Thermal Conductivity of Superconducting Tin Films in a Magnetic Field*†

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We have measured the magnetic field dependence of the thermal conductivity of superconducting tin films in a parallel field ranging from zero to above the critical fields, and at temperatures from 0.3 to 1°K. The electron mean free path l ranged from 18 to 85% of the bulk coherence length ξ_0. The Ginzburg–Landau parameter κ was sufficiently enhanced by the effect of the short mean free path that in the thicker films the the surface sheath region of de Gennes and Saint James was observed. An expression is given for the field dependence of the thermal conductivity in this region, based on theoretical calculations of Caroli and Cyrot and of Maki; this expression, which is strictly valid only in the dirty limit $l/\xi_0 \to 0$, is in good agreement with our experimental results. The field dependence of the thermal conductivity of the thinner films is compared with theoretical expressions derived by Maki. These expressions are also restricted in validity to the dirty limit. Here the agreement between the theory and the data is not as good as for the thick films, but it improves as the experimental values of l approach the dirty limit.

I. INTRODUCTION

THE magnetic properties of superconductors with very short electron mean free paths have been of considerable theoretical and experimental interest in the past several years. In the normal state, impurities reduce the electron mean free path of a metal very sharply. In the superconducting state, impurities decrease the coherence length and increase the penetration depth. Thus a metal which is a type-I superconductor when it is pure becomes type-II with sufficient doping.

Abrikosov and Gor'kov[1] have shown that the introduction of paramagnetic impurities can lead to a superconducting state with no gap in the electronic excitation spectrum. This occurs for a narrow range of impurity concentrations just below that necessary to quench superconductivity entirely. Yet this superconducting state shows many of the remarkable properties of ordinary superconductors, such as infinite dc conductivity and persistent currents. Properties which directly reflect the gap, such as the exponential temperature dependence of the specific heat and thermal conductivity, the optical absorption, and the tunneling characteristics, are substantially modified. Tunneling measurements by Reif and Woolf[2] and specific-heat measurements by Finnemore *et al.*[3] agree with the Abrikosov-Gor'kov theory.

Maki,[4] de Gennes[5] and others have shown that there is a formal correspondence between the effect of magnetic impurities and the effect of a magnetic field on a superconductor with short electron mean free path. In both cases the perturbation acts with opposite sign on the electrons forming a Cooper pair. The lifetime of a Cooper pair is limited by the presence of such a pair-breaking interaction. When the lifetime is sufficiently short, that is for sufficiently high magnetic impurity concentrations or a sufficiently high field, states at the gap edge are broadened in energy enough to fill the gap. The region formerly occupied by the gap in the density of states is diminished relative to the normal-state value, and there is a broad peak near the position of the gap edge in the pure superconductor. The persistence of long-range order and the associated supercurrents are related to this decrease in the density of states. The results of Abrikosov and Gor'kov make it clear that long-range order and the superconducting state can exist without an energy gap.

The calculation of the transport properties of a superconductor with a BCS[6] electronic excitation spectrum is a very straightforward matter in principle. In this case a simple Boltzmann transport calculation is possible. In the gapless region, however, it is not possible to associate a narrow band of energies with a momentum near the Fermi momentum, because of the energy broadening. Thus the quasiparticle approximation breaks down, making a Boltzmann transport calculation inapplicable. The necessity for a less direct calculation of the transport properties makes experimental verification of these calculations important.

Maki and Fulde[7] have made a detailed study of the correspondence between the paramagnetic impurity problem and the situation in a superconductor with

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[1] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **39**, 1781 (1960) [English transl.: Soviet Phys.—JETP **12**, 1243 (1961)].
[2] F. Reif and M. A. Woolf, Phys. Rev. Letters **9**, 315 (1962); Rev. Mod. Phys. **36**, 238 (1964); Phys. Rev. **137**, A557 (1965).
[3] D. K. Finnemore, D. L. Johnson, J. E. Ostenson, F. H. Spedding, and B. J. Beaudry, Phys. Rev. **137**, A550 (1965); W. R. Decker, D. T. Peterson, and D. K. Finnemore, Phys. Rev. Letters **18**, 899 (1967).
[4] K. Maki, Physics **1**, 21 (1964).
[5] P. G. de Gennes, Physik. Kondensierten Materie **3**, 79 (1964).
[6] J. Bardeen, L. N. Cooper, and J. R. Schreiffer, Phys. Rev. **108**, 1175 (1957).
[7] K. Maki and P. Fulde, Phys. Rev. **140**, A1586 (1965).

short electron mean free path in a magnetic field. They found the correspondence to be valid except in the calculation of spin susceptibility. Predictions of other properties can be expressed in terms of the pair lifetime, which can be calculated for the situation under consideration.

Experimentally testing various calculations based on the Abrikosov-Gor'kov theory of paramagnetic impurities is an arduous task. One is commonly interested in the dependence of the property in question on the impurity concentration, and this requires a comparison of the behavior of many different samples. Corresponding information may be obtained from a single sample with short mean free path by measuring the parameter in question as a function of applied field. de Gennes and Tinkham[8] have noted that experiments on a superconductor with a short mean free path in a magnetic field might actually be a better test of the Abrikosov-Gor'kov theory, because Abrikosov and Gor'kov assume a model which ignores impurity-impurity correlations and other parasitic effects which might arise from interactions between the magnetic impurities, and which might play an appreciable role in determining the properties of real samples.

In this experiment we study the thermal conductivity of thin tin films as a function of magnetic field. The films, formed by vacuum deposition of pure tin upon glass substrates kept at 77°K during evaporation, have short electron mean free paths due to imperfections in their structure. The magnetic properties of these films should be those predicted by the Abrikosov-Gor'kov theory as generalized by de Gennes and Maki.

We believe that the experiments described in this paper are the first to provide a definitive test of existing theories of the thermal conductivity of superconductors with short electron mean free path in a high magnetic field, because of our measurement of all of the relevant parameters and our choice of materials. We have avoided using lead films; the electron-phonon coupling is strong enough that one might not expect the theoretical calculations to be accurate for lead.

Section II of this paper is devoted to a description of some of the theoretical calculations of thermal conductivity which should describe our results. We make no attempt at a complete derivation and discussion of these results; we merely quote results and discuss limitations of the calculations. In Sec. III we discuss past experiments dealing with the thermal conductivity of superconductors in high magnetic fields. Section IV gives a brief discussion of our experimental apparatus and techniques; these are described more completely elsewhere.[9] In Sec. V we give and discuss the results of our experiments.

[8] P. G. de Gennes and M. Tinkham, Physics **1**, 107 (1964).
[9] J. E. Smith, Jr., thesis, University of Illinois, 1967 (unpublished).

II. THEORY

A. General Remarks

The electronic thermal conductivity of a superconductor with short electron mean free path in a magnetic field has been calculated in two limiting situations. Maki[10] considers film samples which are sufficiently thin that the order parameter is independent of position. This is equivalent to requiring that the inequality $d \ll \xi(T)$ be satisfied, where d is the film thickness and $\xi(T)$ is the temperature-dependent coherence length characteristic of the scale upon which variations in the order parameter are energetically favorable. Maki's calculation treats all fields up to the critical field of the film. His results are most easily compared with experiment at low temperatures.

Caroli and Cyrot[11] have calculated the thermal conductivity in a field for specimens in which the order parameter is position-dependent. Their calculation is restricted to the region where $\langle \mid \Delta(\mathbf{r}) \mid^2 \rangle \ll \Delta_{00}^2$, where $\Delta(\mathbf{r})$ is the order parameter at position $\mathbf{r}$, $\langle\ \rangle$ indicates an average over the volume of the sample, and Δ_{00} is the order parameter in zero field at zero temperature. This effectively limits their calculation to the vicinity of a second-order phase transition, such as occurs at H_{c2} or H_{c3}.

In the rest of this section we discuss these calculations in greater detail, with emphasis upon their application to our experiments. Throughout this paper we use units in which $\hbar = c = k_B = 1$, where k_B is the Boltzmann constant.

B. Situations where $\Delta(\mathbf{r})$ is Independent of Position

The thermal conductivity of a superconductor in the presence of a supercurrent flow has been calculated by Maki[10] from the Abrikosov-Gor'kov theory.[1] He treats the case where the film is thin enough that $\Delta(\mathbf{r})$ is independent of position, and the phase transition is of second order. The validity of his calculation is restricted to the limit in which the electron mean free path l is much less than ξ_0, the coherence length appropriate for infinite mean free path. He shows that the effect of a supercurrent flow is equivalent to that of a tangential magnetic field, and applies his results to the problem of the field dependence of the thermal conductivity.

In the limit of zero field, Maki's results reduce to those of earlier calculations by Bardeen, Rickayzen, and Tewordt[12] of electronic thermal conductivity in the absence of a magnetic field. At low temperatures ($t=$

[10] K. Maki, Progr. Theoret. Phys. (Kyoto) **31**, 378 (1964); **31**, 731 (1964).
[11] C. Caroli and M. Cryot, Physik. Kondensierten Materie **4**, 285 (1965).
[12] J. Bardeen, G. Rickayzen, and L. Tewordt, Phys. Rev. **113**, 982 (1959).

$T/T_c \ll 1$) his general results can be expressed in relatively simple forms. Let us define

$$\alpha = (2\tau/3\Delta)\, p_F (e/m)^2 (aH)^2, \tag{2.1}$$

where $\tau = l/v_F$, v_F is the Fermi velocity, p_F is the Fermi momentum, and aH is given by the average of the squared vector potential $\mathbf{A}^2$ over the volume V of the superconductor:

$$(aH)^2 = V^{-1} \int_V \mathbf{A}^2 d^3r. \tag{2.2}$$

For a film parallel to the y-z plane, located in a field of magnitude H applied in the z direction, $\mathbf{A}$ is given by

$$\mathbf{A} = (0, Hx, 0), \tag{2.3}$$

where x is measured from the mid-plane of the film.

