Effect of Magnetic Field on Thermal Conductivity and Energy Gap of Superconducting Films*

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We have measured the change in the thermal conductivity of superconducting tin, indium, and lead films upon application of a magnetic field in the plane of the film. These experiments were undertaken to explore the dependence of the energy gap upon magnetic field and to determine the thermodynamic order of the field-induced transition in films. Within the range of temperatures available to us (0.35 T_c to 0.65 T_c) the thermal conductivity of indium and tin films increases nearly as H^2. In films of thickness $d \geqq 2800$ Å the thermal conductivity jumps at H_c to the normal state value, indicating a first-order phase transition in thin films, consistent with the Ginzburg-Landau (GL) theory. If the effect of a field upon the superconducting state can be adequately represented as a change of the ϵ_0 of BCS, we may use the theory of Bardeen, Rickayzen, and Tewordt to compute $\epsilon_0(H)$ from our data. At $T=0.65\ T_c$ we find $\epsilon_0(H)/\epsilon_0(H=0)=[1-(H/H_c)^2]^{1/2}$ in agreement with the GL prediction. At $T=0.35\ T_c$ however, $\epsilon_0(H)/\epsilon_0(0)=1-(H/H_c)^2$ provides a more satisfactory fit to our data. Orientation of the field $\perp$ and $\parallel$ to the direction of heat flow produces the same effect on the thermal conductivity to $\pm 1\%$. This is interesting in view of Bogoliubov's prediction of a $\mathbf{p}_F \cdot \mathbf{v}_{\text{drift}}$ term in the excitation spectrum of a current-carrying superconductor. When the field is not parallel to the surface of the film the thermodynamic transition is still sharply defined, but H_c is reduced. Thin lead films gave results similar to those of indium and tin films except that at low fields the field-dependent conductivity increased more slowly than H^2 at low temperatures.

I. INTRODUCTION

IT is now well accepted on both experimental[1,2] and theoretical[3,4] grounds that near T_c the superconducing transition of a thin film in a magnetic field is of second order. The predictions of the Ginzburg-Landau-Gor'kov theory[3–6] (GLG), applicable here, are in good agreement with experimental results. At reduced temperatures $t=T/T_c \ll 1$, however, the GLG theory is inapplicable.[7] Bardeen[8] has made a calculation which leads to a first-order transition at very low temperatures, while Nambu and Tuan[9] find a second-order transition for a very thin film at all temperatures.

The elegant experimental measurements of the field dependence of the energy gap employing the tunnel effect[1,2] have generally been limited to a few metals at moderately high reduced temperatures and to the case of fields applied parallel to the film surface. Only recently, while this report was in preparation, have measurements been extended to lead films at low reduced temperatures by Douglass and Meservy.[10] The seexperiments support our findings, to be reported here, that the transition for a thin film remains second order even at very low temperatures, and they also find a similar field dependence of the energy gap at low temperatures. It should perhaps be noted that the tunnel-effect measurements selectively indicate the effective energy gap at the film surface for electrons moving normal to the surface.

We have developed an independent experimental method to study the thermodynamic parameters of a superconducting film in a magnetic field. This method consists of measuring the effect of an externally applied magnetic field on the thermal conductivity of a superconducting thin film. A preliminary report of our results on tin and indium films has been published elsewhere.[11] The experiments were then extended[12] to a wider range of experimental conditions and to another metal, lead. We report these more extensive experiments here. The experimental data reveal the thermodynamic order of the transition by inspection. By using the relation derived by Bardeen, Rickayzen, and Tewordt[13] (BRT) the data may be inverted point by point to give $\epsilon_0(H)$, the field-dependent energy gap averaged through the film.

The external field has been applied at various angles with respect to the plane of the film with unexpected results, and the relative directions of the field and the heat flow in the plane of the film have been varied in a search for vestiges of the anisotropy of the energy gap

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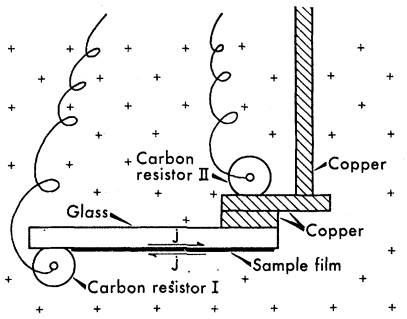

FIG. 1. Sample and thermometer mounting arrangement.

in a current-carrying superconductor predicted by Bogoliubov.[14]

II. EXPERIMENTAL METHOD

A. Low-Temperature Arrangement

The use of carbon resistance thermometers,[15] with their low thermal inertia and high sensitivity, makes it possible to measure the low-temperature thermal conductivity of thin metal films deposited on glass substrates. During our experiments, the temperature drop along the film is typically 0.1°K with 10^{-7} W total heat transport along the sample film and substrate. Under these conditions a change of 2 μdeg in the temperature drop along the film is detectable.

The sample and thermometer arrangement is shown in Fig. 1. A $\frac{1}{2}$-W carbon-composition resistor is prepared for use as a thermometer-heater (I) by grinding a flat surface until the resistance material just becomes visible. The lead wires are cut off short, and lengths of No. 42 Formvar insulated manganin wire are attached with nonsuperconducting solder. The thermal conductivity of these lead wires is negligible in our experiments. The flattened surface of the resistor is glued with GE-7031 cement at one end of the glass sample-film substrate. Using the same cement, the opposite end of the substrate is attached to a copper heat sink, which is in turn connected to the lid of the experimental chamber. A similarly prepared second resistor, to be used as a reference thermometer (II), is similarly glued to the copper heat sink.

