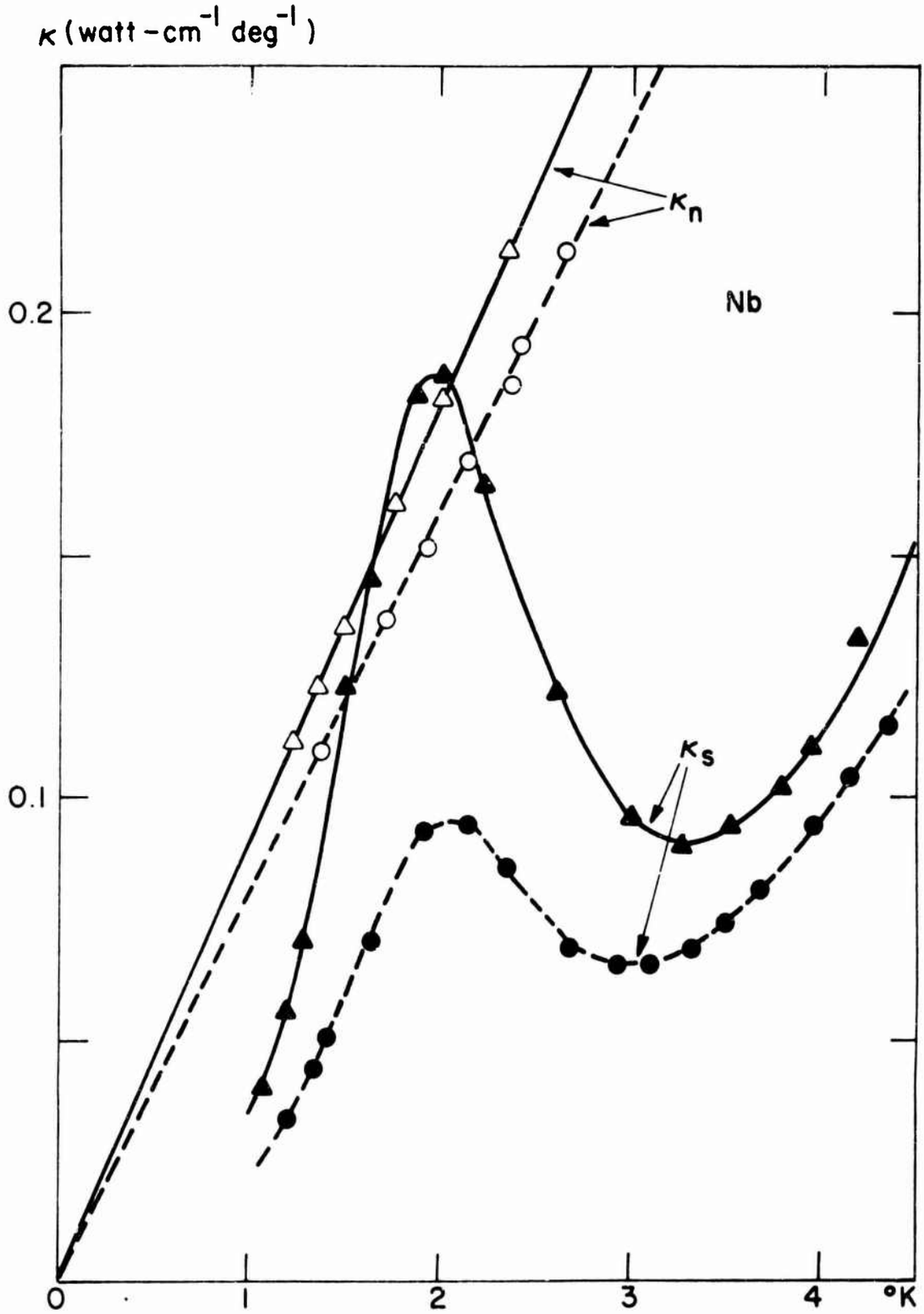

Fig. 25. Thermal conductivity of a niobium single crystal in the normal and superconducting states before (———) and after (---) neutron irradiation.[8]