For $\alpha < 1$ the energy gap is nonzero. At low temperature Maki finds

$$\frac{K(H)}{K_n} = \frac{4}{\pi^2} (\alpha^{-2/3} - 1) \left(\frac{\omega_0}{T} + 4 + 6 \frac{T}{\omega_0} \right) e^{-\omega_0/T}, \tag{2.4}$$

where

$$\omega_0 = (1 - \alpha^{2/3})^{3/2}. \tag{2.5}$$

Δ is a function of the applied field, and is given implicitly by

$$\ln(\Delta/\Delta_{00}) = -\tfrac{1}{4}\pi\alpha - \alpha^{-2/3}(1-\alpha^{2/3})^{1/4} \times (2\pi/3)^{1/2} (T/\Delta)^{3/2} e^{-\omega_0/T}. \tag{2.6}$$

In the BCS theory, we have $2\Delta_{00} = 3.53 T_c$. The energy gap ω_0 goes to zero as α goes to 1; for $\alpha < 1$, the thermal conductivity depends upon $\exp(-\omega_0/T)$. The expressions in Eqs. (2.4)–(2.6) for a superconductor with an energy gap are valid if $\alpha^{2/3}$ is large compared to T/Δ, and is not too near zero or 1.

For $\alpha > 1$ the excitation spectrum is gapless, and the thermal conductivity is given by

$$[K(H)/K_n] = (1-\alpha^{-2}) + \tfrac{1}{5} 7\pi^2 \alpha^{-4} (1-\alpha^{-2})^2 (2+\alpha^{-2}) \times (T/\Delta)^2, \tag{2.7}$$

where Δ is the solution of

$$\ln(\Delta/\Delta_{00}) = -\operatorname{arccosh}\alpha - \tfrac{1}{2}[\alpha \arcsin \alpha^{-1} - (1-\alpha^{-2})^{1/2} - \tfrac{1}{6}\pi^2 \alpha^{-2} (1-\alpha^{-2})^{-1/2} (T/\Delta)^2. \tag{2.8}$$

Equations (2.4)–(2.8) are valid only in the low-temperature limit, $T/\Delta \ll 1$.

Maki also considers the effect of the relative directions of heat flow and magnetic field. He finds that such effects vanish as $(\tau\Delta)$, in agreement with Morris and Tinkham's[13] experimental results.

C. Situations where $\Delta(\mathbf{r})$ is Position-Dependent

Caroli and Cyrot[11] calculate the thermal conductivity in a magnetic field in situations where $\Delta(\mathbf{r})$ varies with position. This treatment is applicable to thicker films, for which $d > \xi(T)$. Such a situation arises in the surface sheath region, where the order parameter goes continuously to zero as one goes away from the surface of the film into the normal interior.

Caroli and Cyrot's calculations are valid for situations in which $\Delta \ll T_c$; this occurs near H_{c2} and H_{c3}. They carry their calculations to order $\langle |\Delta(\mathbf{r})|^2 \rangle$, and their result is

$$K(H) = K_n - [\sigma \langle |\Delta(\mathbf{r})|^2 \rangle / 2e^2 T] - (2/\rho) \times [\psi^{(1)}(\tfrac{1}{2}+\tfrac{1}{2}\rho) + (2/\rho)\psi^{(2)}(\tfrac{1}{2}+\tfrac{1}{2}\rho)], \tag{2.9}$$

where σ is the electrical conductivity, $\rho = (1/2\pi T) \times (1/\tau_k)$ ($\tau_k \equiv$ pair lifetime), and $\psi^{(m)}(z)$ is the mth derivative of the digamma function $\psi(z)$.[14]

Maki[15] has calculated the average of the squared order parameter for a thin film in the surface sheath region:

$$\langle |\Delta(\mathbf{r})|^2 \rangle = \frac{eT}{\sigma} d^{-1} \left(\frac{\pi}{1.18 e H_{c3}} \right)^{1/2} \left(\frac{H_{c3} - H}{\kappa_2^2(T) - 0.156} \right) \times [\psi^{(1)}(\tfrac{1}{2}+\tfrac{1}{2}\rho)]^{-1}. \tag{2.10}$$

Using this result with Eq. (2.9), we arrive at an expression for $K(H)$ in the surface sheath region near H_{c3}:

$$\frac{K(H)}{K_n} = 1 - K_n^{-1} (2ed)^{-1} \left(\frac{\pi}{1.18 e H_{c3}} \right)^{1/2} \times \left(\frac{H_{c3} - H}{\kappa_2^2(T) - 0.156} \tfrac{1}{2}\rho \right) \left(1 + \frac{2}{\rho} \frac{\psi^{(2)}(\tfrac{1}{2}+\tfrac{1}{2}\rho)}{\psi^{(1)}(\tfrac{1}{2}+\tfrac{1}{2}\rho)} \right). \tag{2.11}$$

The requirement "near H_{c3}" is more precisely stated as: (1) $\langle |\Delta(\mathbf{r})|^2 \rangle / T^2 \ll 1$; and (2) H is of such magnitude that we are in the surface sheath region, i.e., greater than both H_{c2} and H_{cf}, and smaller than H_{c3}. H_{cf} is the critical field of a thin film, which is increased by size effects.

Guyon, Meunier, and Thompson[16] have shown that for films with $d \gg \xi(T)$, the pair lifetime is given by

$$1/\tau_k = 0.59 DH, \tag{2.12}$$

where D is the diffusion coefficient ($D = v_F l/3$ for a spherical Fermi surface). Straightforward evaluation of ρ is difficult because of uncertainties in the determination of the parameters involved. However, ρ_c, its value at H_{c3}, is given implicitly by

$$-\log(T/T_c) = \psi(\tfrac{1}{2}+\tfrac{1}{2}\rho_c) - \psi(\tfrac{1}{2}). \tag{2.13}$$

Equation (2.12) shows that ρ is proportional to H, so for purposes of computation we can calculate ρ from

$$\rho = \rho_c (H/H_{c3}). \tag{2.14}$$

[13] D. E. Morris and M. Tinkham, Phys. Rev. **134**, A1154 (1964).

[14] H. T. Davis, *Tables of Higher Mathematical Functions* (The Principia Press, Inc., Bloomington, Ind., 1933), Vol. I, p. 285.

[15] K. Maki, Phys. Rev. **148**, 370 (1966); note that in Eq. (30) of this work the factor $[2\kappa_2^2(T) - 3.12]^{-1}$ should be $[2\kappa_2^2(T) - 0.312]^{-1}$.

[16] E. Guyon, F. Meunier, and R. S. Thompson, Phys. Rev. **156**, 452 (1967).

The behavior of the curve $K(H)/K_n$ is not readily apparent from the analytic form of Eq. (2.11). We have evaluated Eq. (2.11) numerically in the range of validity of this expression and under the experimental conditions appropriate for this work. We find that in this range $K(H)/K_n$ approaches unity at H_{c3} almost linearly. These results are plotted and discussed more fully in Sec. V of this paper with our experimental results.

It must be emphasized that all the calculations of thermal conductivity in a magnetic field presented in this section are strictly valid only in the limit $l \ll \xi_0$. Strassler and Wyder[17] have calculated the density of states for a broader range of l in small particles and find small, but non-negligible changes from the dirty-limit expressions for rather small values of l/ξ_0, such as 0.1. No such calculation of thermal conductivity seems to have been performed, but one would expect corresponding changes in the thermal conductivity with increasing mean free path. The values of l/ξ_0 in real samples are large enough that this limitation on the validity of the theoretical predictions must be noted.

III. PAST EXPERIMENTS

Early measurements of the thermal conductivity of thin superconducting films in a magnetic field were done by Morris and Tinkham.[13] They studied films of tin, indium, and lead, working above 1°K. They were hampered in analyzing their results by the lack of theoretical treatments of the field dependence of the thermal conductivity at the time of their work. They attempted to use the calculation of Bardeen, Rickayzen, and Tewordt (BRT)[12] of the thermal conductivity of a BCS superconductor, assuming that these results could be applied to the problem of the field dependence of the thermal conductivity by simply allowing the BCS energy gap to be field-dependent. This is equivalent to scaling the energy dependence of the BCS single-particle excitation spectrum by a field-dependent scaling factor; the shape of the excitation spectrum is assumed unchanged except for this scaling. Using this effective gap approximation, Morris and Tinkham obtain the field-dependent energy gap from their experimental data. As we have discussed earlier, the effect of a field on a superconductor with a short mean free path is now thought to be inaccurately described by the effective gap approximation; but the results of Morris and Tinkham are in qualitative agreement with Ginzburg-Landau theory calculations of Douglass,[18] and with tunneling measurements by Douglass and Meservey,[19] and by Giaever *et al.*[20] They found no anisotropy with relative direction of heat flow and applied field, in agreement with Maki's later calculations.[10]

Observations have been made of the superconducting surface sheath of de Gennes and Saint James by thermal conductivity measurements on films. Mochel and Parks[21] studied thick ($d=16\,000$ Å) films of $In_{0.95}Pb_{0.05}$, and Seidel and Meissner[22] studied lead films. There was no surface sheath in Morris and Tinkham's samples. Their tin and lead films were too thin, so that H_{cf} was in all cases greater than H_{c3}. In their indium films, the Ginzburg-Landau κ was less than 0.417, so no surface sheath appeared. (In pure indium κ_0 is only 0.05, and their electron mean free paths were too long to produce κ greater than 0.417).