The experimental chamber is placed in the lowest part of the interior of a conventional, liquid-nitrogen shielded, glass Dewar for liquid helium use. A thin-walled stainless-steel tube extends from the experimental chamber to the top of the Dewar. This tube is used to evacuate the chamber; it also carries No. 40 manganin wires for connection to the thermometers. Since the usual power input to the heater-thermometer during the experiments is only $\sim 10^{-7}$ W, thermal anchoring of the manganin leads to the inside of the chamber lid and radiation baffling in the pumping tube above the chamber are both essential. The chamber is sealed to its copper lid with a Woods metal joint. When this alloy is cooled below ~8°K, it becomes superconducting.[16] In order to prevent the superconducting diamagnetism and trapped flux at the joint from disturbing the magnetic field applied to the sample film, the sample is suspended near the bottom of the $4\frac{1}{2}$-in.-long chamber from a copper rod directed downward from the copper lid.

B. Thermometry

The thermometers used were Allen-Bradley $\frac{1}{2}$-W nominal 100-Ω resistors, connected in a wheatstone-bridge circuit. Satisfactory cancellation of temperature drifts was achieved without special matching of the reference and heater resistors. The resistance of the reference thermometer was measured as a function of the vapor pressure of the helium bath over the range 1.2–4.2°K at a small enough current to prevent appreciable heating above the bath temperature. The results could be approximated closely by a relation of the form $\ln R = A + B/T$, where $A = 2.89$ and $B = 3.26°$.

The insensitivity of the resistance thermometers to magnetic fields was checked during several experimental runs. If the magnetic field is increased to several times the critical field of the experimental film, any changes in the thermometer bridge balance above the critical field may be attributed to magnetoresistance in the thermometers. This is so because any effect of the magnetic field on the thermal resistance of the experimental films, which have electron mean free paths ~800 Å, would in the normal state be negligible even at the maximum field applied. In the case of a film of relatively low critical field the resistance bridge balance was unaffected by an increase from $H = 400$ Oe to $H = 800$ Oe. In another experiment, increase of the field from 7500 to 15 000 Oe produced only a small shift in the resistance thermometer bridge balance. These results are consistent with the behavior of similar resistors as determined by Clement and Quinnell.[15] They found that magnetoresistance effects were small and proportional to H^2. Further, we expect the small magnetoresistance of the thermometer heater and the reference thermometer to nearly cancel in measurements of resistance bridge balance.

The relation between power input and resistance change was measured separately for the heater thermometer and the reference thermometer in several experiments. The temperature rise of the reference thermometer at a given power input was only about 10% of that of the heater thermometer at the same power level. We may conclude that the thermal resistance of the re-

[14] N. N. Bogoliubov, Zh. Eksperim. i Teor. Fiz. **34**, 58 (1958) [English transl.: Soviet Phys.—JETP **7**, 41 (1958)].

[15] J. R. Clement and E. H. Quinnell, Rev. Sci. Instr. **23**, 213 (1952).

[16] D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952).

sistors themselves and of the glue used to fasten them in place amounts to $\sim\frac{1}{10}$ of the thermal resistance of the sample film and substrate. For example, at 1.2° and a power input of 0.09×10^{-6} W, the temperature rise of the heater thermometer was ~0.060° and of the reference ~0.006°. This gives a value of $dP/dT=1.5\times10^{-5}$ W/deg for the reference thermometer. Berman[17] established that in the 100-Ω $\frac{1}{2}$-W Allen-Bradley resistor (the same type and value as we have used) $dP/dT=5.2\times10^{-5}$ W/deg. The difference is accounted for by the fact that thermal contact was made to only a fraction of the surface of the resistor in our experiments.

C. Temperature Stability

The initial (unsuccessful) experiments were attempted at 1.3°K, without a reference thermometer. A monotonic, but not perfectly uniform, decrease of the bath temperature at the rate of ~1 mdeg/min during the measurements resulted from the decreasing helium film creep as the liquid-helium level declined. The resulting drift in the thermometer resistance overwhelmed the temperature changes expected from the desired effect of a magnetic field. Attempts were made to stabilize the bath temperature with an electronic regulator consisting of a separate resistance thermometer in a 33-cps ac bridge, followed by a tuned amplifier, lock-in detector, and dc heater in the liquid helium. Although satisfactory long-term stability was achieved, amplifier noise in the heater produced objectionable variations over periods shorter than a minute. Since the total experimental effect is ~5 mdeg, the noise level should be less than 50 μdeg to ensure an adequate signal/noise ratio.

With the introduction of the reference thermometer in a bridge circuit with the thermometer heater, the effective drift rate was decreased by a factor of 10, even without special matching of the resistors. This permitted data to be taken without the use of any noise-producing feedback stabilization schemes.

Temperatures of 1.2°K were reached by pumping at 300 liters/min with a conventional rotary vacuum pump. Operation at 1.7°K was attained by adjustment of a valve in the pumping line until the temperature drift rate at the desired temperature was reasonably low. When operation near 2.1°K was desired, a Cartesian manostat was connected in the helium vapor pumping line. A 1-cu-ft ballast tank was connected in the pumping line between the Dewar and the manostat to reduce fluctuations in the pressure above the helium bath which were caused by the oscillation of the manostat throttle.

Spatial nonuniformity of the bath temperature and bubbling of the helium usually results in intolerable temperature fluctuations of the sample if operation is attempted above the λ point of the helium bath. However, it was possible to conduct experiments at the normal boiling point (4.22°K) by leaving the bath completely undisturbed and isolated from vibration for three hours after the liquid-helium transfer. By that time, the bubbling produced only a relatively small rapid fluctuation of the signal; however, the temperature drop along the film had to be increased to ~0.6°K (several times the low-temperature values) to obtain an adequate signal-to-noise ratio.