TABLE 1 **Characteristics of Investigation Specimens**

Specimen	Orientation	Diameter, mm	$10^{11}\rho_0$, Ω·cm	d/l*	T/K_n ($T\to 0°K$)	$10^6\alpha_0$	$\rho_0/L\alpha T_c^3$	K_s/K_n $T/T_c=$ 0.9	0.8	0.6
Sn-1	[001]	2.6	1±0.5	2.6	—	} 2.8	0.25÷0.35	0,83	0.7	0,48
Sn-2	[001]	1.1	1.65±0,2	1.7	—					
Sn-3	[001]	1,5	6.1	8.6	—	5	1	0,89	0.77	—
Sn-4	[110]	2,1	1.2 ±0.5	2.5	—	2.0	0,3÷0.5	0,75	0,6	—
Tl-7	30°**	1.6	2.4 ±0,3	1	0,7	30(±10%)	0.14÷0,2	0.86	0.67	0.35
Tl-8***	30°	0.9	4,5	1	1.8	35	0.28	0,84	0,74	0.46
Tl-1	80°	1	8.1	2.2	} 3	35	0.6	0.9	0,82	0.47
Tl-2	40°	1.3	6.5	4.7						
Tl-3	20°	1	26	6.7	11	48	1,6	0,9	0.80	0.62
Tl-4	80°	1.1	50	13.5	20	56	2,6	0.95	0.86	0.64

*Rough values. For Sn we took $\rho_0 l = 1.05 \times 10^{-11}$; anisotropy is neglected. Tl we took $\rho_0 l = 4 \times 10^{-11}$ as a result of an analysis of the results of measuring ρ for specimens Tl-7 and Tl-8.

**Angles made with the hexagonal axis.

***Obtained by etching specimen Tl-7.

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)

U.S. Army Electronics Command
Fort Monmouth, New Jersey

2a. REPORT SECURITY CLASSIFICATION

Unclassified

2b. GROUP

3. REPORT TITLE

THERMAL CONDUCTIVITY OF SUPERCONDUCTORS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Technical Report

5. AUTHOR(S) (First name, middle initial, last name)

Irving N. Greenberg

6. REPORT DATE

December 1969

7a. TOTAL NO. OF PAGES

54

7b. NO. OF REFS

76

8a. CONTRACT OR GRANT NO.

b. PROJECT NO.

c. DA-1-T0.61102.B.1A.01.26

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

ECOM-3200

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT (1)

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11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

Institute for Exploratory Research
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13. ABSTRACT

This report is one of a series which is intended to inform the reader on the present status of the thermal conductivity in solid materials. The first of the series was USAELRDL Technical Report 2361, dated May 1963, which gave a general overall picture of the field but specifically discussed the conductivity of dielectric solids (insulators). This was followed by Technical Report ECOM-2799, dated February 1967, which dealt with concepts mainly applicable to metals, such as: a. The electronic component of thermal conductivity and its relation to the free electron theory. b. The relationship between electrical and thermal conductivity, as exemplified by the Wiedmann-Franz-Lorenz law, and the limitations of the law. c. Electron-lattice wave scattering, and the restrictions on the theory. Next in the series was Research and Development Technical Report ECOM-2932, dated February 1968, wherein considerations mainly applicable to semiconductors and semimetals were discussed, such as:

a. The influence of carrier concentration and degeneracy on the thermal conductivity of both extrinsic and intrinsic semiconductors, and on the Wiedmann-Franz-Lorenz law. b. The electronic component of the thermal conductivity, in terms of both holes and electrons, for an extrinsic semiconductor. c. The transport properties of an intrinsic semiconductor. d. The thermal resistance in semiconductors arising from free electrons (holes).

After this, Research and Development Technical Report ECOM-3026, dated September 1968, was written. This treated the lattice component of thermal conductivity in metals,

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14 KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Superconductivity Theory and Experiment Two-fluid model Alloys with paramagnetic impurities Retect detector						

13. Abstract (Cont)

alloys, and semiconductors and the influences affecting it. Phonon scattering processes were described by a relaxation time.

Since all intrinsic resistivities are proportional to $C^2 \sum_j C_j^2$, and since the coefficients C_j cannot be obtained from first principles, the lattice component was expressed in terms of the intrinsic electronic component of thermal conductivity. The residual thermal resistivity was also considered. The influence of the ideal or intrinsic electronic thermal resistivity and that of the residual thermal resistivity on the total thermal conductivity was discussed. A rather detailed discussion was given of the methods of separating the measured thermal conductivity into the electronic and lattice components. The intrinsic lattice component of thermal conductivity and influences affecting it were considered rather completely. A fairly exhaustive treatment of the effect of crystal imperfections on the lattice thermal conductivity was given.

In the present report we discuss the thermal conductivity of superconductors from the viewpoint of theory set forth in the previous reports plus considerations from the theory of superconductivity.

ESC-FM 1658-63