Mochel and Parks derived and used an expression for $K(H)$ of a film with surface sheaths. That expression is somewhat different from Eq. (2.11). They assumed that the average thermal conductivity of the whole film, including both the superconducting and normal regions, can be approximated by

$$K(H)=d^{-1}[2d_{ss}(H)K_{ss}(H)+d_n(H)K_n], \quad (3.1)$$

where $d_{ss}(H)$ is the thickness of the surface sheath, $d_n(H)$ is the thickness of the normal interior of the film, $K_{ss}(H)$ is the thermal conductivity of the portion of the film in the surface sheath, and K_n is the thermal conductivity of the normal state. $d_{ss}(H)$ and $d_n(H)$ are both functions of field, and are related by the condition

$$2d_{ss}(H)+d_n(H)=d. \quad (3.2)$$

$K_{ss}(H)$ is given by Eq. (2.9) with an appropriate expression for $\langle |\Delta(\mathbf{r})|^2 \rangle$, where this quantity is now defined as the average of the squared order parameter in the superconducting regions of the film only, excluding the part of the film that is in the normal state. The derivation of this expression, due to Maki, is unpublished; Caroli and Cyrot[11] quote the result without derivation. At the critical field, $d_{ss}(H)$ is equal to $\xi(T)$. Its field dependence is not well established at this time, so evaluation of Eq. (3.1) below H_{c3} is not possible. Mochel and Parks's expression for the slope of $K(H)$ at H_{c3} is in good agreement with the temperature dependence of their experimental results. They made no attempt to calculate $K(H)$ or its slope for lower fields.

We have tried to fit Seidel and Meissner's data to both our Eq. (2.11) and to Mochel and Parks's expression for $K(H)$ without success. Both of these expressions for $K(H)$ have the same temperature dependence, which is not in agreement with Seidel and Meissner's data on lead. For lead to show anomalous transport properties is not unusual, however.[23]

Parks, Zumsteg, and Mochel[24] have shown that thermal conductivity measurements can be used to

[17] S. Strässler and P. Wyder, Phys. Rev. **158**, 319 (1967).
[18] D. H. Douglass, Jr., Phys. Rev. Letters **6**, 346 (1961).
[19] R. Meservey and D. H. Douglass, Jr., Phys. Rev. **135**, A24 (1964).
[20] I. Giaever, Phys. Rev. Letters **5**, 147 (1960); I. Giaever and K. Megerle, Phys. Rev. **122**, 1101 (1961).
[21] J. M. Mochel and R. D. Parks, Phys. Rev. Letters **16**, 1156 (1966).
[22] T. Seidel and H. Meissner, Phys. Rev. **147**, 272 (1966).
[23] V. Ambegaokar, Phys. Rev. Letters **16**, 1047 (1966).
[24] R. D. Parks, F. C. Zumsteg, and J. M. Mochel, Phys. Rev. Letters **18**, 47 (1967).

determine H_{c1} (the lower critical field) and H_{c2} in type-II superconductors. They studied very thick (16 000 Å) $In_{0.95}Pb_{0.05}$ films with 50 Å layers of Mn on either surface. The Mn layers destroyed the surface sheath. The film thickness was chosen so that d was much greater than the characteristic lengths of the superconducting material. The thin-film structure allowed observation of the electronic thermal conductivity without the interference of a large phonon component. The relative sizes of the thickness and the characteristic lengths of the superconductor ensured that the critical fields measured were not influenced by sample size. In the same experiment they observed that the thermal conductivity in the mixed state had a strong anisotropy, which vanished below H_{c1} and above H_{c2}. Thermal conductivity is higher parallel to the vortex lines than perpendicular to them, presumably due to the continuous paths of normal material forming the cores of the vortex lines.

Dubeck, Lindenfelt, Lynton, and Rohrer[25] have measured the field dependence of the thermal conductivity of a bulk, type-II superconductor. With an appropriate expression for the pair lifetime, the calculations of Caroli and Cyrot are applicable to this situation near the second-order phase transition, i.e., near H_{c2}. Dubeck *et al.* were primarily interested in the behavior of the thermal conductivity near H_{c1} (which reflects the entry of flux lines into the sample), and have few points near H_{c2}. These points are in qualitative agreement with Caroli and Cyrot, but they are too few in number to allow quantitative comparison.

Our experimental measurements are the first to provide a definitive test of many aspects of the theories of thermal conductivity outlined in this paper. Maki's calculations of the thermal conductivity of thin films are most readily evaluated at temperatures very low compared to T_c. The measurements of Morris and Tinkham are the only other ones on films of the proper thickness for comparison with Maki's calculations, but their measurements were all made above 1°K, and are far from Maki's low-temperature limit. Mochel and Parks worked with thicker films, and do not give enough data for comparison with Eq. (2.11), the expression for the thermal conductivity of a thin film in the surface sheath state. They give only the reduced thermal conductivity (thermal conductivity divided by normal-state thermal conductivity). Comparison with Eq. (2.11) requires knowledge of the magnitude of both $K(H)$ and K_n.

IV. EXPERIMENTAL APPARATUS AND PROCEDURE

A. Sample Preparation

The samples used in these experiments were thin films of tin, prepared by vacuum deposition of tin upon a very thin glass substrate. The substrate had to be thin to minimize the background thermal conductance. During the evaporation the films were kept at about 77°K to promote the formation of a film composed of very fine crystallites. This caused the films to have very short electron mean free paths, and restricted the lattice component of the thermal conductivity. Films were prepared upon two identical substrates at the same time. One was used for the thermal conductivity measurements, and the other was used for film thickness measurements by multiple-beam optical interferometry.

The substrates were number 00 Pyrex glass slides, with dimensions 2.5 by 2.5 by 0.0076 cm. Before making a sample the slides were cleaned with detergent and water, followed by distilled water, a hot (130°C) solution of chromic acid, more distilled water, and then were placed for a day in a vapor degreaser which used isopropyl alcohol as an operating fluid.

The sample substrate and an identical dummy substrate were clamped to the bottom of a liquid-nitrogen reservoir in the vacuum chamber of an evaporator. The sample substrate was unmasked; the dummy was masked so a strip of metal 0.8 mm wide could be deposited across the substrate. The two substrates were located 10 cm above, and equidistant from the vapor source, which was a molybdenum boat filled with 99.999% pure tin. The pressure in the vacuum chamber was about 2×10^{-7} Torr before evaporation of the sample; during evaporation this rose to about 10^{-6} Torr, and immediately fell back to its earlier value after the evaporation. The sample was allowed to warm to room temperature in the vacuum system to minimize contamination due to condensation of water vapor, air, and whatever else might have been present when the sample was removed from the vacuum system.

After the sample was removed from the vacuum system, the dummy was prepared for the interferometric film thickness measurement by removing the mask and coating the whole substrate, including the tin strip, with a 1000 Å layer of silver to give it a high and uniform reflectivity; this silver layer was vacuum deposited in the same evaporator. Then the thickness of this dummy sample was measured to within 50 Å by multiple-beam interferometry.[26]

B. Low-Temperature Apparatus

The cryostat is shown in Fig. 1. It was especially designed and constructed to measure thermal conductivity as a function of a magnetic field applied parallel to the plane of a thin-film sample. The apparatus incorporated a He^3 refrigerator for operation in the temperature range from 0.3 to 1°K. A field up to 25 kOe was provided by a superconducting solenoid. A

[25] L. Dubeck, P. Lindenfeld, E. A. Lynton, and H. Rohrer, Rev. Mod. Phys. **36**, 110 (1964).

[26] S. Tolansky, *Multiple-Beam Interferometry of Surfaces and Thin Films* (Oxford University Press, London, 1949).

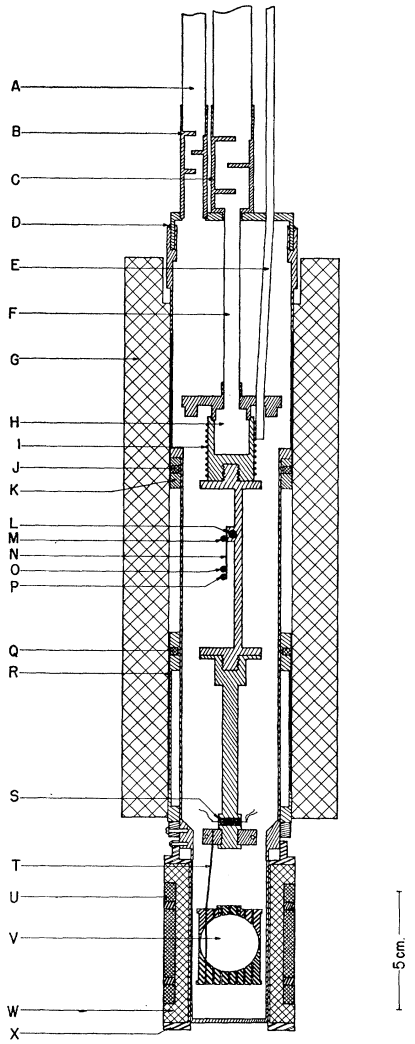

FIG. 1. Cross section of cryostat. A, cryostat pump-out line; B, light trap; C, light trap; D, Cd–Bi solder joint; E, electrical leads; F, He^3 pumping line; G, superconducting solenoid; H, He^3 evaporator; I, electrical heating coil (bifilarly wound); J, wrapped Helmholtz coil; K, coil form for wrapped Helmholtz coil; L, carbon resistance thermometer; M, carbon resistance thermometer; N, sample and substrate; O, carbon resistance thermometer; P, sample heater (carbon resistor); Q, wrapped Helmholtz coil; R, extension of coil form; S, carbon resistance thermometer; T, copper wires (only one of 24 shown, for clarity); U, salt pill measuring coil secondary; V, salt pill; W, salt pill measuring coil primary; and X, measuring coil form.

wrapped Helmholtz pair,[9,27] wound of superconducting wire, produced a field up to 1000 Oe normal to the plane of the film to allow precise adjustment of field direction. A paramagnetic salt pill was used as a primary thermometer, and carbon resistors were used as secondary thermometers. A bifilarly wound electrical heater provided precise temperature regulation. The apparatus was designed and constructed to minimize distortion of the magnetic field in the region of the sample; the use of magnetic materials was kept to a minimum, and the salt pill was located as far as possible from the sample. In use, the apparatus shown in Fig. 1 was in a liquid He^4 bath which could be cooled to 1.1°K by pumping.

