Thermal Conductivity of Superconducting Indium Alloys near the Upper Critical Field*

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The thermal conductivity of several indium-bismuth specimens has been measured as a function of magnetic field and temperature between 0.3 and 4.2°K. The main emphasis is on the region near the upper critical field, where a linear variation of the electronic thermal conductivity with magnetic field is expected. The experimental results are in good agreement with the calculations of Caroli and Cyrot above a reduced temperature of 0.4, but, below that temperature, the experimental values of the slope are lower than the theoretical values by up to 30%. It is possible to account for the discrepancy by assuming a more rapid variation with temperature of the parameter κ_2/κ than that which is theoretically expected. For the comparison with theory, it was necessary to separate the electronic and lattice conductivities, and to analyze the lattice term into its contributions from the various scattering mechanisms. A correction could then be made for the field variation of the lattice conductivity. From the critical fields, the product of the electronic mean free path and the residual electrical resistivity was determined to be $0.56\times10^{-11}\ \Omega\ \text{cm}^2$. The data also lead to a value for the coherence length of indium of 3540 Å.

INTRODUCTION

IF the thermal conductivity of a type-II superconductor is measured as a function of magnetic field it is, under certain circumstances, observed to go through a deep minimum. Minima in the variation of the thermal conductivity with field can also occur when an intermediate-state structure exists and since the early measurements focused on the intermediate state the distinctive behavior of type-II superconductors was not at first recognized.[1] The first observations which unambiguously showed the presence of a minimum in the absence of an intermediate state were those of Sladek[2] who prophetically used the term "mixed state" long before the vortex structure of type-II superconductors was known.

A detailed analysis of the variation of the thermal conductivity with field was attempted by Dubeck, Lindenfeld, Lynton, and Rohrer[3] for their own measurements on indium alloys as well as for the earlier ones of Sladek. They showed that the behavior could be understood at least qualitatively by considering the spatially averaged energy gap and its variation with field, with the help of the dependence of the thermal conductivity on the energy gap as calculated by Bardeen, Rickayzen, and Tewordt.[4] They demonstrated that the phonon conductivity should be expected to drop abruptly as the magnetic field is increased beyond the lower critical field H_{c1}, while the electron conductivity increases relatively slowly towards its value in the normal state which it reaches at the upper critical field H_{c2}. In the common case where the conductivity is mainly by phonons in the superconducting state and mainly by electrons in the normal state, the passage through the mixed state will then result in a minimum, whose depth will depend on the magnitudes of the two components of the thermal conductivity.

Soon afterwards Caroli and Cyrot[5] pointed out that the use of an average energy gap was inappropriate near the upper critical field, since, in fact, there was no energy gap in that region. They made a calculation which took into account the magnetic field as well as the spatial variation of the order parameter. They found that the electronic thermal conductivity should depend linearly on field near H_{c2}, in agreement with the experiments but in contrast to the prediction of the average energy-gap analysis.

A quantitative comparison of the measured and calculated slopes showed the measured slopes to be consistently low, with the discrepancy greatest in the most impure specimens. Further measurements were made by Lindenfeld, Lynton, and Soulen,[6] who demonstrated that the phonon conductivity and its variation with field should not be neglected even near the upper critical field and showed that better agreement between theory and experiment could be obtained if this variation is taken into account. Except for somewhat doubtful measurements on one specimen in the He^3 range, their work was done between 1.5°K and T_c. The limited temperature range made it difficult to analyze the thermal conductivity into its various components and limited the precision of their analysis. They concluded that theory and experiment agreed within about 25%. Similar measurements, also on indium alloys above 1.5°K, were reported by Muto, Noto, Mamiya, and Fukuroi.[7] The present experiments were therefore undertaken over a

