first penetration of the ac field into the sample defines the dc field at which the critical current, in the model illustrated in Fig. 2, is reached. However, because of experimental factors such as precise identification of the transition point and other points discussed in the paper, we felt the χ'' peak was the best "all-around" point to use for the transition. After submission of this paper Fink,[12] and Rollins and Silcox[13] have discussed the χ' and χ'' transitions in great detail. From Fink's work one gets the relation that $h_c=0.385\ H_{ac}$. Hence the critical current values on this argument should be given by $0.385\ H_{ac}=0.4\pi J_c$. This would then reduce all our current values by over a factor of 2.5. h_c is defined by Fink as the vertical height from $4\pi M=0$ to point (2,6) in the high-field hysteresis loop (curve B) in Fig. 2. This is of course just the point at which any increase in dc field will cause χ' to deviate from $-1/4\pi$, as discussed in the paper.

[12] H. J. Fink, Phys. Rev. Letters **16**, 447 (1966).
[13] R. W. Rollins, J. Silcox, Bull. Am. Phys. Soc. **11**, 224 (1966).

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Thermal Conductivity of Thick Pure Lead Films for the Study of Surface Superconductivity*†

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The differential thermal conductivity of lead films in a magnetic field parallel to the plane of the film has been measured in the temperature range 1.2 to 4.2°K. The thicknesses of the films (from 2500 to 7000 Å) have been selected so that the expected volume of the superconducting surface regions is an appreciable volume fraction of the sample. The fraction of material remaining in the surface superconducting state just above the film's critical field is related to the measured thermal conductivity via a simple phenomenological model. The analysis allows a heuristic determination of the product of the thickness of the superconducting surfaces and the square of the order parameter at the surface. The results are compared with the recent calculations of Fink and Kessinger. Well defined values of H_c and H_{c3} are obtained. Some hysteresis is observed near H_c in a decreasing magnetic field, and the role of phonons in the heat transport is manifest, but its contributions above H_c is negligible when compared with the electronic contribution to the thermal conductivity.

I. INTRODUCTION

SURFACE superconductivity[1] was predicted by Saint James and de Gennes for type-II superconductors[2] for magnetic fields up to $1.69H_{c2}$. At H_{c2} the magnetic field completely fills the interior of a type-II superconductor, keeping the interior in the normal state. The Saint James–de Gennes superconducting surface layer is expected to have a thickness of the order of the superconducting coherence[3] distance ξ. The existence of surface superconductivity in type-II superconductors is well established.[4]

Remnant superconducting properties have also been observed in type-I superconductors above the bulk thermodynamic critical field H_c. Among the indications of this phenomenon were the microwave surface resistance[5] on pure bulk lead, the magnetization[6] in dilute alloys of the Bi-Pb system, and electron tunneling[7] in thick pure films of lead. These experiments have been interpreted in terms of surface superconductivity mainly on the basis of the observation that superconductivity exists for external fields up to $H\approx 1.7\ H_{c2}$, where even for a type-I superconductor H_{c2} is taken as $\sqrt{2}\kappa_{G.L.}H_c$. ($\kappa_{G.L.}$ is the dimensionless Ginsburg-Landau parameter.) The purpose of this work is to investigate the superconductivity of pure lead below and above H_c by measurements of the thermal and electrical conductivity. The significance of the thermal conductivity approach is that it may be used to demonstrate directly that the thickness of the superconducting region is of the order of the coherence distance.[8]

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† Supported in part by the National Science Foundation.
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[1] D. Saint James and P. G. de Gennes, Phys. Letters **7**, 307 (1963).
[2] V. L. Ginsburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz **20**, 1064 (1950).
[3] A. B. Pippard, Proc. Roy. Soc. (London) **A203**, 210 (1950).
[4] E. Guyon, A. Martinet, J. Matricon, P. Pincus, Phys. Rev. **138**, A746 (1965); and paper by the Orsay Group on Superconductivity (to be published), and their references.
[5] B. Rosenblum and M. Cardona, Phys. Letters **9**, 220 (1964); **13**, 33 (1964).
[6] A. Paskin, M. Strongin, P. P. Craig, and D. G. Schweitzer, Phys. Rev. **137**, A1816 (1965).
[7] Y. Goldstein, Phys. Letters **12**, 169 (1964); and *Proceedings of the IX International Conference on Low Temperature Physics* (Plenum Press, Inc., New York, 1965).
[8] T. Seidel and H. Meissner, Bull. Am. Phys. Soc. **10**, 59 (1965); Physics Letters **17**, 100 (1965) and Proceedings of the Fifth Thermal Conductivity Conference, Denver; III-D-I, Oct. 1965 (unpublished).

The thickness of the superconducting surface layer in pure lead is expected at low temperatures to be of the order of $\xi_0=740$ Å (see Ref. 9). For bulk specimens, one would therefore expect to measure a value of the thermal conductivity just above H_c which is within a few percent of the normal-state thermal conductivity. However, if the thickness of the sample is only several times the thickness of the superconducting surface, then the value of thermal conductivity just above H_c should be significantly smaller than the normal-state thermal conductivity. If one anticipates surface superconductivity in the sense of Saint James and de Gennes, then, as the thickness of the specimen is reduced from ~ 10 to 3 coherence distances, we should observe progressively stronger superconducting properties just above H_c. Finally, if the value of the order parameter in the superconducting surface layer for a field just above H_c is not much less than the zero-field order parameter, then a film whose thickness is roughly equal to that of two Saint James–de Gennes-like layers will exhibit essentially superconducting properties just above H_c.