C. Magnetic Field

A magnetic field up to 25 kOe was generated parallel to the plane of the sample by a superconducting solenoid, labeled G in Fig. 1. This solenoid was operated in the persistent mode. The field strength was determined from the solenoid current, using the field-current ratio provided by the manufacturer and subsequently verified in this laboratory by use of a Hall probe[28] which had been calibrated at 4.2°K in a liquid-nitrogen-cooled solenoid of well-known calibration.[29]

The trimming coil system, labeled J and Q in Fig. 1, provided a field up to 1000 Oe normal to the plane of the sample. This superconducting coil system was a wrapped Helmholtz pair, as described by Sarwinski.[9,27] It was calibrated by using the Hall probe described above.

The uniformity of the field produced by the solenoid, as reported by the manufacturer, was within 0.002% over the volume of the sample. The theoretical uniformity of the wrapped Helmholtz pair over the volume of the sample was $\pm 0.1\%$.

The correction of the field direction provided by the wrapped Helmholtz pair was typically 1′ or 2′. To make this correction, we relied on the fact that the critical field of a thin film is much less for a field directed normal to the plane of the film than for a field parallel to the film.[30] We applied a field approximately parallel to the sample of such magnitude that the thermal conductivity was about half-way through its transition from the superconducting to the normal-state value. The direction of this field was then slowly changed. When this direction passed through the plane of the film, the thermal conductivity was at a minimum, because at this point the applied field was the smallest fraction of the critical field. The ratio of the current in the trimming coil to that in the solenoid was noted at this point, and this ratio was maintained in further measurements on the sample in question. (A new alignment was necessary every time the cryostat was disassembled, since the alignment of the coils could change upon reassembly.) This technique allowed alignment of the field to within 0.1′. The minimum in the thermal conductivity of the thicker films was broader, but the transition to the normal state was sharper. These two factors offset each other, and the

[27] R. J. Sarwinski thesis, University of Illinois, 1966 (unpublished).

[28] The Hall probes are model HA-11 Hall generators, produced by American Aerospace Controls, Inc., Farmingdale, N.Y.

[29] This magnet is in the laboratory of Professor D. E. Mapother. It is described in D. C. Hopkins, thesis, University of Illinois, 1962 (unpublished).

[30] M. Tinkham, Phys. Rev. **129**, 2413 (1963).

precision was about the same for all samples reported upon in this work.

D. Temperature Measurement and Control

The primary thermometer for the temperature range 0.3–1°K was a Curie-law thermometer. The paramagnetic salt was chrome methalamine alum. The susceptibility of this salt was determined by measuring the mutual inductance of a set of coils surrounding the salt sample. The mutual inductance was measured using a ballistic Hartshorn bridge. The Curie-law thermometer was calibrated from 1.1 to 2.2°K against the 1958 helium vapor pressure scale, and this calibration was extended to 0.3°K by using the Hebb-Purcell and Onsager corrections. Calibration and use of this thermometer is described in greater detail elsewhere.[9,31]

Carbon resistance thermometers were used as secondary temperature standards below 1°K. The resistors were Speer resistors, 470 Ω and $\frac{1}{2}$ W, which previous experiments have shown to be good thermometers in this temperature range. The resistances of the thermometers were calibrated against the Curie-law thermometer by using an ac Wheatstone bridge and lock-in amplifier.

The magnetic thermometer and the resistance thermometers were recalibrated every time they were warmed above 77°K.

Coarse temperature regulation was achieved by manual adjustment of valves which controlled the pumping speed for the He^4 bath or the He^3 evaporator. Fine control was achieved by use of an electronic regulator.[32] The input signal for this was the ac error signal from the ac bridge system described above; the regulator supplied a current to a 200-Ω heater wound bifilarly around the He^3 evaporator. Regulation was typically ± 15, 35, and 530×10^{-6} °K at 0.3, 0.5, and 0.8°K, measured at the thermometer labeled L in Fig. 1.

E. Thermal Conductivity Measurement

Other workers[13,21,22,24] have measured the thermal conductivity of thin tin films by using one carbon resistor as both sample heater and thermometer attached to one end of the sample, the other end of which was attached to the refrigerator. Then measurement of the power dissipated in the carbon resistor and the temperature rise of the resistor allows simple calculation of the thermal conductivity. This method of measurement of thermal conductivity is analogous to the measurement of electrical conductivity by a two-terminal technique. Precision in the electrical measurement is limited by the effect of lead resistances; the analog of this limitation in the measurement of thermal conductivity is the uncertainty caused by thermal resistance between the sample and the thermometer-heater. The temperature drop which appears across the boundary between the resistor and the sample may be an appreciable fraction of the temperature difference between ends of the sample. It is generally not possible to make corrections for this effect in the calculation of thermal conductivity, so this temperature drop contributes to the uncertainty in measurement of temperature difference. Results of Morris and Tinkham[13] indicate that this effect is negligible in their measurements above 1°K. Below 1°K, however, thermal contact becomes much more difficult, and this limitation becomes increasingly serious.[33]

We used a method of thermal conductivity measurement analogous to a four-terminal measurement of electrical conductivity. Three carbon resistors, labeled M, O, and P in Fig. 1, were attached to the sample, and one end of the sample was attached to the sample holder. P served as a sample heater, analogous to the current source in the four-terminal electrical measurement. Resistors M and O were the thermometers analogous to potential leads. The sample holder was the heat sink, analogous to the current sink.

The resistors were Speer carbon resistors, 470 Ω and $\frac{1}{2}$ W. Each was prepared for use by grinding away the varnish and composition insulation on one side down to the point where a thin line of carbon was visible, giving the resistor a D-shaped cross section. Resistors M and O were further ground so that their resistances were the same within 0.1 Ω at room temperature.

Manganin leads were attached to the resistors, using cadmium-bismuth eutectic solder.[34] While this solder has a critical temperature above the temperature at which some of our measurements were made, it has an extremely small critical field, of the order of several Oe. The regions of the $K(H)$ curves of interest in this experiment lie at significantly higher fields, where the cadmium-bismuth solder is in the normal state, and is no longer a source of field distortion. The leads were 0.05 mm in diameter and 10 cm long; this length was chosen to keep the total thermal conductance of the leads less than 1% of the thermal conductance of the substrate.

The flattened sides of the resistors were glued with GE 7031 to the thin film in the positions indicated in Fig. 3. We chose to fasten the resistors directly to the thin film rather than to the substrate, to minimize thermal contact problems. The thermometer resistors

[31] D. K. Finnemore, thesis, University of Illinois, 1962 (unpublished).

[32] C. Blake and C. E. Chase, Rev. Sci. Instr. **34**, 984 (1963).

[33] H. R. Hart, Jr. and J. C. Wheatley, Intern. Bull. Inst. Froid Annexe **1**, 311 (1958); A. C. Anderson, G. L. Salinger, and J. C. Wheatley, Rev. Sci. Instr. **32**, 1110 (1961).

[34] Cerro Sales Corporation, 300 Park Avenue, New York 22, N.Y. This alloy is a good, low-melting-point solder for use in situations where the superconducting property of conventional tin-lead soft solder is objectionable. Cd–Bi eutectic alloy is superconducting, with a transition temperature between 0.5 and 1°K. It has a very low critical field, of the order of several oersted.

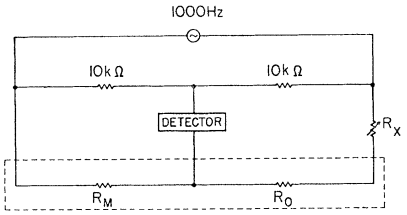

FIG. 2. Temperature-difference bridge circuit. Elements inside dashed line are in cryostat.

were typically about 7 mm apart; the heater was as close to the end of the sample as possible, and the lower thermometer was as close to the heater resistor as possible, without actually touching it. We were careful to avoid a common puddle of glue, which could introduce a high thermal conductance between the heater and lower thermometer. Visual inspection revealed no damage to the samples, and any which might have been present and invisible could affect only a very small portion of the sample. The leads were soldered to the resistors before mounting the resistors on the sample, to avoid damage to the sample by the solder flux. The same resistors were used in the same positions for all measurements reported in this work.

After the resistors were mounted on the sample, this was mounted in the cryostat. It was glued to a small projection on the sample holder, using GE 7031. The contact area was 0.4 cm^2.

Current was supplied to the sample heater by batteries, and was controlled by a variable resistance in series with the batteries and heater. Power input was determined by measuring and multiplying heater current and voltage. To account for Ohmic heating in the leads to the heater, a procedure due to Neighbor[35] was used. If we assume that half of the Ohmic heat generated in a lead flows into the heater and the other half back to the point where the lead is thermally grounded, this effect is accounted for by including the voltage drop across one of the two identical current leads with the voltage drop across the heater resistor. We therefore attached one potential lead right at the heater resistor and the other one at the point where the opposite current lead was thermally grounded. Neighbor discusses limitations of this procedure; they are negligible in the present application.

The temperature drop along the sample was measured by the two thermometers M and O. These resistors were calibrated at the same time as thermometer L, using a second, identical ac bridge system. Thermal contact between the sample holder and resistor O was poor, since it was provided entirely by the sample and substrate. (The thermometers were calibrated only between 0.3 and 0.8°K, when the cryostat was evacuated.) During the calibration, care was exercised that resistor O was in thermal equilibrium with the sample holder after changing temperature. Five minutes generally seemed to be adequate for achieving this equilibrium. To minimize errors caused by Ohmic heating of the thermometers due to the bridge current, the power dissipation was kept less than 2×10^{-12} W in the measurement of these resistances.

Using the thermometer calibration curves, the temeprature drop was related to the resistance difference between resistors M and O. This difference was measured by the bridge circuit shown in Fig. 2. The 10 000-Ω resistors were matched to within 0.1%. The bridge was balanced by adjusting R_x. When it was balanced, R_x was equal to the difference between R_O and R_M, the resistances of thermometers O and M. The resistors used as thermometers had negative temperature coefficients of resistance, so O, located at the hot end of the sample, had lower resistance. While the two thermometers were well matched in resistance at room temperature, they differed slightly at our working temperatures; they were chosen so that $R_M > R_O$. The detector of the bridge circuit was a lock-in amplifier driving a strip-chart recorder. The signal-to-noise ratio of this system was high enough that we could detect resistance differences of less than 1 in 10 000 Ω.