* Supported by the National Science Foundation.
[1] See, for example, K. Mendelssohn and C. A. Shiffman, Proc. Roy. Soc. (London) **A255**, 199 (1960).
[2] R. J. Sladek, Phys. Rev. **97**, 902 (1955).
[3] L. Dubeck, P. Lindenfeld, E. A. Lynton, and H. Rohrer, Phys. Rev. Letters **10**, 98 (1963).
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[5] C. Caroli and M. Cyrot, Phys. Condensed Matter **4**, 285 (1965).
[6] P. Lindenfeld, E. A. Lynton, and R. Soulen, in *Proceedings of the Tenth International Conference on Low Temperature Physics, Moscow, 1966*, edited by M. P. Malkov (Proizvodstrenno-Izdatel'skii Kombinat, VINITI, Moscow, 1967), p. 396.
[7] Y. Muto, K. Noto, T. Mamiya, and T. Fukuroi, J. Phys. Soc. Japan **24**, 992 (1968).

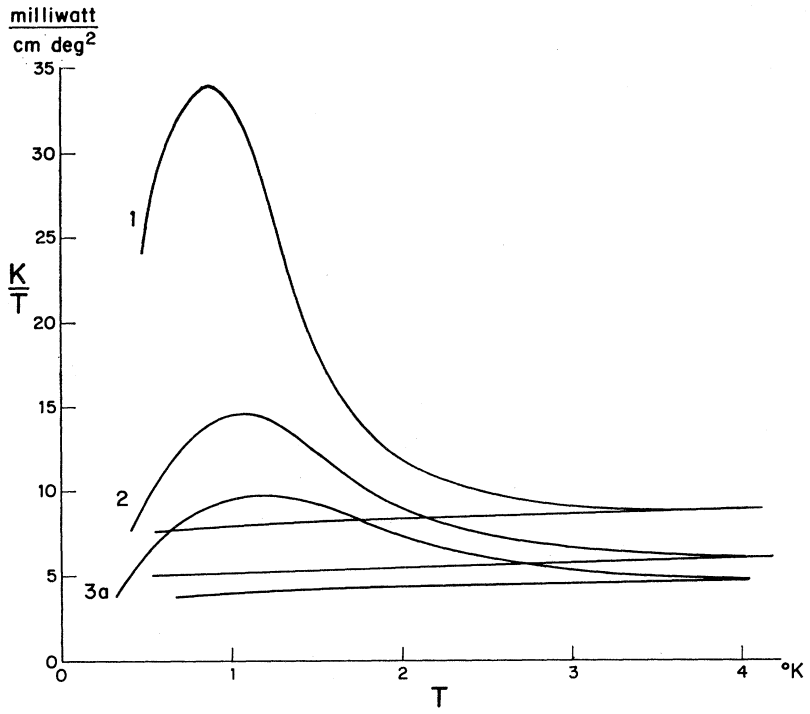

FIG. 1. Thermal conductivity of specimens 1, 2, and 3a plotted as K/T against T. In each case the upper curve represents the results in the superconducting state and the lower curve the results in the normal state.

wider temperature range, to make possible a more detailed analysis and a more precise comparison with the calculations of Caroli and Cyrot.

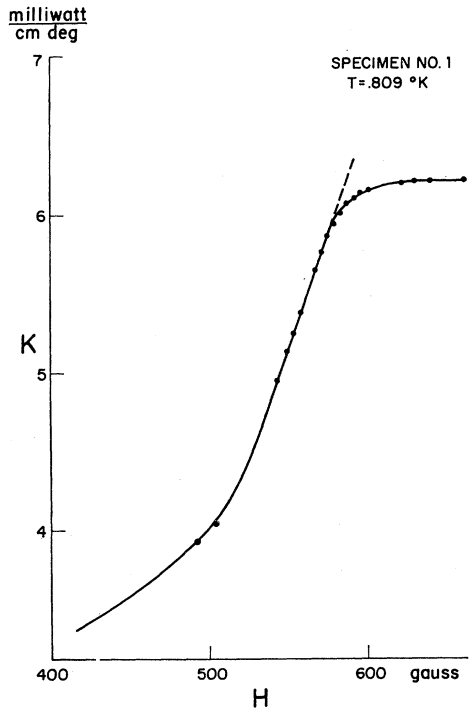

FIG. 2. Example of a curve of thermal conductivity against field.