[17] R. Berman, Rev. Sci. Instr. **25**, 94 (1954).

D. Temperature Drop and Critical Field Spread

The approximate temperature drop along the film during the experiments at various temperatures is shown in Table I. The increase in ΔT at higher temperatures was necessary to maintain the signal/noise ratio in the presence of greater uncontrolled temperature fluctuations and decreasing thermometer sensitivity. The percentage difference in the critical fields at the hot and cold ends of the film which result from the difference of temperature is also shown in Table I. These values were determined from the appropriate bulk critical field curves.

TABLE I. Temperature drop along experimental films and corresponding spread in critical fields.

Mean temperature	ΔT	$\Delta H_c/H_c$ Indium	Tin	Lead
1.2°	0.06°	1.5%	1.0%	0.2%
1.7°	0.1°	4%	3.5%	0.6%
2.1°	0.15°	10%	7%	1.3%
4.5°	0.6°			15%

E. Magnetic Field

A high-power water-cooled Helmholtz pair produced fields up to 1000 Oe. This relatively high-field, iron-free system was employed to permit precise control of the direction of the field by using auxiliary trimming coils, in order that the effect of applying the field slightly out of the plane of the sample film could be investigated. The terminals of the trimming coils could be connected by a rotary switch to taps on a low-resistance nichrome strip wired in series with the main coil pair. In this way the angle of the resultant field, independent of amplitude, could be adjusted in 0.02° steps up to ±4°. In experiments on films with critical fields greater than 1000 Oe, conventional iron-core electromagnets were used. The resulting uncontrolled angle of the field with respect to the plane of the film is less than 1° and apparently it has no major effect upon the experimental results for these very thin films, as may be seen in Fig. 11.

F. Sample Films

Sample films were produced by rapid evaporation onto glass substrates held at 77°K, after thorough ion-bombardment cleaning of the substrate surface.

The substrates were No. 0 microscope-cover glasses about 0.11 mm thick which had been broken into pieces about 5 mm×15 mm, suitable for our experiments. The substrates were washed in a saturated solution of detergent, rinsed in hot tap water, and air dried. The substrate was then clamped against the surface of an unfilled cold trap inside the vacuum chamber. The chamber was evacuated and an intense (20 mA) high-voltage (5000 V) glow discharge was operated for 5 min to heat and clean the substrate by ion bombardment. Then the pressure was reduced to 3×10^{-6} mm Hg and the substrate was cooled to 77°K by filling the attached cold trap. The vacuum pumping line contained a liquid nitrogen cooled baffle to rule out contamination of the vacuum chamber by condensation of oil vapor.

A tantalum evaporation boat containing the preweighed and pre-fused sample charge was rapidly heated to about 1400°C and the film evaporation took place in a period ranging from 1 sec for a 3-mg charge (giving a 1300-Å film) to 6 sec for a 30-mg charge. The source-to-substrate distance was only 2 in. The deposition rate of over 1000 Å/sec, along with the residual gas pressure of less than 10^{-5} mm Hg, ensured that the flux of residual gas molecules was a great deal smaller than that of the metal atoms during the evaporation. Films prepared under these conditions should therefore be quite pure. Cooling of the substrate during the evaporation is necessary to prevent migration of the metal atoms after they first strike the surface.[18] After the films were warmed to room temperature and removed from the vacuum, they were annealed at room temperature for at least one week. (The lead films were annealed in vacuum to retard oxidation.)

The sources and purities of the metals used in evaporation of the experimental films are given in Table II.

TABLE II. Metal sources and purities.

Metal	Supplier	Stated purity
Indium	Indium Corporation of America	99.999%
Lead	A. D. Mackay	99.999%
Tin	Johnson, Matthey	99.999%

Films ranging in thickness from 250 to 12 000 Å were prepared. Thickness was estimated from the measured critical field and published data relating the critical field to film thickness. As described above, all films were deposited on substrates cooled to 77°K. In all cases it was possible to prepare films which were mirror-like in appearance with very little diffuse reflectivity, in contrast to results of room-temperature evaporations.[18] No structure was visible under magnification of 1500 diameters except a fine granularity.

A 250-Å indium film showed no noticeable deterioration after seven months exposure to the atmosphere. A 700-Å tin film similarly exposed for four months showed no visible deterioration. Oxidation of lead films, however, was more rapid. The experimental film designated Pb I was exposed to the atmosphere for approximately 5 h while Pb II was exposed approximately $\frac{1}{2}$ h. In order to determine the durability of lead films and the extent of deterioration produced by atmospheric exposure while preparing for an experiment, measurements have been made of the transmission of 0.9-μ radiation through a lead film of about 180-Å thickness, as a function of the duration of exposure to the atmosphere. The results may be roughly interpreted as a decrease in thickness of the metallic film due to oxidation, resulting in decreased reflection and increased transmission. We assume that Z, the impedance per square, is inversely proportional to d, the film thickness. Then, for transmission $T\ll1$, $T\sim Z^2\sim1/d^2$. On this basis, during the period between 15-min and 2 h after the beginning of exposure to the atmosphere, Δd was ~7 Å. After one day Δd was ~20 Å, and the oxidation of the film proceeded at ~7 Å per day for the next week. Now, PbO is a semiconductor, not an insulator as the above analysis has assumed; also, the estimation of d_0 from the weight of the evaporated Pb charge may be somewhat in error. Nevertheless we may safely conclude that the atmospheric oxidation of the Pb films used in our experiments was of negligible importance.