Our method of taking measurements eliminated the calibration of thermometer M from the data analysis. With no power applied to the sample heater, the bridge was balanced. Then R_x was increased by an amount corresponding to the desired temperature drop. The heater power was then adjusted to balance the bridge. Assuming that either (1) the temperature rise at thermometer M due to the heat flux was negligible, or (2) the temperature dependences of R_M and R_O were the same, this measurement of the temperature difference was independent of the calibration of thermometer M. Condition (1) is favored by the location of thermometer M on the thin film directly above the part of the substrate which was glued to the sample holder. Condition (2) was satisfied to within experimental error.

The measurement of relative thermal conductivities for varying magnetic field at a fixed temperature was made independent of the calibration of either thermometer by using a constant temperature drop, and varying the heat flux as the thermal conductivity changed. Then the problem was reduced to simply maintaining a constant resistance difference by adjusting power applied to the sample heater.

The principal difficulties associated with the technique were associated with the length of the thermal time constants. At 0.3°K, where the situation was worst, the time constants were on the order of several minutes. This means that after the equilibrium of the system was upset by a change of field, temperature, heater power, or other disturbance, one had to wait several time constants, on the order of 10 min, to determine whether the bridge was balanced or unbalanced. Generally, changes in thermal conductivity

[35] J. E. Neighbor, Rev. Sci. Instr. **37**, 497 (1966).

between experimental points were small enough that the proper heater power could be determined in two or three approximations.

The error signal of the temperature difference bridge was recorded on a chart recorder, as was the error signal to the ac bridge system used with resistance thermometer L. These recordings gave an indication of equilibrium. To make it possible to take data at a reasonable rate, the following criteria for acceptable bridge balance were used: (1) The chart recorder reading the error signal of the temperature difference bridge was required to be within a certain range about zero, shown in Table I in terms of the resulting uncertainty $\delta(\Delta T)$ in temperature drop ΔT at the normal operating temperatures shown in the table; (2) it was required to stay within this range for one time constant and show no tendency to leave it; (3) the ac bridge system indicating T was required to show no gross fluctuations in its recorded error signal during this period. The usual short-term variations in the operating temperature are also shown in Table I.

TABLE I. Relative uncertainties in T and ΔT at typical operating temperatures.

T, °K	δT, μ°K	(ΔT), °K	$\delta(\Delta T)$, °K
0.3	15	0.0275	0.00030
0.5	37	0.0540	0.00016
0.8	530	0.111	0.00033

V. RESULTS AND DISCUSSION

A. General Features

Raw data in this experiment yielded $\dot{Q}$, the power input to the sample heater, versus H, the applied field. As the field was varied, $\dot{Q}$ was adjusted to maintain a constant temperature drop along the sample. Thus $Q(H)$ is simply proportional to the thermal conductance of the sample shunted by the substrate and the electrical leads. $\dot{Q}(H)$ was measured at several temperatures in the range 0.3 to 1°K for each sample. The resulting curves may be characterized very generally by an initial low value of $\dot{Q}$ at $H=0$, which increases very slowly at low fields. In the region of the critical field of the sample, $\dot{Q}$ rises quickly to a value characteristic of the normal state. After reaching this value, $\dot{Q}$ is independent of field at all fields used in this work.

For comparison with theory we want to extract from these data the electronic thermal conductivity of the thin-film sample as a function of applied field. We must eliminate background due to the conductance of the substrate, the electrical leads, and the phonons in the sample. This is possible because the only significant field-dependent contribution to the heat flow is the electronic thermal conductivity of the thin-film sample. The thermal conductivity of the glass substrate is independent of magnetic fields of the magnitude used in this experiment. Any field dependence of the contribution of the electrical leads should be very slight, and should be negligible in the present situation because of the small magnitude of the thermal conductance of the leads compared with the total heat flow.

Any field dependence of the thermal conductance of the substrate or electrical leads would give structure in the $\dot{Q}(H)$ curves which would be the same for each sample. No such structure was observed. One run was made on a sample which was very thin and electrically discontinuous; in this case the thermal conductance, due to the leads and substrate alone, was independent of field within the precision of this experiment.

In thin films formed upon cold substrates, the phonon contribution to the thermal conductivity is a negligible fraction of the normal-state electronic contribution. This is contrary to the behavior of bulk specimens, where the phonon contribution is often much larger than the electronic contribution. Films which are formed upon cold substrates are characterized by very small crystallite size. This results in extremely short phonon mean free paths, limiting the phonon conductivity.[21]

Previous experiments, which have found the electronic component of the heat flow to be dominant in samples similar to ours, have all been performed at higher temperatures than our experiments. The density of phonons is proportional to T^3, so the phonon thermal conductivity decreases more rapidly than the normal-state electronic thermal conductivity. In our experiments, the field-dependent part of the phonon thermal conductivity is therefore even smaller compared to the normal-state electronic thermal conductivity, and we feel justified in ignoring it in our calculations.

A field-dependent phonon conductivity might be expected to cause an initial decrease in the total thermal conductivity of the superconducting sample as the field is increased from zero. This is due to the increase in electron-phonon scattering as the number of unpaired electrons increases with increasing field. No such effect was observed in any of our measurements.

Since the field-dependent part of $\dot{Q}(H)$ is entirely due to the electronic conductivity, we can calculate the field-dependent part of the electronic thermal conductivity, $K(H)$, from $Q(H)$:

$$K(H)-K(0)=(L/dW\Delta T)[\dot{Q}(H)-\dot{Q}(0)]. \quad (5.1)$$

L is the distance between the thermometers on the sample. W is the width and d the thickness of the sample, and ΔT is the temperature drop between the thermometers. Using the BRT[12] expression for K_s/K_n in zero field we then set

$$K(0)/K(H>H_c)=(K_s/K_n)_{\mathrm{BRT}}. \quad (5.2)$$

Equations (5.1) and (5.2) are solved for $K(H)$. The BRT value of K_s/K_n is less than 0.02 throughout the temperature range studied in this work, so slight devi-

TABLE II. Sample properties.[a]

d	T	T/T_c	ΔT	$10^{-5}K_n$	l	$(K_s/K_n)_{BRT}$
3900	0.28	0.075	0.0275	0.724±0.050	1090±83	2.35×10^{-8}
	0.49	0.132	0.0540	1.226±0.096	1060±90	2.03×10^{-4}
3000	0.30	0.081	0.0255	0.548±0.043	771±66	1.15×10^{-7}
	0.50	0.134	0.0565	0.718±0.073	606±64	2.41×10^{-4}
	0.81	0.218	0.1136	1.037±0.134	540±72	1.58×10^{-2}
1300	0.29	0.078	0.0173	1.355±0.146	1970±242	5.37×10^{-8}
	0.50	0.134	0.0356	1.713±0.223	1440±206	2.41×10^{-4}
	0.78	0.210	0.0803	2.490±0.403	1350±236	1.24×10^{-2}
1200	0.31	0.083	0.0279	0.435±0.053	592±75	1.86×10^{-7}
	0.52	0.140	0.0586	0.559±0.100	453±82	3.91×10^{-4}
	0.84	0.226	0.1154	0.819±0.198	411±101	1.98×10^{-2}
600	0.29	0.078	0.0290	0.949±0.198	1380±291	5.37×10^{-8}
	0.50	0.134	0.0464	1.112±0.301	938±254	2.41×10^{-4}
	0.61	0.164	0.0759	1.066±0.401	737±278	1.84×10^{-3}
	0.80	0.215	0.1057	2.056±0.785	1080±415	1.45×10^{-2}

[a] Temperatures are in °K, lengths in Å, and K_n is in cgs units.

ations from this theoretical expression would make a negligible contribution to the uncertainty in $K(H)$.

Knowledge of the electron mean free path l is necessary for analysis of the data. We have calculated l from the electronic thermal conductivity in the normal state by using the approximate relation

$$K_n=\gamma T v_F l/3, \tag{5.3}$$

where γ is the Sommerfeld constant in the free-electron-theory expression for the specific heat, and v_F is the Fermi velocity. According to BRT, l is unchanged in the transition from the normal to the superconducting state.

For v_F in Eq. (5.3) we use a value calculated[36] from anomalous skin effect measurements of Faber and Pippard.[37] In such measurements the product $\omega^2\sum_\infty{}^3$ is determined, where ω is the angular frequency of the measurement and $\sum_\infty$ is the real part of the surface conductivity in the extreme anomalous limit at frequency ω. In terms of this product,

$$v_F=3\pi^3\omega^2\sum_\infty{}^3/e^2\gamma. \tag{5.4}$$

Faber and Pippard's measurements on bulk, polycrystalline tin give $\omega^2\sum_\infty{}^3=17.8c^6$ (Gaussian). Using $\gamma=1.75\times10^4$erg/(°K^2 mole)[31] and the molar volume of tin, 16.064 cm^3/mole,[31] we obtain $v_F=0.65\times10^8$ cm/sec. Tin has a highly anisotropic Fermi surface, so this measurement on a polycrystalline sample represents some sort of average over the Fermi surface. Lacking detailed knowledge of the structure of our samples, this average value of v_F is probably as good as any for our calculations.

Values of l are given in Table II. Note that there is no systematic variation of l with film thickness, indicating that l is limited by bulk effects rather than by sample size. In the case where electron scattering is predominantly by impurities, imperfections, and grain boundaries or sample boundaries, the mean free path should be independent of temperature. On the other hand, if scattering from phonons were the limiting process, the mean free path would vary inversely as the phonon density, or as T^{-3}. The values of l determined from our measurements have a systematic temperature dependence which would suggest the presence of a large amount of phonon scattering. This seems unlikely in the present case, however. In good, single-crystal tin, where the scattering is almost certainly phonon-limited. l has been observed to be as large as a millimeter at 1°K.[38] This is much larger than values of l observed in this experiment. It therefore seems unlikely that phonon scattering plays an appreciable role in determining l. Equation (5.3) is a result of the free-electron theory, and part of the apparent temperature dependence of l may be due to failure of this simple model in the present situation.