Since it has been indicated that studies of the thermal conductivity are potentially interesting, it is worth while to compare the contribution of the electronic and the phonon conductivities for pure lead films of thicknesses less than one micron. For the normal state, the ratio of electron to phonon conductivities is much greater than 1. This can be understood by comparing the thermal conductivities for electrons with that for phonons. Both can be obtained from the relation $\kappa=\frac{1}{3}cvl$, where c, v, and l are the specific heat, the velocity and the mean free path of phonons or electrons. For our pure films, electron mean free paths are found to be at least equal to the thickness of the film, while the phonon mean free path may be expected to be equal to or somewhat less than the specimen thickness.[10] The Fermi velocity is $\sim 10^3$ times the phonon (sound) velocity, while the electron and phonon specific heats are comparable for lead in the temperature range of interest. It follows that the thermal conductivity of lead films results mainly from the heat transport by the electrons. Furthermore, the electrons are scattered almost entirely by static imperfections including diffuse boundary scattering, since the residual resistance is independent of the temperature.

We are interested in the manner in which the electronic thermal conductivity changes from its zero-field superconducting value to the normal-state value at constant temperature under an increasing magnetic field. By a suitable choice of materials (e.g., pure Pb as compared with pure In), of their thicknesses, and of the temperature, one is able to distinguish type-I superconductors with $\kappa_{\mathrm{G.L.}}<0.42$ from type I with $\kappa_{\mathrm{G.L.}}>0.42$, and probably both of these from type-II superconductors.

[9] For a typical evaluation of ξ_0 for pure lead see P. Hilsch and R. Hilsch, Z. Physik **180**, 10 (1964).

[10] K. Mendelsohn, Can. J. Phys. **34**, 1315 (1956).

II. DESCRIPTION OF EXPERIMENT

Following the ideas expressed above, thin-film samples were prepared by evaporation of the metal onto glass substrates and their thermal and electrical resistances were measured as a function of the magnetic field for various temperatures.

For the thermal-conductivity measurements the method of Morris and Tinkham[11] was used, to obtain the normalized differential thermal conductivity $\Delta\kappa=[\kappa(H)-\kappa(0)/[\kappa_n-\kappa(0)]$, where $\kappa(H)$ is the film's thermal conductivity in a parallel applied magnetic field H, $\kappa(0)$ that in zero field, and κ_n that in a magnetic field large enough to completely destroy all traces of superconductivity. The differential method allows the conductance of the glass substrate to be subtracted out. The electrical resistance of a separate specimen is measured using a four-terminal method.

The samples were prepared by evaporation in vacuum (2×10^{-6} Torr) onto "00" Corning cover-glass slides at room temperature of the dimensions 0.0075 cm$\times$0.4 cm $\times$1.0 cm. During evaporation, the substrates for thermal and electrical specimens were positioned in the same plane and far enough from the evaporation source so that the thicknesses of the films on the two substrates are identical. The substrates to be used for the thermal-conductivity measurements were prepared before the evaporation by cementing 0.1-W Allen-Bradley resistors (100 Ω at room temperature) onto the side of the glass opposite the side bearing the film. Thus, the film is a uniform slab of material whose area is identical to that of the glass substrate, and since the film itself is untouched, there is no mechanical damage to the film. The resistors were used as heater-thermometer and reference thermometer. The resistors were suitably prepared to give a large contact area to the glass.

The electrical-resistance measurements were made on a well-defined area scribed out with a razor blade so that the current and potential leads could be kept separate and so that no penumbra effects would falsify the electrical transitions.

A cryostat was used which is schematically shown in Fig. 1. The samples were cemented to an OFHC copper rod which was screwed into the bottom of the inner He vessel. Both the rod and the samples were aligned parallel to a uniform magnetic field of a precision-wound niobium solenoid. The region containing the specimens had a magnetic field which was uniform to 1 part in 10^3; the alignment of the samples with respect to the field was within 1.5°. The solenoid produced fields up to 6500 G. The temperature of the samples could be varied from 1.1 to 5°K by controlling the vapor pressure over the bath of the inner vessel. A long-time temperature stability was obtained by using a temperature controller described previously,[12] and tem-

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

[12] H. Meissner, Phys. Rev. **109**, 668 (1958).