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. Electron Mean Free Path

An estimate of the electron mean free path Λ_e in the experimental films will be useful in the interpretation of our data. According to BRT[13] the mean free path of the electronic excitations is unaffected by the transition to superconductivity. We may determine Λ_e in the normal state from the relation for thermal conductivity $K_n=\frac{1}{3}C_{en}v_F\Lambda_e$ where the electronic specific heat $C_{en}\approx4\times10^{-4}\times T$ cal/mole-deg for both tin and indium,[19] and $v_F\approx10^8$ cm/sec is the Fermi velocity. A direct measurement of K_n is impractical because of the dominant thermal conductance of the glass substrate. It is possible, however, to determine experimentally the ratio of the thermal conductivity of the films to that of the substrate and combine this information with published values of the thermal conductivity of glass, K_{gl}, in order to find K_n. We will denote by r the fractional change in the total conductance of the film plus substrate combination when the film is driven into the normal state by a field $H\geq H_c$. The quantity r is measured experimentally as the change in the thermometer bridge balance position upon application of $H\geq H_c$ (i.e., the total "signal") divided by the shift in bridge balance position resulting from increase in the bridge power in-

[18] L. Holland, *Vacuum Deposition of Thin Films* (John Wiley & Sons, Inc., New York, 1956), pp. 206–208.

[19] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1953).

put from a small value up to the full operating current. When r is combined with the published values[20] of the temperature dependent ratio K_s/K_n of the thermal conductivities of the superconducting and normal states,[16] and with d and D, the thickness of the film and of the substrate, we may determine $K_n/K_{gl}=rD/(1-K_s/K_n)d$. Then $\Lambda_e=3K_n/C_{en}v_F$. The thermal conductivity of the glass, K_{gl}, needed in this calculation, is estimated from a value[19] of $K_{gl}=5\times10^{-4}$ W/cm-deg at 2°K, and the assumption that $K_{gl}\sim T^{1.3}$ at liquid-helium temperatures.[21] The resulting values for K_{gl} were used in the computation of the Λ_e values quoted in Table III.

TABLE III. Data leading to estimates of electronic mean free paths Λ_e in the experimental films. Symbols are defined in text. In all cases thickness of glass substrate $D=0.11$ mm.

Sample	d (Å)	T (°K)	Heater power (μW)	r	$\frac{K_s}{K_n}$[a]	K_{gl} (mW/cm-deg)	K_{gl}' (mW/cm-deg)	Λ_e (Å)
SnII	2600	1.2°	0.09	0.2	0.1	0.26	0.11	600
SnIII	700	1.2°	0.08	0.046	0.1	0.26	0.07	500
InII	1600	1.7°	0.3	0.07	0.39	0.40	0.18	600
		1.8°	0.1	0.07	0.45	0.40	0.20	600
		2.1°	0.22	0.11	0.61	0.55	0.73	1600
		2.14°	0.85	0.07	0.64	0.58	0.5	800
InIII	650	1.25°	0.14	0.05	0.16	0.26	0.2	600
		1.7°	0.11	0.07	0.33	0.40	0.12	1000
		2.1°	1.3	0.016	0.65	0.55	0.58	600
InIV	4000	1.2°	0.09	0.41	0.14	0.26	0.26	800
		2.1°	1.3	0.10	0.67	0.55	0.44	600

[a] From Ref. 16, p. 83, Fig. 29.

Note that Λ_e has a value of 600–900 Å, and seems to be constant with increasing film thickness between 650 Å (InIII) and 4000 Å (InIV). This indicates that Λ_e is limited by imperfection and impurity scattering rather than boundary scattering in these films. In either case, Λ_e would be independent of temperature. Thus, the range of calculated values of Λ_e at different temperatures in the same film gives an indication of the lack of precision in the determination of Λ_e.

Phonon scattering of the electrons is negligible in our films. The phonon-limited K_{eg} would be $2.56\times10^3/T^2$ W/cm-deg in tin, according to the compilation of Klemens.[22] From $K_e=(1/3)\gamma T v_F\Lambda_e$ we may calculate at 1.2°K, $\Lambda_{eg}\approx0.4$ cm, and at 2.1°K, $\Lambda_{eg}\approx0.075$ cm.

An independent experimental estimate of the thermal conductivity of the glass substrate, K_{gl}', also listed in Table III, was made from the power input to the heater, the resulting temperature change in the thermometer resistance, and the approximate dimensions of the substrate. We ascribe the difference between K_{gl} and K_{gl}' at the lower temperatures to poor calibration of the thermometer resistance as a function of temperature. This calibration does not affect the normalization or interpretation of the experimental data; it was used only in the computation of K_{gl}' and in the estimation of the temperature difference between the ends of the film during the experiments (Table I).

B. Temperature Variation of H_c/H_{cb}

We note an increase in H_c/H_{cb} with temperature in all of the experimental films, (see Figs. 2, 5–8). This may be anticipated as a result of the increase in λ with temperature, since H_c/H_{cb} is determined by the ratio λ/d. The effect has been studied in detail by Appleyard *et al.*[23] and by Alekseyevsky[24]; their results are discussed by Shoenberg.[16] Our measurements of H_c are limited to temperature $T<0.7\ T_c$ where the changes of λ are relatively small, and our results are only of sufficient accuracy to show an agreement in sign and order of magnitude with the expected effect. Our results fall between $(H_c-H_{cb})/H_{cb}\sim\lambda(T)\sim[1-(T/T_c)^4]^{-1/2}$, which applies for thick films ($d\gg\lambda$), and $H_c/H_{cb}(T)\sim[1-(T/T_c)^2]^{1/2}$, predicted by Pippard[25] for very small specimens.