Morris and Tinkham[13] have also reported values of l for tin films produced by techniques similar to ours. Their values of l are consistently lower than ours, but the difference has a simple explanation: They assumed $v_F=10^8$ cm/sec, compared with our use of 0.65×10^8 cm/sec. Their results showed no temperature dependence.

Data in most cases were taken as the field was decreased in a stepwise fashion from the highest field on the $K(H)$ curve. Several runs were made in both increasing and decreasing fields to check for hysteresis. The curves were completely reversible in all cases,

[36] C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), p. 315. We assume diffuse reflection at the surface of the sample.

[37] T. E. Faber and A. B. Pippard, Proc. Roy. Soc. (London) **A231**, 336 (1955).

[38] N. V. Zavaritskii, Zh. Eksperim. i Teor. Fiz. **39**, 1571 (1960) [English transl.: Soviet Phys.—JETP **12**, 1093 (1961)].

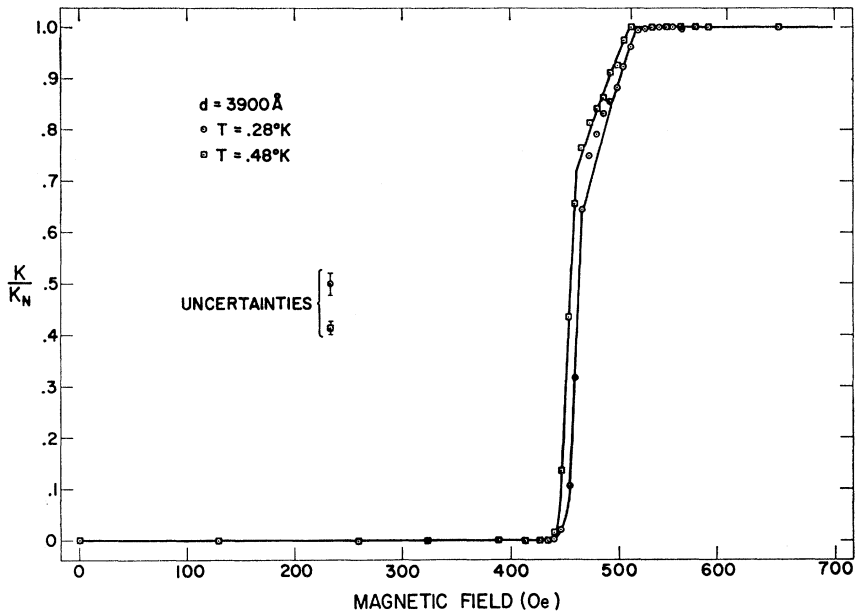

FIG. 3. Reduced thermal conductivity versus magnetic field for the 3900 Å tin sample.

indicating a lack of flux trapping and superheating or supercooling.

B. Behavior of the Thicker Films

The measurements made on our thickest samples, which were 3900 and 3000 Å thick, are most readily explained by existing theory. These samples are thick compared to both $\xi(T)$ and $\lambda(T)$, and satisfy the Ginzburg-Landau criterion for a first-order phase transition to the normal state in a magnetic field, which should be accompanied by a discontinuous change in $K(H)$.[18]

Figures 3 and 4 show results for these samples. They are characterized at all temperatures by the fact that $K(H)$ is independent of field almost up to the point where a first-order phase transition occurs; at this point there is a nearly discontinuous jump in $K(H)$. However this jump is not to K_n, the thermal conductivity of the normal state. A layer at each face of the film persists in the superconducting state, and has reduced thermal conductivity. This is the surface sheath state of de Gennes and Saint James. In this state the thermal conductivity continuously approaches K_n as the field approaches H_{c3}, indicating a second-order phase transition.

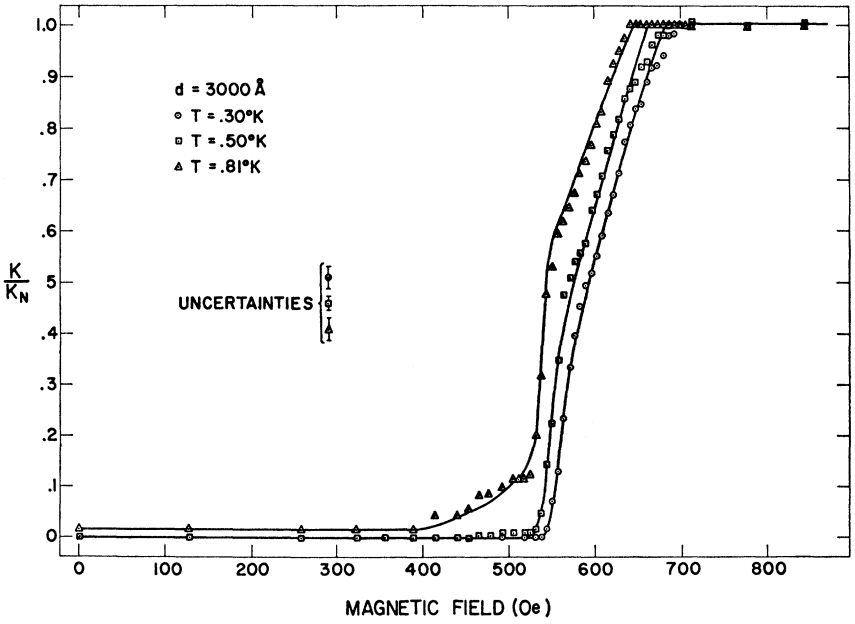

FIG. 4. Reduced thermal conductivity versus magnetic field for the 3000 Å tin sample.

TABLE III. Characteristics of thicker films.[a]

Experimental parameters						Theoretical $\kappa_1(T)$[c]		
d	T	H_{cf}	$\lambda(T)$	H_{c3}	$\kappa_1(T)$[b]	for $\eta=1$	for $\eta=1.5$	for $\eta=2$
3000	0.29	585±17	1370±60	682±22	0.94±0.03	0.66	0.68	0.71
	0.50	568±17	1340±60	663±22	0.92±0.03	0.73	0.75	0.78
	0.78	545±16	1310±60	645±21	0.93±0.03	0.74	0.76	0.78
3900	0.30	463±14	1200±70	517±18	0.71±0.02	0.49	0.51	0.54
	0.50	456±14	1190±70	509±17	0.71±0.02	0.49	0.51	0.54

[a] All fields are in Oe, lengths in Å, and temperatures in °K.
[b] $\kappa_1(T)$ is derived from the London relation, Eq. (5.5).
[c] Theoretical values of $\kappa_1(T)$ are given for three values of η, the ratio of s-wave mean free path to transport mean free path.

The jump which we have identified as a first-order phase transition is not discontinuous, but has a width of about 5% of the critical field. In part this is accounted for by the effect of the temperature gradient. If this were the sole cause, we would expect widths of about 0.3, 0.5, and 1.3% of H_c at 0.3, 0.5, and 1°K, respectively. Possible causes for the rest of the broadening are variations in film structure and thickness, and strains, all of which can cause local variations in the critical field.

Ittner has treated the problem of the critical field of a thin film which has a first-order phase transition.[39] He found the London theory result to be valid, provided that the penetration depth was properly generalized to include the effects of finite electron mean free path and the nonlocal relation between current and vector potential. In terms of such an effective penetration depth $\lambda(T)$ and the bulk critical field $H_{cb}(T)$, the critical field $H_{cf}(T)$ of a film of thickness d is given by

$$[H_{cf}(T)/H_{cb}(T)]^2 = \{1+[2\lambda(T)/d]\tanh[d/2\lambda(T)]\}^{-1}. \quad (5.5)$$

Using data of Finnemore and Mapother[40] for $H_{cb}(T)$ of bulk tin, we have solved Eq. (5.5) for $\lambda(T)$. These results are shown in Table III. The values of H_{cf} shown in this table correspond to the midpoint of the steep rise in $K(H)$. Ittner[39] has calculated $\lambda(T)$ as a function of l and d for tin films. He finds the temperature dependence to be very nearly that predicted by the two-fluid model:

$$\lambda(T)=\lambda(0)[1-(T/T_c)^4]^{-1/2}. \quad (5.6)$$

He gives the dependence on l and d in a plot of $\lambda(0)$ versus d for $l=\infty$, 10 000, and 1000 Å. Precise comparison of our results with this calculation is difficult because of the uncertainties in our values of l, and because of the extrapolation for $l<1000$ Å in the 3000 Å sample, but the agreement is fair.

The region between H_{cf} and the point where $K(H)$ reaches K_n is the surface sheath state. The upper end of this region is the surface critical field given by[41]

$$H_{c3}(T)=2.39\kappa_1(T)H_{cb}(T). \quad (5.7)$$

This expression is valid only for $d>1.8\xi(T)$, a condition easily satisfied by these samples. Using once again the results of Finnemore and Mapother[40] for $H_{cb}(T)$, we have solved Eq. (5.7) for $\kappa_1(T)$. Eilenberger[42] has calculated $\kappa_1(T)$ theoretically for a variety of conditions of temperature and mean free path in bulk specimens. His calculations depend upon the ratio of transport mean free path to s-wave mean free path. There is no way to determine this ratio for our samples, but he suggests that the best choice is probably 1.5. In Table III we show experimental values of $\kappa_1(T)$ and those determined theoretically by Eilenberger.