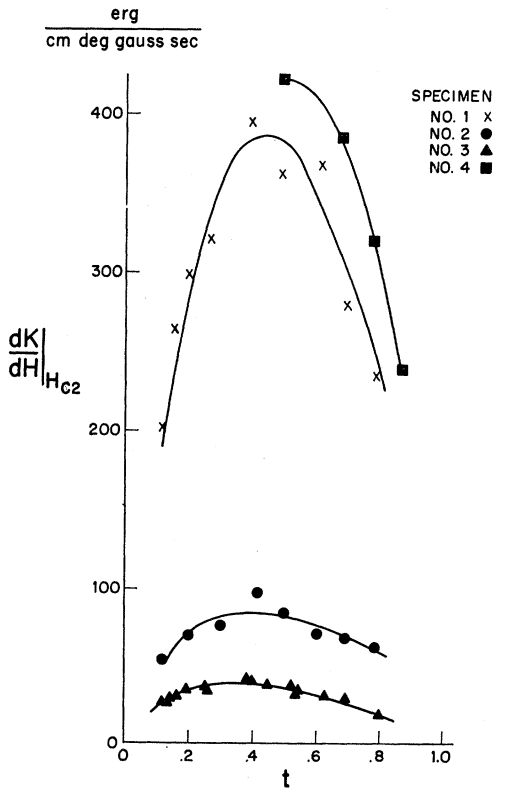

FIG. 3. Measured slopes $(dK/dH)_{H_{c2}}$ as a function of reduced temperature.

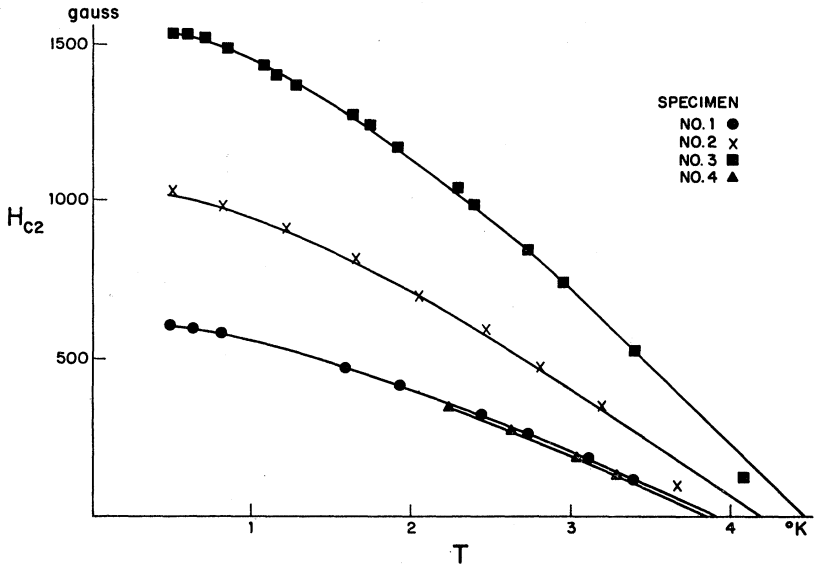

FIG. 4. Variation of the upper critical field with temperature for specimens 1–4.

It should be noted that we are here dealing only with the case where the electronic mean free path is small compared with the coherence length. In pure materials, where this is not so, the results are quite different.[8]

SPECIMENS AND APPARATUS

The specimens were made of 99.999% indium and bismuth (American Smelting and Refining Co.). The ingredients were melted together, mixed, and quenched in water. The specimens were extruded rods, $\frac{1}{8}$ in. diam, several inches long, and annealed for at least a week in helium-filled Pyrex tubes.