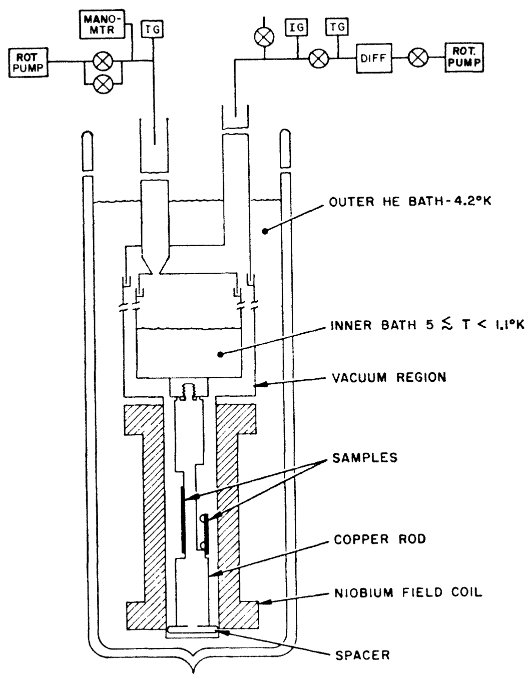

FIG. 1. Schematic drawing of cryostat and auxiliary equipment.

perature fluctuations were held to less than 50 μdeg by using an RC smoothing network in the feedback circuit. The vacuum region was kept at a pressure of $\sim 10^{-6}$ Torr during the runs.

The pair of temperature-sensitive resistors are used as the heater-thermometer R_1 and a reference thermometer R_2, in order to measure the changes in thermal conductivity of the metal film. R_2 and part of the glass substrate are cemented to the copper finger which is in contact with the inner helium bath. R_2 is electrically insulated but in thermal contact with the block. The lead resistances were a small fraction of R_1 or R_2 and the resistors were matched to within about 5%. R_1 and R_2 form one side of a Wheatstone bridge. The ratio of R_1 and R_2 (designated r) was measured first in the limit of zero power to the bridge and in zero magnetic field $r_0(0)$, then with a finite operating current through the bridge and in zero field $r(0)$; then the ratio was measured at various values of the magnetic field $r(H)$. The differential thermal conductivity was computed from these measurements using the formula:

$$\Delta\kappa(H)=\frac{r(H)-r(0)}{r(H_c)-r(0)}\,\frac{r_0(0)-r(H_c)}{r_0(0)-r(H)}, \qquad (1)$$

where, for the case of several critical fields, H_c is taken as the highest, H_{c3}. In deriving this formula, account is taken of the fact that the power developed in the heater-thermometer (i^2R_1) depends upon the value of R_1 for the particular value of the field at which the measurement is being made.[13] Measurements were made with the Wheatstone bridge under null conditions and well after the steady state was established.

III. EXPERIMENTAL RESULTS

The data for the thermal and electrical transitions of our 3500-Å thick In film are given in Fig. 2. They are compared with the published data of Morris and Tinkham[11] (MT) for the same metal and roughly the same thickness (4000 Å). Both exhibit sharp transitions and there is only one critical field. That is, the critical fields determined from electrical and thermal measurements agree with each other. The experimental agreement between our data and those of MT is seen to be satisfactory. The data on indium are presented to show that we do reproduce the results of MT on thick films, and also to allow for a direct comparison with the Pb results. It is seen in Fig. 2 that Pb shows a structure in the transition, while In does not.

The data on the 7000 Å Pb film for three temperatures are given in Fig. 2; the electrical and thermal transitions at lower temperatures (2.13 and 1.2°K) show that there is essentially no change in $\Delta\kappa$ until $H=H_c$. Here, H_c is the film critical field associated with the jump in $\Delta\kappa$. The thermal transition is not complete until H_{c3}, where the electrical resistance rises from zero. These measurements indicate that (at lower temperatures) about 40% of the specimen remains superconducting at H_c. All the electrical transitions were highly reversible, while the thermal transitions showed hysteresis in the vicinity of H_c. The data are sufficient to establish values of H_{c3} and H_c, and also suggest a linear region between H_c and H_{c3} for $\Delta\kappa$. Note the initial decrease in $\Delta\kappa$ for $H<H_c$, which has been overemphasized by the change in scale. The decrease is less than 3% of the total change and less than 0.05% at temperatures below 2°K. The residual resistance ratio $R_{300}/R_{4.2}$ of this specimen is 190.

Figure 3 shows the thermal and part of the electrical transitions for a 4500-Å Pb film. Different power levels were used for the thermal measurements at some temperatures, demonstrating that $\Delta\kappa$ is independent of the temperature gradient. At lower temperatures it is seen that 60% of the specimen remains superconducting at H_c. Again at low temperatures there is essentially no change in $\Delta\kappa$ until $H=H_c$, while the nearly linear region is now more firmly established for $H_c<H<H_{c3}$. A departure from linearity close to H_{c3} is observed. The electrical transitions are highly reversible in the region of R/R_n shown, while the thermal transitions are nearly reversible for $H>H_c$. The "crosses" are data for decreasing field; all other points are data for increasing field. A hysteresis occurs at H_c. For electrical transitions

[13] A detailed description of the experimental procedures can be found in T. E. Seidel, Ph.D. thesis, Stevens Institute of Technology, Hoboken, New Jersey, 1965. Microfilm copies (No. 65-12585) available from Microfilms, Inc., 313 First Street, Ann Arbor, Michigan.