Pippard[25] and Ginzburg[6] have predicted substantial superheating and supercooling effects in films a few penetration depths thick. In several experiments we approached the transition from above and also from below and found no detectable hysteresis. This may be a result of the thermal gradient along our films, or of their crystalline imperfection.

C. Behavior of Very Thin Films

The results of our experiments are easiest to interpret in the case of very thin films ($d<\lambda$). The applied field penetrates almost uniformly, and ϵ_0 is also expected to be essentially uniform.

Figure 2 shows results for thin (~700 Å) films of tin and indium. For both metals, the thermal conductivity K increases nearly as H^2 up to the critical field, the thermal conductivity in the superconducting state joins smoothly onto the field-independent conductivity of the normal metal. The location of the shoulder at this point fixes H_c for the pruposes of normalizing the data. The absence of any discontinuity at H_c indicates that the superconducting transition in a magnetic field is second order for films of this thickness, in contrast to the first-order transition of bulk superconductors in a field. In other words, since K is related

[20] For tin and indium, K_s/K_n as a function of T/T_c, measured in bulk samples, is in good agreement with the theoretical calculation of BRT for the case of electronic thermal conductivity with lattice-defect scattering dominant. Boundary scattering would give essentially similar results. In the films we have studied, even if we neglect defect scattering, the electronic mean free path would be limited by boundary scattering to a few thousand angstroms at most, and thus we can have considerable confidence in the applicability of the experimental and theoretical bulk metal values of K_s/K_n.

[21] D. Bijl, Physica **14**, 684 (1949).

[22] P. G. Klemens, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1956), Vol. XIV, p. 245.

[23] E. T. S. Appleyard, J. R. Bristow, H. London, and A. D. Misener, Proc. Roy. Soc. (London) **A172**, 540 (1939).

[24] N. E. Alekseyevsky, J. Phys. USSR **4**, 401 (1941).

[25] A. B. Pippard, Phil. Mag. **43**, 273 (1952).

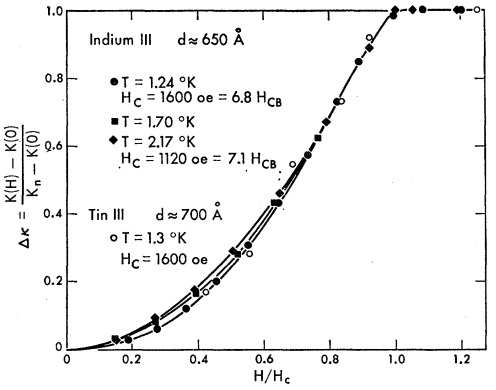

FIG. 2. Change of thermal conductivity of thin superconducting films with field. Note that the phase transition is of second order for films of this thickness.

directly to the gap width, we can infer that the gap closes continuously to zero when a field is applied to a thin film, whereas in a bulk sample it drops discontinuously from nearly the full value (~98% even at the surface) to zero.

The measured dependence of K upon H may be used to compute a dependence of the energy gap upon field in a simple way if the electronic term K_e is primarily limited by scattering of electrons by lattice imperfections. Under these conditions the ratio of the thermal conductivity in the superconducting state K_{es} to that in the normal state K_{en} is given by Bardeen, Rickayzen, and Tewordt[13] as their Eq. (3.6). This may be written

$$\frac{K_{es}}{K_{en}}=G(\epsilon_0/kT)=\int_{\epsilon_0}^{\infty}E^2(\partial f/\partial E)dE\Big/\int_0^{\infty}E^2(\partial f/\partial E)dE,$$

where $f(E/kT)$ is the Fermi function. The function $G(\epsilon_0/kT)$ is plotted in Fig. 3. If we assume that the effect of a field upon the superconducting state can be adequately represented as a change of the ϵ_0 of BCS, then the observed quantity $\Delta\kappa$ plotted in Fig. 2 should be given by

$$\Delta\kappa=\frac{K_{es}(H)-K_{es}(0)}{K_{en}-K_{es}(0)}=\frac{G[\epsilon_0(H)/kT]-G[\epsilon_0(0)/kT]}{1-G[\epsilon_0(0)/kT]}.$$

This relation was used to invert the experimental data on indium III, point-by-point, to yield $\epsilon_0(H)$, with the result shown in Fig. 4. Because $G(\epsilon_0/kT)$ initially drops only cubically as ϵ_0/kT increases from zero (see Fig. 3), the gap must drop more steeply to zero near H_c than the approach of $K_{es}(H)$ to K_{en} there. A rather steep final drop $\sim(H_c-H)^{1/2}$ in the gap near H_c is necessary to reproduce the almost linear approach of K_{es} to K_{en} observed at that point.

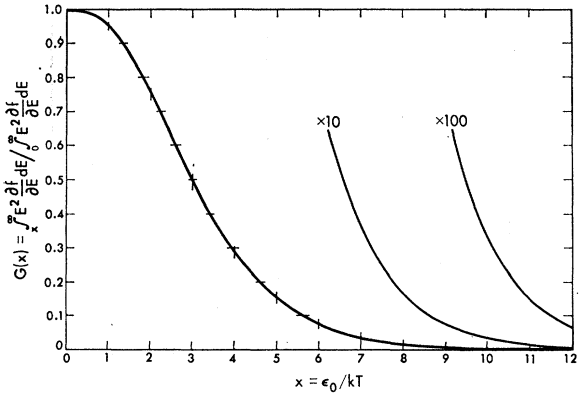

FIG. 3. The function $G(\epsilon_0/kT)$ relates the normalized thermal conductivity to the energy gap, according to the theory of Bardeen, Rickayzen, and Tewordt.