Both the experimental and theoretical values of $\kappa_1(T)$ are greater than 0.417, the threshold for the existence of a surface sheath state, as expected. But we see that there are large discrepancies between the theoretical and experimental values, the measured values being larger in all cases. This has a number of possible explanations: (1) There are large uncertainties in the experimental determinations of $\kappa_1(T)$ and l, particularly l. In addition to the uncertainties shown in Table III, v_F has no single value in a highly anisotropic metal such as tin. Since we have no way of estimating the resulting uncertainty, it is not included in those listed in Table III. (2) There is also the question raised by Eilenberger, of the proper choice of the ratio of transport mean free path to s-wave mean free path. (3) The generalized Ginzburg-Landau parameter $\kappa_1(T)$ should depend on film thickness in a thin-film superconductor with nonlocal electrodynamics. $\kappa_1(T)$ is of the order of $\lambda(T)/\xi(T)$, and we know that $\lambda(T)$ is enhanced in a sufficiently small specimen. Eilenberger's calculations are for bulk specimens, and do not take such effects into account.

We might also note that the measured values of $\kappa_1(T)$ all indicate the materials should be type-II superconductors. But the film thicknesses are suffi-

[39] W. B. Ittner, III, Phys. Rev. **119**, 1591 (1960).
[40] D. K. Finnemore and D. E. Mapother, Phys. Rev. **140**, A507 (1965).
[41] D. Saint James and P. G. de Gennes, Phys. Letters **7**, 306 (1963).
[42] G. Eilenberger, Phys. Rev. **153**, 584 (1967).

ciently small that $H_{cf}>H_{c2}$, and the type-II character does not affect the properties of the films.

The thermal conductivity of the film in the surface sheath region is given by Eq. (2.11). The surface sheath state is one in which the order parameter $\Delta(\mathbf{r})$ has its maximum value at the surface of the specimen, falling off towards the interior of the specimen. The thermal conductivity, which is a function of $\Delta(\mathbf{r})$, varies with position in the film. This expression represents an average value of $K(H)$ for the whole film, the quantity actually calculated by means of Eqs. (5.1) and (5.2).

To evaluate Eq. (2.11) and compare it with experimental results, we substitute $\kappa_1(T)$, determined experimentally using Eq. (5.7), for $\kappa_2(T)$. Calculations by Caroli, Cyrot, and de Gennes[43] indicate that in the dirty limit, $l\ll\xi_0$, this introduces an error which is much smaller than the uncertainty in $\kappa_1(T)$. ρ is given by $\rho=\rho_c(H/H_{c3})$, where ρ_c is derived from a numerical solution of Eq. (2.13). The measured value of K_n is used, and H_{c3} is chosen to give the best fit of Eq. (2.11) to the experimental data. Only H_{c3} is treated as an adjustable parameter in this comparison of theory with experiment. $\kappa_1(T)$ and consequently $\kappa_2(T)$ are functions of this choice of $H_{c3}(T)$. The portions of the solid lines in Figs. 3 and 4 representing the surface sheath regions are plots of Eq. (2.11). In Figs. 5 and 6 this region is shown in somewhat greater detail.

The theory predicts a sharp break in the $K(H)$ curve at $H_{c3}(T)$, but experimentally we find a slightly rounded approach to the normal state. A likely cause of this rounding is a variation in $H_{c3}(T)$ with position in the sample, due to variations in film thickness and structure, and due to the temperature gradient along the sample.

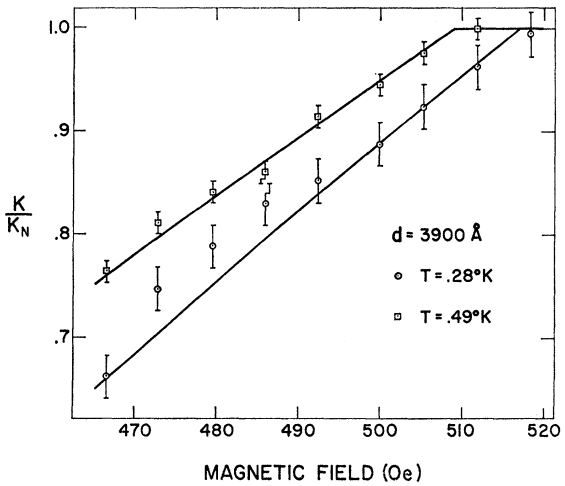

FIG. 5. Reduced thermal conductivity versus magnetic field in the surface sheath region for the 3900 Å tin sample. The solid lines are theoretical calculations.

[43] C. Caroli, M. Cyrot, and P. G. de Gennes, Solid State Commun. **4**, 17 (1966).

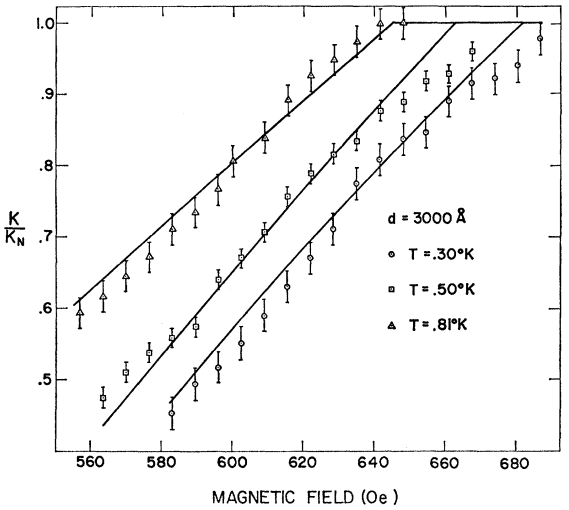

FIG. 6. Reduced thermal conductivity versus magnetic field in the surface sheath region for the 3000 Å tin sample. The solid lines are theoretical calculations.

Equation (2.11) has been derived with the assumption that $\langle|\Delta(\mathbf{r})|^2\rangle$, given by Eq. (2.10), is small. This condition is best satisfied near H_{c3}, because $\langle|\Delta(\mathbf{r})|^2\rangle$ goes continuously to zero as H approaches $H_{c3}(T)$. For this reason we have chosen to give more weight to points nearer $H_{c3}(T)$ (but out of the rounded region) in cases where a uniformly good fit to all points in the surface sheath region is not possible.

At the lower end of the surface sheath region the theoretical value of $\langle|\Delta(\mathbf{r})|^2\rangle/\Delta_{00}^2$ is of the order of 0.2. (Δ_{00} is the order parameter in zero field and zero temperature.) The agreement between experiment and theory is surprisingly good in view of this apparent failure to satisfy the requirement of a small order parameter. The calculation by Caroli and Cyrot of $K(H)$ is a power-series expansion in powers of $\langle|\Delta(\mathbf{r})|^2\rangle$, carried to first order only. Higher-order terms have not been calculated, and we have no reason to assume that they are large under the conditions covered by our experiments.

Both the calculation by Caroli and Cyrot[11] and Maki's[15] calculation of $\langle|\Delta(\mathbf{r})|^2\rangle$ are valid only in the dirty limit, $l\ll\xi_0$. Guyon[44] has suggested that the expression for $\langle|\Delta(\mathbf{r})|^2\rangle$ might be corrected for nonzero values of l, using the results of Guyon, Meunier, and Thompson.[16] These corrections would in all cases be less than 10% in our samples. Because of our poor knowledge of l, uncertainties in the corrections are actually greater than the corrections themselves. Furthermore, this would still leave the relation between $K(H)$ and $\langle|\Delta(\mathbf{r})|^2\rangle$ uncorrected. Because of these uncertainties, we have decided to present only the theoretical expressions which are consistently in the dirty limit. These provide a surprisingly good fit to the experimental data.

[44] E. Guyon (private communication).

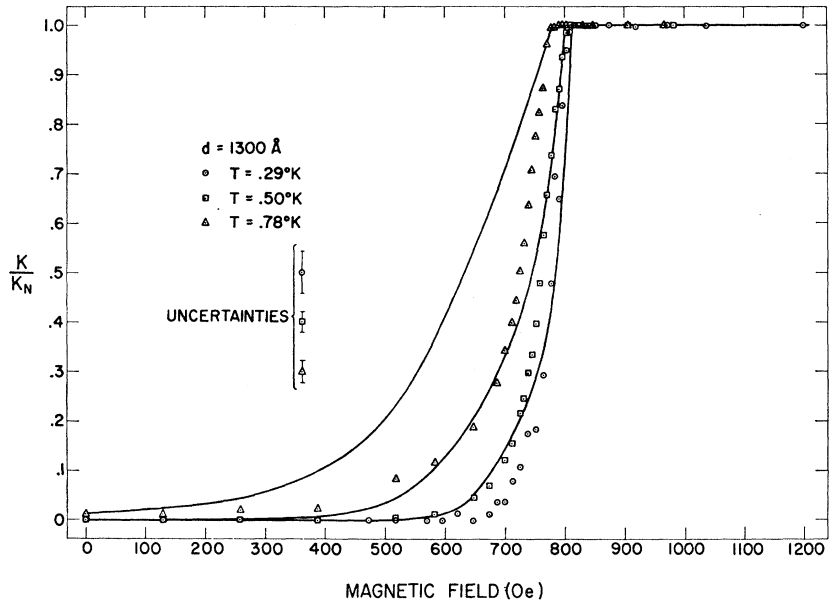

FIG. 7. Reduced thermal conductivity versus magnetic field for the 1300 Å tin sample. The solid lines are theroetical calculations.

C. Behavior of the Thinner Films

In this section we consider samples showing second-order phase transitions to the normal state in a magnetic field. Such behavior is observed in thin films; the Ginzburg-Landau theory predicts that the transition should be of second order for $d<(\sqrt{5})\lambda(T)$. Maki's[10] calculations of thermal conductivity, discussed in the second section, apply to such samples. His results are strictly valid only when (1) the phase transition is second order, (2) $\Delta(\mathbf{r})$ is independent of position, that is, $d\ll\xi(T)$, and (3) $l\ll\xi_0$.

We have measured the thermal conductivity of samples which were 1300, 1200, and 600 Å thick. These data are plotted in Figs. 7, 8, and 9. The solid lines are the results of our numerical evaluation of Maki's theoretical expressions, with field values normalized to agree with experiment for at least one temperature as H approaches H_{cf}; the same normalization is used at all temperatures.