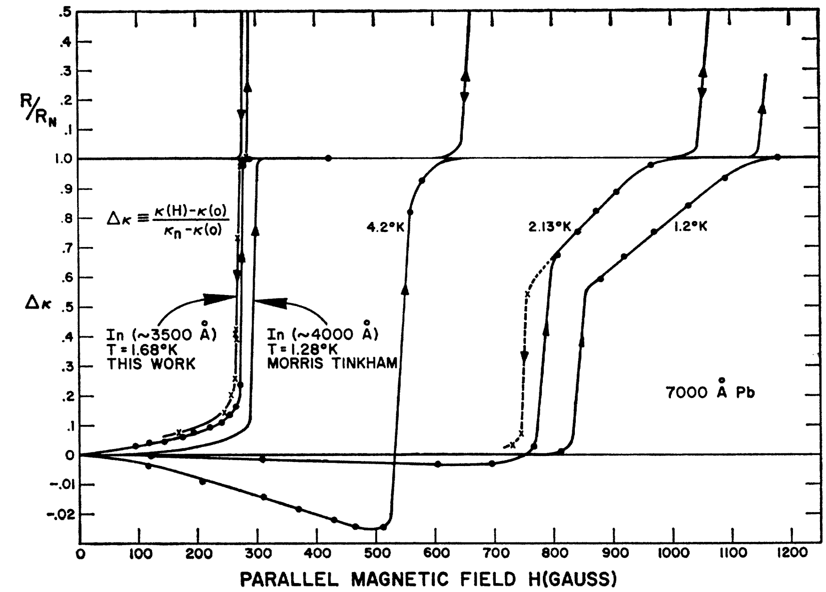

FIG. 2. Plot of the normalized electrical resistance R/R_n and of the normalized thermal conductivity $\Delta\kappa$ against the value of magnetic field, which is aligned parallel to the plane of the specimen and parallel to the directions of electrical and thermal current. Data for the indium are indicated; the other data are those of a 7000-Å Pb film. Crosses indicate data for decreasing magnetic field. All other data are for increasing field. Note the change in scale for $\Delta\kappa < 0$.

this is characteristic of thick superconducting films which undergo a first-order phase transition. The residual resistance ratio $R_{300}/R_{4.2}$ of this specimen is 140.

Figure 4 shows the transitions for the 2500-Å film. It is seen that, as the thickness of the film approaches the total thickness of the superconducting surface layers, the transitions are broadened and the jumps at lower temperatures are washed out. There is no well-defined region of linearity for $\Delta\kappa$ between H_c and H_{c3}. The difference $\Delta\kappa$ increases already below H_c in a manner comparable with the behavior of the 3500-Å In sample. This increase results from the decrease of the value of the order parameter[11,14] below H_c as H approaches H_c. The residual resistance ratio was 80 for this sample.

An oxidation experiment was carried out on this (the thinnest) sample to be sure that the transitions were not dominated by oxide-induced effects.[15] Data were first taken after the sample was exposed to air for only 6 h after fabrication; a second run was made after 3 additional days of oxidation in air. The value of "H_{c3}" defined by the onset of electrical resistance was within 1% of the earlier run. The thermal transition also matched the earlier run to within 1% at all values of the

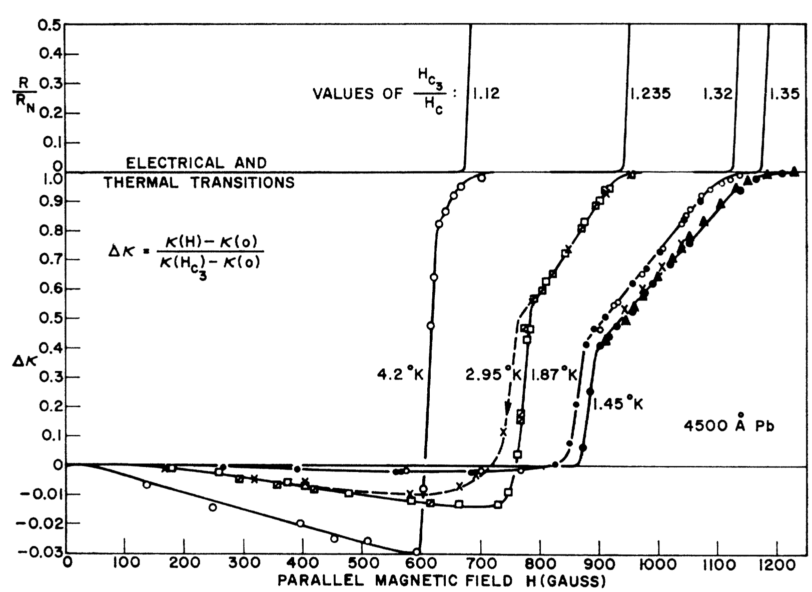

FIG. 3. Plot of R/R_n and of $\Delta\kappa$ against the parallel magnetic field for a 4500 Å film. The crosses are data obtained in decreasing field. Different points for the same temperature (e.g., 2.95°K curve shows squares with and without a diagonal line)represent measurements at different but small temperature gradients. Note the change in scale $\Delta\kappa < 0$.

[14] D. H. Douglass, Jr., Phys. Rev. Letters **7**, 14 (1961).
[15] L. J. Challis, Phys. Letters **13**, 20 (1964).