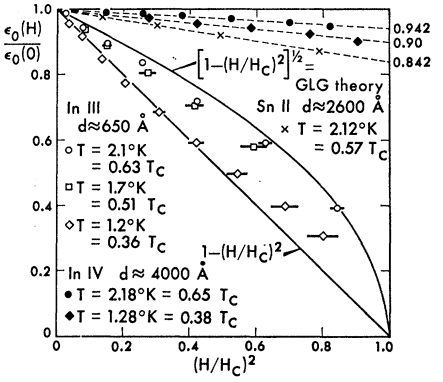

FIG. 4. Magnetic field dependence of superconducting energy gap for several tin and indium films computed from the data in Figs. 2, 6, 7, and 8, assuming that the energy gap is independent of position in the film. The curve $[1-(H/H_c)^2]^{1/2}$ is that given by the GLG theory in the limit of very thin films.

The difficulty of distinguishing between a broadened transition because of film inhomogeneity and a truly rounded approach to K_{en} because of the form of $G(\epsilon_0/kT)$ results in an uncertainty in the choice of H_c. The bars on the plotted experimental points in Fig. 4 indicate the size of this uncertainty.

Our results for the dependence of the energy gap upon magnetic field in a thin film are qualitatively similar to those from the more direct tunnel experiments of Giaever and Megerle[1] and of Douglass,[2] although their data were taken at higher reduced temperature and in a different metal (aluminum). From our data shown in Fig. 4, we see that $\epsilon_0(H)/\epsilon_0(0)$ seems to approach $1-h^2$, where $h=H/H_c$, at low temperatures, but it is moderately well fitted at $T/T_c=0.63$ by $(1-h^2)^{1/2}$. The latter form is that given by Douglass[4] based on the Ginzburg-Landau-Gor'kov (GLG) theory, which is expected to hold near T_c. We also note that our data at $T/T_c=0.36$ deviate from $1-h^2$ and approach $(1-h^2)^{1/2}$ when the gap has dropped so that $\epsilon_0(H)<kT$. This behavior indicates that the GLG approach becomes successful, as expected,

when there is a large amount of thermal excitation present.

We may find the approximate value of d/λ for In III from the GLG theory. Ginzburg[6] has shown that the solution of the Ginzburg-Landau equations, in the limit $d<\lambda$, leads to $H_c=(24)^{1/2}(\lambda/d)H_{cb}$. For In III, $H_c/H_{cb}\approx 7$, so that $d\approx 0.7\lambda$. The sevenfold increase in critical field over the bulk value shows that the field penetration must be very nearly complete, so that we are in this case observing the effect of a field in the thin film limit.

D. Behavior of Thicker Films

The film indium II (Fig. 5) of intermediate thickness $d\approx 1800$ Å, is still thin enough to display a second-order transition, but the increase of K near H_c is much faster than H^2. This behavior may be explained in terms of an increase of the penetration depth λ as the gap decreases,

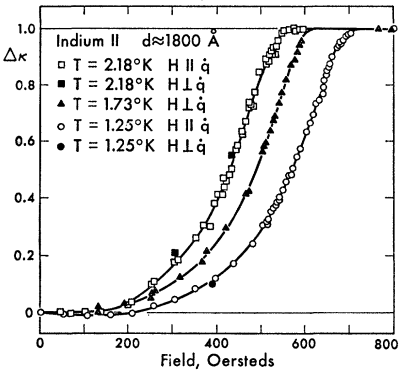

FIG. 5. Change of thermal conductivity of a superconducting film of intermediate thickness with magnetic field.

as would be expected on the basis of sum-rule arguments.[26] Since the film thickness is comparable to the electron mean free path (≈ 600 Å in this sample according to Table III) which determines the coherence length ξ, we expect the energy gap to be only weakly dependent on position in the film. We may then apply the approach of Pippard,[25] considering the balance between condensation energy and magnetic energy to determine the gap (or order parameter) as a function of field. Taking into account the dependence of film susceptibility on (d/λ) and the dependence of λ on ϵ_0, one is led to expect a change in the form of $\epsilon_0(H/H_c)$ of the observed sense for films with $d>\lambda$. A similar conclusion follows from the GLG theory, as discussed by Douglass.[4]

In Fig. 6 we see the experimental results on a moderately thick film, tin II. The data taken at 2.12° shows a variation of K with H which is purely quadratic (within 1%) up to the critical field. At this point $\Delta\kappa=24\%$. With a further increase of field, K increases rapidly

[26] M. Tinkham and R. A. Ferrell, Phys. Rev. Letters **2**, 331 (1959).

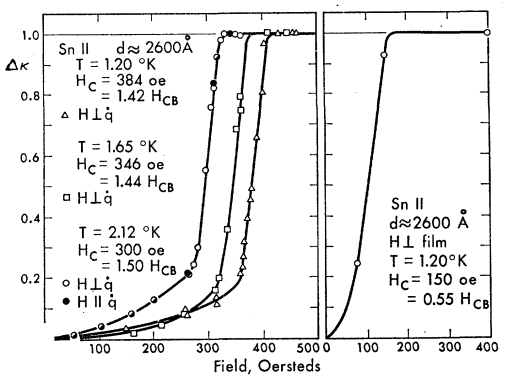

FIG. 6. Change of thermal conductivity of a 2600-Å tin film with magnetic field at various temperatures. Because of poor temperature stabilization, we have little confidence in the 1.20 and 1.65°K curves except for the determination of critical fields. The right-hand curve is for **H** perpendicular to the film plane.

up to the normal-state conductivity. The breadth of the transition can be accounted for partly, but not completely, by the difference in temperature of the ends of the film. We do not have much confidence in the 1.2 and 1.65° curves, except for the points which determine the transition, because the temperature stabilization was poor during those particular runs.