Morris and Tinkham[13] associated a first-order phase transition with a discontinuity in $K(H)$ at H_{cf}; for a second-order transition $K(H)$ is expected to be continuous through the transition. We find this criterion difficult to apply at low temperatures. In the case of films which should show a discontinuity in $K(H)$, the

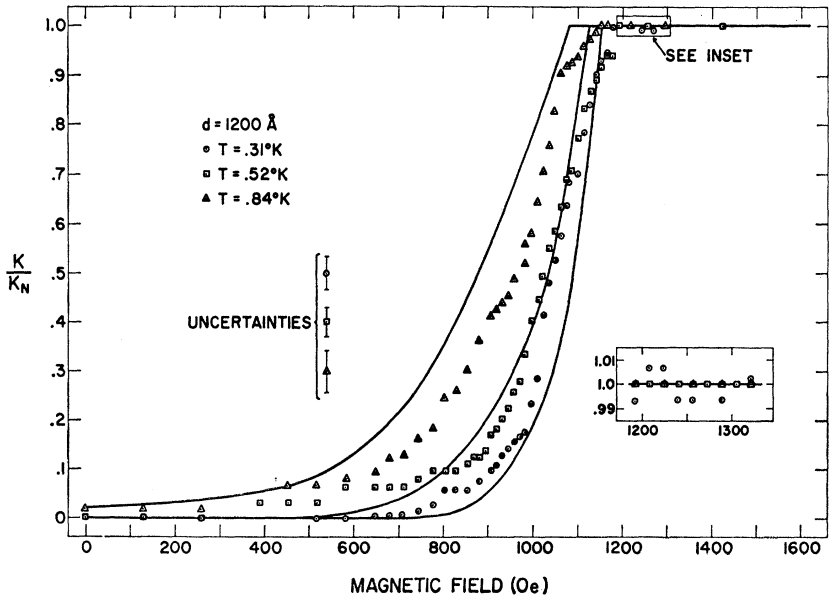

FIG. 8. Reduced thermal conductivity versus magnetic field for the 1200 Å tin sample. The solid lines are theoretical calculations.

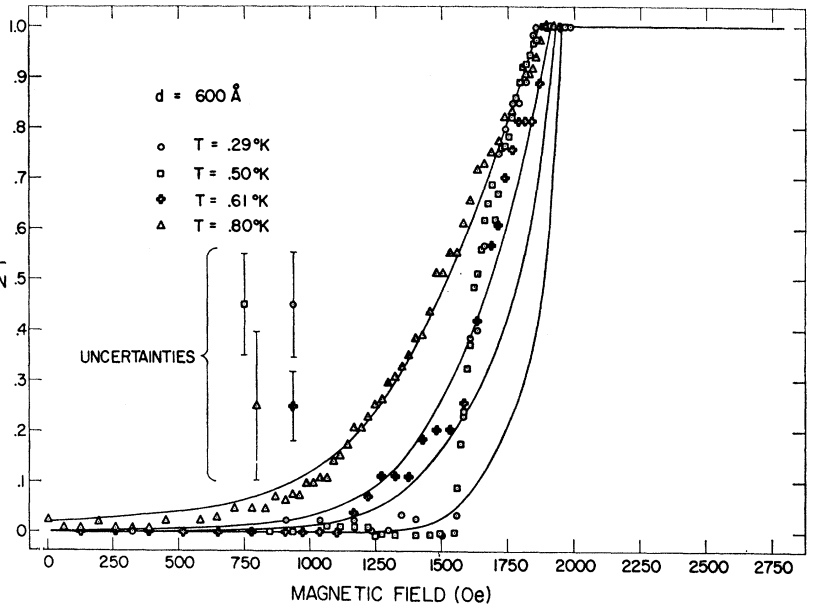

FIG. 9. Reduced thermal conductivity versus magnetic field for the 600 Å tin sample. The solid lines are theoretical calculations.

jump is always broadened somewhat for the reasons discussed in the last section. Maki's[10] calculations indicate that as the temperature is lowered the final rise of $K(H)$ to K_n should become steeper, and this type of behavior is very hard to distinguish from a broadened first-order transition.

Since the $K(H)$ plots do not unambiguously identify the order of the phase transition, more consideration of this question is necessary. Let us first consider the 1300 Å sample in detail. If we assume the transition to be of first order in this sample, then we can solve Eq. (5.5) for $\lambda(T)$. This assumption leads to an effective penetration depth of about 900 Å. The Ginzburg-Landau theory would then indicate the transition to be of first order only if $d>2000$ Å.

We might also calculate an effective penetration depth from the Ginzburg-Landau theory rather than from Eq. (5.5), which is derived from the modified London theory. de Gennes[45] has used the Ginzburg-Landau theory to show that for a thin film with a first-order transition $H_{cf}(T)$ and $\lambda(T)$ are related by Eqs. (5.8) and (5.9):

$$\left(\frac{H_{cf}(T)}{H_{cb}(T)}\right)^2\left(1+\frac{\epsilon f+\sinh\epsilon f}{\epsilon f(1+\cosh\epsilon f)}-\frac{4}{\epsilon f}\tanh\tfrac{1}{2}(\epsilon f)\right)=f^4, \tag{5.8}$$

$$1+\frac{1}{6}\frac{f^2}{1-f^2}=\frac{1}{3}\frac{\epsilon f[1-\cosh\epsilon f]}{\epsilon f-\sinh\epsilon f}. \tag{5.9}$$

In these equations $\epsilon=d/\lambda(T)$, and f is the reduced order parameter. For our present purposes we merely treat f as a parameter to be eliminated in the solution of Eqs. (5.8) and (5.9). de Gennes has shown that when the phase transition is of second order, no physical solution of these equations exists. We find this to be the case for the 1300 Å sample. We have also carried out this analysis for the 3900 and 3000 Å samples, and we find that the resulting values of $\lambda(T)$ are about 15% smaller than those derived by Eq. (5.5).

Our results indicate that the phase transition in the 1300 Å film is of second order in a magnetic field at all temperatures. The 1200 and 600 Å samples both have shorter mean free paths than the 1300 Å sample, as can be seen in Table II. Ittner's[39] calculations show that these samples should then have larger penetration depths and smaller values of $d/\lambda(T)$. So if the 1300 Å sample has a second-order transition, we may safely assume that these thinner samples, in which the electron mean free paths are shorter, also have second-order transitions.

The field dependence of the thermal conductivity of the 1300 Å sample, shown in Fig. 7, is only qualitatively accounted for by Maki's[10] calculations. The experimental results indicate that the transition begins at somewhat higher fields than the theory predicts, and $K(H)$ then rises more steeply to the normal-state value. This result might be qualitatively explained by the fact that neither the condition $d\ll\xi(T)$ nor $l\ll\xi_0$ is well satisfied. de Gennes[45] calculates the penetration depth in the dirty limit to be

$$\lambda(T)=0.64\lambda_L(0)\{(\xi_0/l)[T_c/(T_c-T)]\}^{1/2}. \tag{5.10}$$

In this expression, $\lambda_L(0)$ is the London penetration depth at $T=0$. $\lambda(T)$ becomes infinite as l/ξ_0 approaches 0. Maki's calculation assumes this result, and so assumes complete flux penetration into the sample.

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

The mean free path of our sample is nonzero, so we expect a shorter penetration depth and more screening of the interior of the sample from the applied field. The thickness is large enough so that we expect a small variation of $\Delta(\mathbf{r})$ with position in the film. In fields below $H_{cf}(T)$ we then expect the order parameter to be slightly higher at the center of the sample than at the edges. This shielding of the interior then delays the beginning of the rise of $K(H)$, and causes a steeper rise of $K(H)$ to the normal-state value, as we have observed.

In the 1200 Å sample, the mean free paths are only about 30% of the mean free paths of the 1300 Å sample Figure 8 shows that the Maki calculation is in better agreement with experiment in this case. The agreement is still not good, but the (expected) improvement as we approach the dirty limit is striking.

It is hard to draw conclusions from Fig. 9, $K(H)$ for the 600 Å sample, because of the large amount of scatter in the data. In this case the background due to substrate and electrical leads was far larger than the electronic thermal conductivity of the thin film. The 0.8°K data have far less scatter than our estimated uncertainty would predict. These data are in good agreement with the theoretical curve for this temperature. Results at lower temperature show larger scatter and poorer agreement with theory. The larger scatter at lower temperatures is due to long thermal time constants, which made it difficult to achieve equilibrium in this sample.

Maki's[10] calculations predict the onset of gaplessness at applied fields $H \approx 0.95 H_{cf}$. Theory predicts no singular behavior in $K(H)$ at this point,[10] in agreement with our experimental results.

Our results seem to approach the behavior predicted by Maki as the samples approach the dirty limit, but detailed explanation of our results would require a theory which treats nonzero values of l.

D. Conclusions

The dirty-limit calculations of thermal conductivity in a magnetic field have been compared with experiments. In the case of thick films, the Caroli and Cyrot[11] calculation is in very good agreement with experiment. This agreement extends over a broader range of field than is required by the theoretical calculations, and to mean free paths clearly outside the dirty limit.

We have also discussed the dependence of the penetration depth and Ginzburg-Landau κ on mean free path and sample size. The uncertainties in these calculations do not allow any firm conclusions about the validity of theory, but their general agreement with theory lends support to our interpretation of the behavior of the thick films.

Maki's[10] calculations apply in the case of thin films. Here the agreement is not as good as the thick-film case, but the data show better agreement with theory as we approach the dirty limit, as one would expect.

It would be interesting to see the calculations extended to longer mean free paths. For thick films the range of field strength over which we find good agreement is surprisingly large. Parks, Zumsteg, and Mochel,[24] working with thick, type-II films in which the surface sheath had been suppressed by a thin layer of Mn on each face of the film, found the thermal conductivity to be a linear function of field throughout the range from H_{c1} to H_{c2}. This discovery and our results indicate that terms higher than first order in $\langle | \Delta(\mathbf{r}) |^2 \rangle$ make only a small contribution to $K(H)$. It would be interesting to see the calculation of Caroli and Cyrot extended to include these higher-order terms.

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