Specimens 1, 2, and 3 were intended to contain nominally 2, 3, and 4% bismuth, respectively. Specimen 3 was measured immediately after annealing ("3a") and again after being stored in vacuum at room temperature for one month ("3b"). The results for the two runs were somewhat different, and we attribute the change to the precipitation of some of the bismuth. In the second run, the normal-state conductivity was higher by about 3% while the conductivity in the superconducting state was lower. (At the maximum of the curve of K/T against T, the conductivity had decreased by about 30%.)

Specimen 4 had a composition similar to that of specimen 1. It was made in order to check the results near T_c with greater precision, and was measured only in a conventional He^4 cryostat. All other measurements were made in a He^3 cryostat which has been described previously.[9]

RESULTS

For each specimen the thermal conductivity was measured as a function of temperature in the superconducting state (without magnetic field) and in the normal state in a sufficiently large field provided by a Nb-Zr solenoid. The results for specimens 1, 2, and 3a are shown in Fig. 1. At selected temperatures the thermal conductivity (K) was measured as a function of longitudinal field (H) near the upper critical field (H_{c2}). A representative curve is shown in Fig. 2. The slopes of the curves of K against H near H_{c2} are shown in Fig. 3. The upper critical field curves (H_{c2} against T) as determined from these measurements, are shown in Fig. 4.

ANALYSIS

The analysis of the results consists of two main parts. The first is to determine the value of κ and its variation with temperature. The second is to determine the variation of the lattice conductivity with field. The procedures which were used are described in the following two sections. The values of the various parameters are shown in Table I.

Determination of Parameters

The transition temperature T_c was determined from the critical field curves. The curves follow the equation[10]

$$\ln(T_c/T)=\psi(\rho_c+\tfrac{1}{2})-\psi(\tfrac{1}{2}), \qquad (1)$$

where ψ is the digamma function, $\rho_c=(\hbar/2k\phi_0)\times(DH_{c2}/T)$, ϕ_0 is the flux quantum, and $D=\frac{1}{3}v_F l$ the diffusion coefficient. Since H_{c2} is proportional to $\rho_c T$, the correct choice of T_c will make $H_{c2}/\rho_c T$ independent of temperature. Accordingly, Eq. (1) was used to calculate ρ_c and hence $H_{c2}/\rho_c T$ as a function of T for various values of T_c. The most nearly horizontal graph of $H_{c2}/\rho_c T$ against T then determined T_c, and incidentally D and $(dH_{c2}/dT)_{T_c}$.

The value of the Ginzburg-Landau parameter κ was

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[10] P. G. de Gennes, *Superconductivity of Metals and Alloys* (W. A. Benjamin, Inc., New York, 1966), p. 270.

TABLE I. Characteristics and parameters of the specimens.

Specimen	1	2	3	4
ρ_0 ($\mu\,\Omega$ cm)	3.27	5.0	6.68	3.15
κ	0.87	1.37	1.82	0.83
T_c (°K)	3.90	4.20	4.45	3.87
D (cm²/sec)	46.7	30.1	21.2	46.3
$\rho_0 l$ ($10^{-11}\,\Omega$ cm²)	0.60	0.54	0.50	0.59
M (10^{-20} cm³/deg⁴ sec⁴)	2.9	5.1	13	
Λ(cm)	0.009	0.0025	0.003	
ξ_0/l	16.5	27	37	16
ξ_0(Å)	3040	2950	2780	2980
ξ_{00}(Å)	3490	3640	3630	3390
l(Å)	184	109	75	186
$(-dH_{c2}/dT)_{T_c}$(G/deg)	235	366	518	236

found from the Gor'kov-Goodman equation, $\kappa=\kappa_0+7.5\times10^3\gamma^{1/2}\rho_0$. For the specific-heat coefficient γ the values of Kinsel, Lynton, and Serin[11] were used, and for κ_0 the value 0.062.[12] The residual resistivity ρ_0 was calculated from the value of K/T in the normal state extrapolated to zero temperature and the Wiedemann-Franz law.