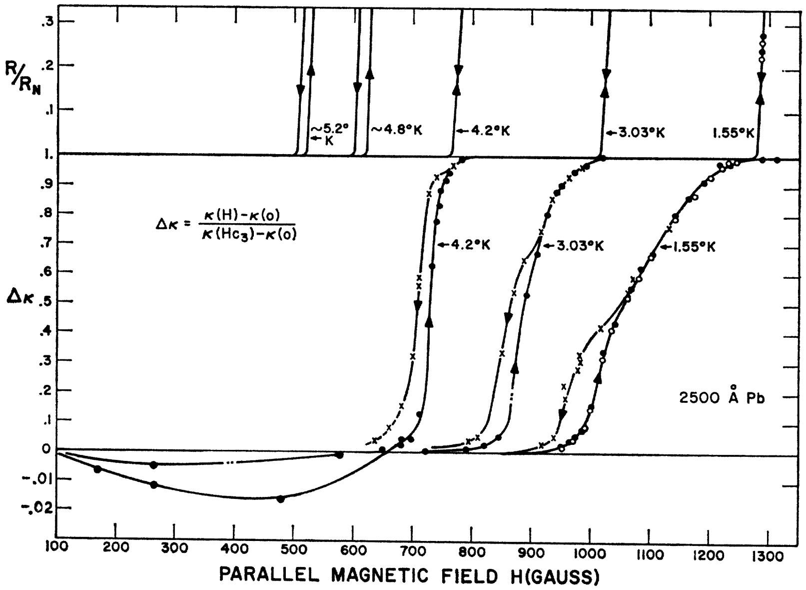

FIG. 4. Plot of R/R_n and $\Delta\kappa$ against the parallel magnetic field for a 2500-Å film. The crosses are decreasing-field data, as the arrows indicate. The solid points are those obtained from measurements made only six hours after film preparation, while the open circles of the 1.55°K curve are data obtained after three days of aging the sample in air at room temperature.

field. A knowledge of the oxidation rates[11] indicates that the oxide thickness is doubled between 6 h and 3 days, from $\sim$20 to $\sim$40 Å. The temperatures for these measurements were reproduced to better than 5 mdeg.

All the films exhibit a first-order phase transition in the magnetic field if $\kappa_{\mathrm{G.L.}}(t)<0.42$ and the thickness of the film is greater than $(\sqrt{5})\lambda$, where λ is the weak-field penetration depth.[2] The thickness of the 2500-Å film is considerably greater than $(\sqrt{5})\lambda$. If there were no surface superconductivity such a pure film should show hysteresis in the electrical transition. This is found above 4.2°K for the 2500-Å film.

The dc resistance measurements were made with currents of 10 to 100 μA, which if confined to the surface regions near H_{c3} correspond to effective current densities of 10 to 100 A/cm^2 for Pb. No dependence of H_{c3} on current density was observed for this range of current densities.

IV. INTERPRETATION OF DATA

Since the decreases in $\Delta\kappa$, which may indicate phonon conduction, are less than a few percent of the total change in $\Delta\kappa$, we neglect phonon conduction in the treatment of this section.

We use a simple phenomenological theory which includes the thickness of the superconducting surfaces and also the value of the order parameter at the surface. It is further assumed that a cross-sectional area corresponding to the area of the superconducting surface layer has a thermal conductance which may be added in parallel to the thermal conductance of the normal interior. Admittedly, this approach is not rigorous for pure lead films, but it will allow us to evaluate the parameters of the system in a heuristic manner. Some of the aspects of a rigorous theory will be suggested in the discussion.

The thickness as well as the order parameter of the surface region will be compared with theoretical values obtained by Fink and Kessinger.[16] For this reason it is convenient to use the definitions of these authors. The thickness of the specimen is d, hence the interior has thickness $(d-2N\xi)$. Here, N is a factor, larger than one, which accounts for the fact that the actual thickness of the superconducting surface layer is greater than the coherence distance ξ; it is defined by the equation

$$N\xi=\int_0^\infty F^2(x)dx/F^2(0)\,, \qquad (2)$$

where x is the distance from the surface of the film and $F(x)=|\psi(x)|/|\psi_{H=0}|$, $F(0)$ is the ratio of the order parameter at the surface to the order parameter in zero-magnetic field, and ξ is a function of the temperature and approaches ξ_0 as the temperature goes to zero. The conductance of the film is written as the sum of the conductance of the surface layers and the interior, giving

$$\kappa(H)=(2N\xi/d)\kappa_s+(d-2N\xi/d)\kappa_n,\quad H\geq H_c,\qquad (3)$$

where κ_s is the conductivity appropriate to the surface region. The choice of the expression for κ_s is difficult. The expression of Bardeen, Rickayzen, and Tewordt[17] (BRT) cannot be used, because our surface layers have a single-particle excitation spectrum different from that of a BRT superconductor; as a matter of fact, the

[16] H. J. Fink and R. D. Kessinger, Phys. Rev. **140**, A1937 (1965) see also H. J. Fink, Phys. Rev. Letters **14**, 853 (1965).