When we apply our method for calculation of the energy gap as a function of field to the 2.12° data, assuming a uniform gap throughout the film, we find the energy gap decreasing exactly as H^2 to $\epsilon_0(H)/\epsilon_0(0)=0.842$ at the critical field (Fig. 4). If we apply the GLG theory we find that the observed critical field ratio $H_c/H_{cb}=1.50$ implies that $d/\lambda=3.6$ and $\epsilon_0(H_c)/\epsilon_0(0)=0.78$. The agreement with the above value of 0.842 is quite good considering that at H_c the gap in the interior of the film should be depressed somewhat less than that at the surface, because in this film the coherence length is limited by Λ_e to a value less than the film thickness.

We next consider the data for In IV (Figs. 7, 8, 9, 10).

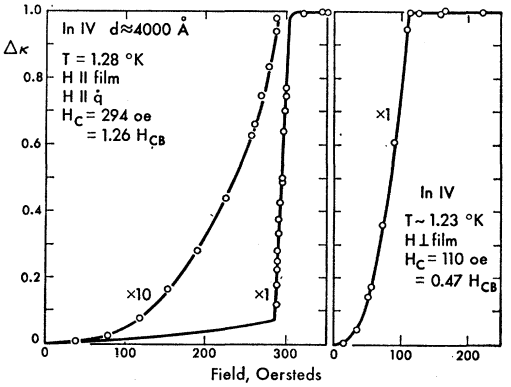

FIG. 7. Change of thermal conductivity of a thick superconducting film with magnetic field, at $T\approx 0.38\ T_c$. The first points are shown on an expanded scale for greater clarity. At the right is the result of applying the field perpendicular to the surface of the film.

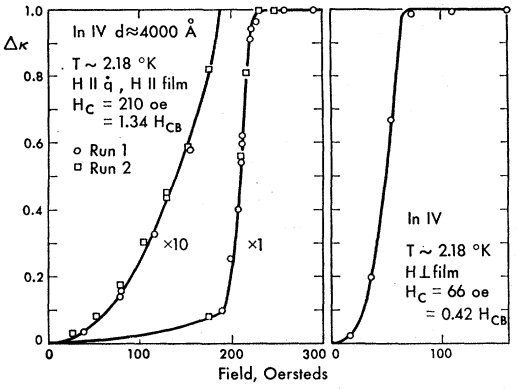

FIG. 8. Change of thermal conductivity of a thick superconducting film with magnetic field, at $T \approx 0.64\ T_c$.

Because of the large film thickness the change in thermal conductivity does not exceed about 10% up to the critical field, and the calculated energy gap variation assuming ϵ_0 is independent of position, i.e., $\xi \gg d$ (Fig. 4) is correspondingly small. The numbers at the right-hand margin of Fig. 4 are found by extrapolating the computed values of the energy gap to H_c at the points shown. These points fall almost exactly on straight lines until we reach the transition region, so we may be confident of the extrapolation. There seems to be a very slight curvature to the $0.38\ T_c$ curve, probably reflecting a trace of the peculiar hysteresis effects which are so prominent in this sample with a field orientation **H** perpendicular to $\dot{\mathbf{q}}$, the direction of heat flow (Figs. 9, 10).

E. Initial Decrease of $\Delta\kappa$

In indium II (Fig. 5) at the lowest temperature we see an apparent initial decrease of thermal conductivity with field. This may be a spurious effect arising from a slow approach to the equilibrium distribution of any trapped flux. We note from Table III that the heater power in our experiments is only about 10^{-6}–10^{-7} W and that r, the total change in thermal conductance of the metal and glass-sample sandwich with magnetic field is between 5 and 40%. Thus, evolution of heat at a rate of only 10^{-10} W (<4 erg/h!) when the field is applied could produce a spurious effect of 1% of the total. Such an evolution of heat could result from induction heating of the film during a slow approach to the equilibrium distribution of trapped flux. In many cases during the experiments, a small effect with a time constant on the order of minutes was noticed in addition to the ordinary thermal relaxation time constant, when the field was increased. This effect did not appear upon decreasing the field or upon increasing H from zero to a value previously exceeded. If indeed this is related to a slow approach to equilibrium in the flux distribution and associated induction heating, the sign of the bridge unbalance produced by the heating would give an apparent depression of $\Delta\kappa$, consistent with the sign of the observed effect.

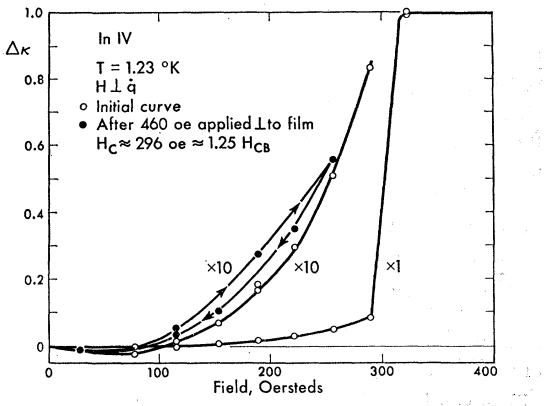

FIG. 10. Hysteresis effects observed in a thick superconducting film.