The results of Caroli and Cyrot are expressed in terms of the ratio of dK/dH to dM/dH at H_{c2} where the slope dM/dH of the magnetizaton curve is related to the temperature-dependent parameter κ_2 defined by Maki[13] by

$$(dM/dH)_{H_{c2}}=[1.16(2\kappa_2^2-1)]^{-1}.$$

We calculated κ_2 from κ and the theoretical temperature dependence of κ_2/κ as calculated by Eilenberger[14] for different values of ξ_0/l. ($\xi_0=0.18\hbar v_F/kT_c$, and l is the electronic mean free path.) The ratio ξ_0/l was determined from Gor'kov's relation[15]

$$\kappa_0/\kappa=\chi(\rho_G),$$

where

$$\chi(\rho_G)=1.173\rho_G^{-1}\{1+(4/\pi^2\rho_G)[\psi(\tfrac{1}{2})-\psi(\tfrac{1}{2}+\tfrac{1}{2}\rho_G)]\},$$

with $\rho_G=0.882\xi_0/l$. (A graph of κ/κ_0 against ξ_0/l is given by Eilenberger.[14]) The values of ξ_0/l for our specimens are shown in Table I. They are so large that the expected temperature variation of κ_2/κ is very close to that for the dirty limit.

As a byproduct of this work, it is now possible to determine ξ_0, l, and hence $\rho_0 l$. We use the Gor'kov relation in the form used, for example, by Guyon, Meunier, and Thompson,[16]

$$\xi^2(t)(1-t)=(0.851)^2\xi_0 l\{1+(4/\pi^2\rho_G)[\psi(\tfrac{1}{2})-\psi(\tfrac{1}{2}+\tfrac{1}{2}\rho_G)]\},$$

where $\xi(t)$ is the temperature-dependent coherence length. The left-hand side can be put equal to $\phi_0/(2\pi T_c)(-dH_{c2}/dT)_{T_c}$ with the help of the relation $\xi^2(t)=\phi_0/2\pi H_{c2}$. The right-hand side is equal to $0.545\,\xi_0^2\chi(\rho_G)$. Hence, we can write

$$\xi_0^2=0.605\times10^{-7}\frac{\kappa/\kappa_0}{T_c(-dH_{c2}/dT)_{T_c}}.$$

We have used this relation to calculate ξ_0 for our specimens, hence l and $\rho_0 l$, with the results shown in Table I.

The values of ξ_0 center about 2900 Å. We can estimate the value ξ_{00} appropriate for pure indium by multiplying ξ_0 by $T_c/3.40$, where 3.40 is the transition temperature of pure indium. (We neglect any change in v_F.) The average value of ξ_{00} is 3540 Å. The average value of $\rho_0 l$ is $0.56\times10^{-11}\,\Omega$ cm².

We have applied the same method of analysis to the critical-field curves of the nine In-Bi specimens of Kinsel, Lynton, and Serin,[11] with the result that $\xi_{00}=3650\pm70$ Å and $\rho_0 l=0.60\times10^{-11}\,\Omega$ cm². We have also estimated $(dH_{c2}/dT)_{T_c}$ from the graphs of Noto, Muto, and Fukuroi,[17] leading to an average value of 3430 Å for ξ_{00}.

It should be noted that this analysis depends strongly on the value of κ_0. ξ_0 is proportional to $1/\sqrt{\kappa_0}$, and in the dirty limit κ/κ_0 is proportional to ξ_0/l. Hence l is then proportional to $\sqrt{\kappa_0}$. The older value for κ_0 of 0.11 would therefore lead to a coherence length 25% lower, and to a value for $\rho_0 l$ one-third higher.