[17] J. Bardeen, G. Rickayzen, and L. Tewordt, Phys. Rev. **113**, 982 (1959).

excitation spectrum is gapless.[4] It seems best to return to an old-fashioned two-fluid model. In this model the electronic part of the thermal conductivity is proportional to the number of normal electrons present, or to $1-n_s$, where n_s is the number density of the superconducting electrons. Connection to the Ginzburg-Landau theory is made by assuming that $n_s \propto |\psi|^2$. For the value of ψ we choose that at the surface, $\psi(0)$ in accordance with Eq. (2). This leads us to express κ_s as

$$\kappa_s(H)=(1-|\psi(0)|^2)\kappa_n. \tag{4}$$

In zero field the whole sample is superconducting and $\kappa(0)=(1-|\psi_{H=0}|^2)\kappa_n$, hence

$$\Delta\kappa=\frac{\kappa(H)-\kappa(0)}{\kappa_n-\kappa(0)}=1-\frac{2N\xi}{d}F^2(0), \quad H\geq H_c. \tag{5}$$

Measurements of $\Delta\kappa$ give information on the value of $N\xi F^2(0)$, the product of the thickness of the superconducting surface layer and the normalized order parameter at the surface.

We may interpret the experimental results to obtain a value for N just above H_c and then use this value to obtain $F^2(0)$ just above H_c, designated by $F_c^2(0)$. The jumps in $\Delta\kappa$ at H_c for the two thicker films are interpreted as meaning that H_c is the field where the interior of the specimen becomes normal. If the sample thickness is reduced to the point where the jump disappears, then we may equate the thickness of that sample with $2N\xi$. If this is done at low temperatures where the value of ξ is ξ_0, then we obtain $N\approx 2$. The film of this particular thickness is taken to be about 2900 Å and $\xi_0=740$ Å for Pb. The experimental results for the thicker Pb films put a lower limit on the value of N just above H_c. Certainly, immediately above H_c, one expects $F_c^2(0)\leq 1$. Using $F_c^2(0)$ as equal to 1 in Eq. (4) leads to $N>1.83$ for the 4500-Å film. The fact that N evaluated in different ways leads nearly to a common value suggests that the data may be treated by using Eq. (4) with $N=2$. At low temperatures we have

$$\Delta\kappa=1-(4\xi_0/d)F_c^2(0), \tag{5a}$$

for H just above H_c. It is also desirable to evaluate

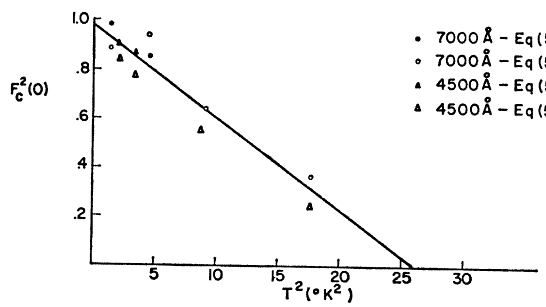

FIG. 5. The square of the order parameter at the surface for fields just above H_c, normalized to the order parameter in zero field $F_c^2(0)$, is plotted against the square of the temperature.

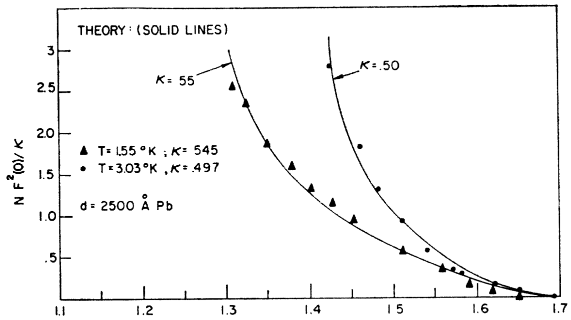

FIG. 6. Plot of $NF^2(0)/\kappa_{G.L.}$ against the magnetic field H/H_{c2}. The points are determined from experiment and Eq. (5), while the curves are those of Fink and Kessinger. The comparison is made for the 2500-Å film at two low temperatures.

$F_c^2(0)$ at higher temperatures. This can be done by using a variety of equations to relate $\xi(T)$ to experimental quantities. N is taken as 2 at higher temperatures also. Using[6] $\xi=\lambda/\kappa_{G.L.}$ and[5] $\kappa_{G.L.}=H_{c3}/1.9\sqrt{2}H_c$, we obtain

$$\Delta\kappa=1-10.7(\lambda/d)(H_c/H_{c3})F_c^2(0). \tag{5b}$$

For λ we take $(390\text{ Å})/(1-t^4)^{1/2}$ where the value 390 Å was determined by Lock[18] and $t=T/T_c$. (T is the temperature and T_c is the critical temperature.) H_c/H_{c3} is determined from our experiment. $F_c^2(0)$ has been computed from the data for H just above H_c using Eq. (5a) and Eq. (5b), and is plotted in Fig. 5 as a function of T^2. The significance is the following: At low temperatures the surface order parameter $\psi(0)$ just above H_c is almost as large as the zero-field order parameter. At higher temperatures the surface-order parameter is considerably smaller than its zero-field value. The plot allows a determination of the temperature above which surface superconductivity does not exist. This temperature is found to be 5.1°K. This result is in reasonable agreement with the microwave measurements,[5] which give $H_{c3}=H_c$ at 5.6°K.