Our result for ξ_{00} is in excellent agreement with $0.18\,\hbar v_F/kT_c$, where $v_F=0.90\times10^8$ cm/sec.[18] The result for $\rho_0 l$ is in good agreement with that obtained from anomalous skin-effect measurements.[19] On the other hand, both results differ strongly from those of a variety of size-effect measurements which lead to a coherence length about one-third smaller and to values for ρl two to three times as large.[20–22] The discrepency between the values from bulk measurements and those on thin films and thin wires has been noted before and has been discussed particularly by Bate, Martin, and Hille,[12] and by Cotti.[22]

Lattice Conductivity

For a comparison with the theoretical results of Caroli and Cyrot it is useful to define the quantities

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[17] K. Noto, Y. Muto, and T. Fukuroi, J. Phys. Soc. Japan **21**, 2122 (1966).

[18] F. W. Smith, thesis, Brown University, 1968 (unpublished).

[19] P. N. Dheer, Proc. Roy. Soc. (London) **A260**, 333 (1961); T. E. Faber, *ibid.* **A241**, 531 (1957).

[20] See, for example, R. D. Chaudhari and J. B. Brown, Phys. Rev. **139**, A1482 (1965); A. M. Toxen, M. J. Burns, and D. J. Quinn, *ibid.* **138**, A1145 (1965); R. S. Thompson and A. Baratoff, Phys. Rev. Letters **15**, 971 (1965); F. J. Blatt, A. Burmester, and B. LaRoy, Phys. Rev. **155**, 611 (1967); F. de la Cruz, M. E. de la Cruz, and J. M. Cortignola, *ibid.* **163**, 575 (1967).

[21] R. T. Bate, B. Martin, and P. F. Hille, Phys. Rev. **131**, 1482 (1963).

[22] P. Cotti, Phys. Condensed Matter **3**, 40 (1964).

$$S_e=(dK_e/dH)_{H_{c2}}(2\kappa_2^2-1)\beta_A,$$
$$S_g=(dK_g/dH)_{H_{c2}}(2\kappa_2^2-1)\beta_A,$$
$$S=S_e+S_g=(dK/dH)_{H_{c2}}(2\kappa_2^2-1)\beta_A,$$

where K is the total measured thermal conductivity and K_e and K_g are the electronic and lattice thermal conductivities, respectively.

The theory gives

$$S_e=\frac{ck}{2e}\rho_c\left(1+\frac{\rho_c\psi''(\frac{1}{2}+\rho_c)}{\psi(\frac{1}{2}+\rho_c)}\right),$$

where ψ is again the digamma function and ψ'' is the tetragamma function. S_e is a function of the reduced temperature only, and is shown as a solid line on Fig. 5, which also shows the measured values of S. The error bars shown for the values of S reflect the uncertainty in the graphical determination of $(dK/dH)_{H_{c2}}$, but do not include the uncertainties in the geometrical factor L/A, or in the value of κ_2, each of which we estimate to be in the neighborhood of 4%. It may be seen that the values of S follow the expected temperature dependence of S_e but are consistently low, with the discrepancy greatest for the most impure specimen.

For a better comparison between theory and experiment it is necessary to know S_g.

The lattice conductivity may be described by the equation

$$K_g=\frac{k^4T^3}{3\pi^2\hbar^3v_s}\int_0^\infty\frac{1}{\sum\tau_K^{-1}}\frac{x^4e^x\,dx}{(e^x-1)^2},\qquad(2)$$

where v_s is the sound velocity, $x=\hbar\omega/kT$, and where the summation is over the reciprocals of the phonon relaxation times appropriate for the various scattering mechanisms. We are here using only the contribution of the transverse phonons, because it can be shown that the conduction by the longitudinal phonons is less by at least an order of magnitude.[23,24] The processes which need to be considered for our specimens are boundary scattering, impurity (mass difference and strain field) scattering, and scattering by the conduction electrons. Since only the electron scattering is affected by the magnetic field it is necessary to analyze the lattice conductivity so as to find the relaxation times for each specimen.