We may also use Eq. (5) to determine the product $NF^2(0)$ and compare the field dependence of this quantity with the calculations of Fink and Kessinger.[16] They have computed $NF^2(0)/\kappa_{G.L.}$. We use the measurements of $\Delta\kappa(H)$ and d, and take ξ as

$$\xi(t)=\lambda/\kappa_{G.L.}=(1+t^2/1-t^2)^{1/2}\xi_0. \tag{6}$$

$\kappa_{G.L.}$ is obtained from $H_{c3}=1.69\sqrt{2}\kappa_{G.L.}H_c$. The choice of 1.69 is used here to conform with Fink and Kessinger's theory. Hence, apart from the assignment of ξ_0 we have determined $NF^2(0)/\kappa_{G.L.}$ from experiment with no arbitrary parameters. The results are shown in Figs. 6 and 7 and are compared with theory.[16]

The agreement with theory for the 2500-Å film is excellent, but must be considered fortuitous at this time. For, first, our thermal-conductivity theory is not

[18] J. M. Lock, Proc. Roy. Soc. (London) **A208**, 391 (1951).

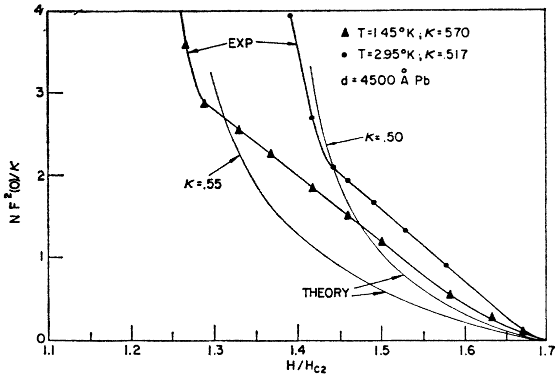

FIG. 7. Plot of $NF^2(0)/\kappa_{G.L.}$ against the magnetic field H/H_{c2} for the 4500-Å film at two temperatures.

rigorous, and second, the application of Fink and Kessinger's results to this thin film is not appropriate, since they use the boundary condition that $\psi(x)\rightarrow 0$ as x goes deep into the interior of the film. The agreement with theory for the 4500-Å film is poorer, but still gives values of $NF^2/\kappa_{G.L.}$ close to those calculated from theory. The results for the 7000-Å film are similar to those for the 4500-Å film.

V. DISCUSSION

A. The Value of $\kappa_{G.L.}$ for the Films

The mean free paths of the films, as determined by the residual resistance ratios, are greater than the film thickness by a factor of 1.3 to 1.7. This indicates some specular reflection and also a long bulk mean free path. The increase in $\kappa_{G.L.}$ due to the finite mean free path may be estimated from Goodman's[19] formula and the residual resistivity of our films.

$$\kappa_{G.L.}=\kappa_0+7.5\times 10^3\gamma^{1/2}\rho \qquad (7)$$

where $\kappa_0=\lambda/\xi=(390\text{ Å})/(740\text{ Å})=0.53$ at the lowest temperatures, γ is the electronic specific-heat coefficient

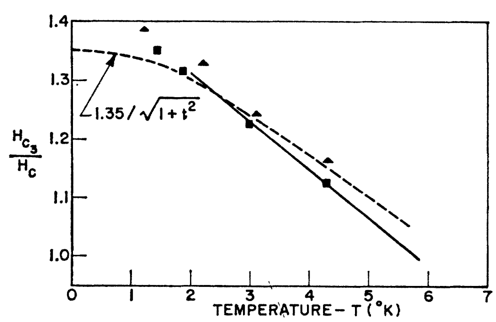

FIG. 8. Plot of H_{c3}/H_c against temperature. The solid line gives the results of Rosenblum and Cardona from microwave measurements on pure bulk lead, the dashed curve is the theoretical "Bardeen" temperature dependence (see Ref. 6). Closed squares 4500-Å film; closed triangles 7000-Å film.

(in erg/cm³ deg), and ρ is the residual resistivity in Ω cm. The difference $\kappa_{G.L.}-\kappa_0=0.05$, 0.065, and 0.116 for our three films of 7000-, 4500-, and 2500-Å thickness, respectively. Thus, $\kappa_{G.L.}$ for our two thicker films is not significantly different from the value for κ_0, and therefore H_{c3}/H_c may be meaningfully compared with results obtained on pure bulk specimens. We have plotted H_{c3}/H_c versus the temperature in Fig. 8 and compared the results with theoretical expectations[6] and with the microwave data.[5] The estimate of $\kappa_{G.L.}$ using Eq. (7) indicates that we have a type-I superconductor with $\kappa_{G.L.}>0.42$. Although our results on H_{c3}/H_c are for films, the film thickness is large enough to give results very close to those obtained for bulk. A comparison with the values of H_{c3}/H_c obtained by tunneling[7] can be made; the values determined by tunneling are higher than the values shown in Fig. 8. This may be due in part to some penumbra on the Pb tunneling strip.

B. Decreases in $\Delta\kappa$ for $H<H_c$

We have attempted to interpret the small decreases of $\Delta\kappa$ for $H<H_c$ as phonon-electron scattering by the phonons in the lead.[8,13] This approach did not account numerically for the observed change and it is concluded, therefore, that at least part of the decrease is due to a modulation[11] of the phonons in the glass substrate by the electrons in the lead. The decrease in $\Delta\kappa$ for the 2500-Å film is smaller than that of the thicker films. For the 2500-Å film the order parameter decreases[14] considerably as H approaches H_c. This causes an increase in the thermal conductivity of the film which offsets the decrease of the thermal conductivity of the substrate.