The first step in the analysis was to separate the electronic thermal conductivities K_{en} and K_{es} in the normal and superconducting states from the total conductivities K_n and K_s to find the lattice conductivities K_{gn} and K_{gs}. It was assumed that K_{en} is equal to L_0T/ρ_0 as given by the Wiedemann-Franz law (with $L_0=2.445\times10^{-8}$ V^2/deg^2). (The effect of the scattering of electrons by phonons can be expected to be small in our specimens.) It was also assumed that $R_e\equiv K_{es}/K_{en}$ was given by

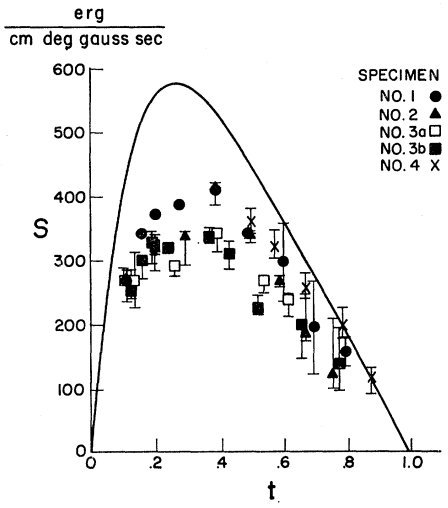

FIG. 5. Measured ratios $S=(dK/dH)_{H_{c2}}\times1.16(2\kappa_2^2-1)$.

the theory of Bardeen, Rickayzen, and Tewordt[4] with $2\epsilon_0=3.7\,kT_c$, so that $K_{gs}=K_s-R_eL_0T/\rho_0$.

The second step was to fit the resulting curves of K_{gn} and K_{gs} as a function of temperature analytically with Eq. (2) to determine the boundary relaxation time $\tau_B=\Lambda/v_s$ (Λ: boundary mean free path) and the impurity relaxation parameter M, related to the relevant relaxation time by $\tau_M^{-1}=MT^4x^4/v_s^3$. In this procedure we used for the electronic relaxation time $\tau_E^{(n)}$ in the normal state the expression $1/ATx$ which by itself would lead to a lattice conductivity proportional to T^2. (Although this may not be the correct temperature dependence,[23,24] this form was judged sufficiently accurate for the present purpose.) For $\tau_E^{(s)}$, the electronic relaxation time in the superconducting state, we used $(\tau_E^{(s)})^{-1}=ATxg(x)$, where $g(x)$ is given by Eq. (5.2) of Ref. 4.

A digital computer was used to perform the integrals of Eq. (2) for various values of Λ and M at a series of reduced temperatures. At each temperature the experimental curve could be fitted by different combinations of the parameters. We therefore plotted the compatible values of Λ and M against each other at each reduced temperature. The intersection of the lines gave the values of Λ and M which best fit the data at all temperatures.

The values of Λ and M were then used to calculate $K_{gm}(H)/K_{gn}$, where $K_{gm}(H)$ is the lattice conductivity in the mixed state. In this calculation we again used Eq. (2), with the elcetronic relaxation time in the mixed state given by $1/\tau_E^{(m)}=\alpha_T(H)$, where $\alpha_T(H)$ is the transverse acoustic attenuation for the mixed state derived by Maki.[25] When H is equal to H_{c2}, this reduces to the normal-state attenuation as derived by Pippard,[26] which can be used to calculate K_{gn}. It is known that there are discrepancies between the experimental determinations

[23] P. Lindenfeld and W. B. Pennebaker, Phys. Rev. **127**, 1881 (1962).
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[25] K. Maki, Phys. Rev. **148**, 370 (1966).
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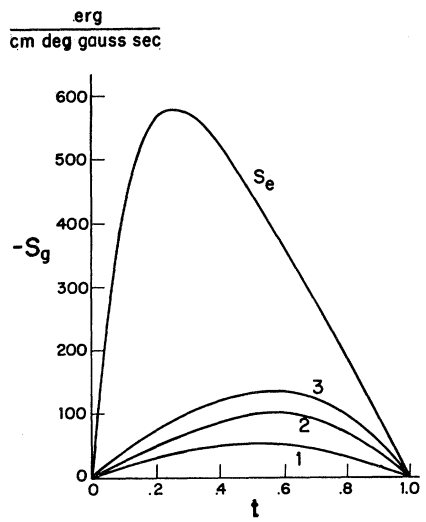

FIG. 6. Calculated ratios $S_g = (dK_g/dH)_{H_{c2}} \times 1.16(2\kappa_2^2 - 1)$ together with the theoretical curve for S_e.

of K_{gn} and the theoretical expression calculated in this way,[23,24] but the calculation of the ratio $K_{gm}(H)/K_{gn}$ is likely to be much better than that of the conductivity itself.

The calculated curves of S_g as a function of the reduced temperature for our specimens are shown on Fig. 6. The effect of S_g on S is greatest, as expected, for the most impure sample, and it becomes smaller as the temperature is reduced.

The values of S_g were subtracted from the experimental values of S to give the results for S_e shown in Fig. 7. The figure shows excellent agreement between theory and experiment down to a reduced temperature of about 0.4, but at lower temperatures our values are consistently below the theoretical values for all specimens.

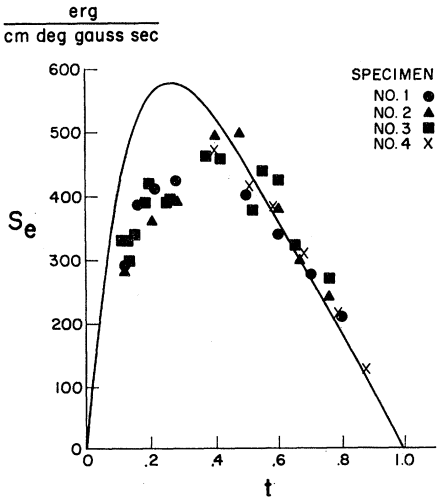

FIG. 7. Corrected ratios $S_e = (dK_e/dH)_{H_{c2}} \times 1.16(2\kappa_2^2 - 1)$.

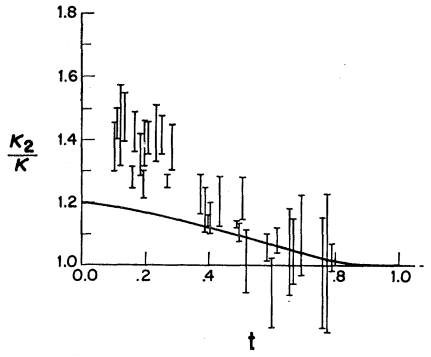

FIG. 8. Values of κ_2/κ which would lead to agreement between theory and experiment for S_e.

It should be noted that in the region of the greatest discrepancy the values of S_g are quite small so that it is quite unlikely that the disagreement could be improved by a better determination of the effect of the lattice conduction.

There is another point of view which may be taken. It is possible to put the burden of the discrepancy on the temperature variation of κ_2 rather than on the formula of Caroli and Cyrot. If it is assumed that the Caroli and Cyrot results are exact, and if the measurements are then used to determine κ_2/κ as a function of temperature, one gets the values shown on Fig. 8. The figure also shows the line expected in the dirty limit, which is close to that expected for our specimens.

The available evidence on the temperature dependence of κ_2/κ is quite contradictory. A more rapid variation than that predicted theoretically was found by Guyon[27] in indium alloys, but a measurement by Fischer and Vieli[28] agreed very well with the appropriate curve of Eilenberger. More recently, Farrell, Chandrasekhar, and Culbert[29] have found high values of κ_2/κ in lead alloys and we refer to their paper for a critical analysis of the experimental and theoretical situation.

It seems that further experiments will be necessary to describe the temperature variation of κ_2, and hence to determine whether there remains a discrepancy between the calculations of Caroli and Cyrot and the experimental results.

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