C. Effective Penetration Depth

A further check of the interpretation used here comes from the numerical value of H_c/H_c(bulk). According to the elementary London theory[20]

$$H_c=H_c(\text{bulk})[1-(2\lambda/d)\tanh(d/2\lambda)]^{-1/2}. \qquad (8)$$

Use of Eq. (8) with H_c defined by the jump in the thermal conductivity leads to values of λ of about 500 Å, which is larger than the weak-field penetration depth λ_0, as one could expect from the use of the London theory. If H_{c3} is used for this calculation, unreasonably large values of λ are obtained.

This calculation also rules out any doubt about the occurrence of an intermediate state.

D. The Influence of Oxide Layers

It is appropriate to give a critical discussion of the influence of oxide layers on the surface of superconducting lead. Ginsburg's[21] surface superconductivity is

[19] B. B. Goodman, I. B. M. J. Res. Develop. 6, 63 (1962).

[20] F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1950), Vol. 1.

[21] V. L. Ginsburg, Phys. Letters 13, 101 (1964).

due to an enhanced electron-electron interaction in the neighborhood of the surface due to a different electron interaction there. Alteration of the surface properties could lead to a higher local transition temperature. In contrast to this, the Saint James–de Gennes surface superconductivity should exist for ideally clean surfaces. One may then ask whether the presence of an oxide layer (20–50 Å in thickness) has an influence on the field-dependent transitions in pure lead.[14]

All of the materials[5–7] under discussion which exhibit remnant superconducting properties above H_c do in fact have a few atomic layers of oxide on their surfaces, as do our own specimens. Challis[14] has interpreted his data to suggest that the presence of the oxide layer is critical for the transition.

It is clear that the intrinsic $\kappa_{\text{G.L.}}$ for lead at low temperatures is ~ 0.5, hence H_{c3} in the Saint James–de Gennes sense should be limited to only $\sim 1.4\, H_c$ for pure lead. Observations[14] of remnant superconducting properties to fields as high as 2 or 5 H_c are not associated with the intrinsic properties of pure lead or the Saint James–de Gennes-like superconducting state for pure lead.

Since our experiment gives values of H_{c3}/H_c which are consistent with the values expected for pure Pb and also demonstrates that the superconducting sheath thickness just above H_c is ~ 1500 Å for each surface, and since our results for the thinnest film are insensitive to the growth of an oxide on reasonable time scales, it seems justifiable to interpret our results as an intrinsic surface superconducting property of pure Pb rather than accepting the phenomenon as a result of the existence of a thin oxide layer.

It may be possible to reinterpret Challis's results so that pure lead with a clean surface does show remnant superconductivity above H_c (see the tail in Fig. 1 of Ref. 14 for $800 \lesssim H \lesssim 1000$ G). One may also entertain the conjecture that the Kapitza resistance is rather insensitive to the surface superconducting state.[14] The tunnel results of Goldstein[7] do suggest to us that lead for $H_c < H < H_{c3}$ is gapless, although the density-of-states peak is in the vicinity of the gap in zero field. Even though the surface superconducting state is gapless, one cannot conclude from this observation alone that the Kapitza resistance should be the same as in the normal state. The order parameter replaces the gap as the primary parameter for a description of the properties of the system.[22] A case in point is that a gapless superconductor would still be expected to have an electronic thermal conductivity less than the normal-state[23] value.

[22] S. Skalski, O. Betbeder-Matebet, and P. Weiss, Phys. Rev. **136**, A1500 (1964).

[23] V. Ambegaokar and A. Griffin, Phys. Rev. **137**, A1151 (1965).

E. On a Microscopic Theory

Our phenomenological procedure is a simplification which is used to allow us to make an initial interpretation, and a strict evaluation of the parameters of the system from our data must await a rigorous thermal-conductivity theory. Such a theory should include the following: (1) the nonlocal properties of the system, (2) the role of diffuse surface and bulk-scattering (3) the question of a quasiparticle approach.

VI. CONCLUSIONS

It has been shown that as the thickness of a pure lead film is reduced, a large fraction of the volume of the material remains in the superconducting state just above H_c. This result directly supports the idea that one observes surfaces superconductivity in the sense of Saint James and de Gennes in pure lead.

The interpretation which is given allows the determination of the thickness of the superconducting surface layer in terms of the coherence distance ξ. It is found that immediately above H_c, the thickness of each superconducting surface is about 2ξ, a result which is in good agreement with the calculations of Fink and Kessinger. This evaluation of the thickness of the surface layer also allows a determination of the order parameter at the surface just above H_c. At low temperatures, the order parameter at the surface is found to be almost as large as the zero-field order parameter.

The field dependence of the product of the thickness of the surface sheath and the surface order parameter has been evaluated from the field dependence of $\Delta\kappa$ for $H > H_c$. The magnitude of the quantity $NF^2(0)$ compares favorably with the calculations of Fink and Kessinger, without the use of an adjustable parameter.

The values of H_{c3}/H_c compare favorably with those obtained by microwave studies and those expected for pure lead. According to the thermal-conductivity measurement, less than $\sim 1\%$ of the volume of the specimen is superconducting above H_{c3}. A two-fluid approach for the field dependence of $NF^2(0)$ does not give good agreement with the calculations of Fink and Kessinger. This suggest that a different basis be found for thermal conductivity.

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