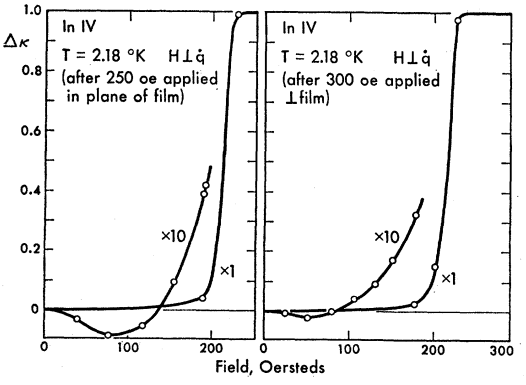

FIG. 9. Change of thermal conductivity of a thick superconducting film with magnetic field applied perpendicular to $\dot{\mathbf{q}}$, the direction of heat flow. At the right, the effect of prior exposure of sample to a large field perpendicular to the film is shown.

Another possible explanation of the long time constant term is heat released during adsorption of helium gas on the thermometer or sample surface when the equilibrium temperature of the heater-thermometer changes. It would be difficult, however, to explain the absence of the effect with decreasing field on this basis.

Yet another explanation might be depression of phonon conductivity by scattering from excitations as the gap decreases. It may be easily shown that the phonon conductivity of the experimental films, if we neglect the substrate, is very small in comparison with the electronic contribution.[27] However, diffuse scattering of the substrate phonons by the electronic excitations in the film when the substrate phonons cross the boundary into the film may lead to an effective "modu-

[27] $K_{\text{electron}} = \frac{1}{3} C_e v_F \Lambda_e$ while $K_{\text{phonon}} = \frac{1}{3} C_p v_p \Lambda_p$. C_e and C_p are comparable in the range 1–4°K in lead, tin, and indium, while $v_F/v_p \approx 10^3$. If $\Lambda_e \approx \Lambda_p \approx d$, then $K_p/K_e \approx 10^{-3}$.

lation" of the phonon conductivity of the substrate. The resultant effect may be comparable to that of the electronic thermal conductivity of the film. This possibility is examined in the following section.

F. Modulation of Phonon Conductivity of Dielectric Substrate

The wavelength of thermal phonons in glass at 1°K is approximately 2000 Å. Thus we may expect almost perfect specular reflection at the optically polished surfaces of our film substrates. Thermal phonons at 1°K have $\nu \approx 1/400$ of the Debye cutoff frequency, and therefore behave essentially as ordinary ultrasonic phonons. Experiment and theory indicate that the acoustical match between quartz and indium is quite good and leads to less than 1% reflection. Therefore, thermal phonons from the glass substrate pass quite freely into an indium surface film. Neglecting electron-phonon scattering in the film, the phonons will be specularly reflected at the smooth film-vacuum surface, and pass back into the glass. The effect of electron-phonon scattering in the indium film is to diffusely reflect the phonons back into the glass. If the phonon mean free path is a significant fraction of the substrate thickness, then the effective change from specular to diffuse surface scattering will materially decrease the thermal conductance of the substrate-film system. As a field-induced transition from the superconducting to the normal state will increase the electron-phonon interaction in the film, it will depress the thermal conductance of the system.

From the known thermal conductivity of glass at 2°K, and the relation $K=\frac{1}{3}Cv\Lambda$, we calculate $\Lambda \approx 5\times10^{-4}$ cm. This is only $\sim 1/20$ of our substrate thickness, and limits the change in the substrate thermal conductance which may be produced by surface scattering to less than $\sim 5\%$.

The degree of diffuse phonon scattering in the film depends, of course, upon the size of Λ_{pe}, the phonon mean free path as limited by electron scattering, compared with the film thickness. We may estimate Λ_{pe} by using the principle of detailed balance and the measured values of K_{ep}, the phonon-scattering limited electronic thermal conductivity, and its temperature dependence. Kittel[19] has done this in the high-temperature limit. Carrying out a similar analysis in the low-temperature limit, one finds $\Lambda_{pe} \approx 10^{-5}$ cm for tin and 10^{-6} cm for lead at 1.2°K. Since our experimental films range from 5×10^{-6} to 4×10^{-5} cm in thickness, substantial diffuse scattering of phonons may occur within the film in the normal state. When the film becomes superconducting, this diffuse scattering will nearly vanish, since most of the electrons in a superconductor at temperatures far below T_c are in the superconducting ground state and thus unable to scatter phonons. Even though the total modulation of the conductance of the substrate is limited to 5% in our case, since the substrate conductance is typically 2 to 10 times that of the film, the partial modulation obtained at moderate fields might well be enough to account for the small decrease in conductance at low fields found for In II (Fig. 5). By employing a substrate which has a larger mean free path than glass, the effect discussed in this section might be made quite large. Use of a material such as crystalline quartz (with Λ of several cm at 2°K) would appear to permit complete dominance of the thermal conductance by surface effects.

G. Hysteresis Effects in a Thick Film

During the measurements made on In IV ($d=8\lambda$) rather peculiar hysteresis effects were observed (see Figs. 9 and 10). These effects appeared only when $\mathbf{H}$ was perpendicular to $\dot{\mathbf{q}}$, the direction of heat flow. There was no detectable hysteresis when $\mathbf{H}$ was parallel to $\dot{\mathbf{q}}$, nor was any comparable hysteresis observed in any experiments with the other (thinner) experimental films. We consider the most reasonable explanation to be scattering of the heat-carrying electronic excitations at normal-superconducting boundaries.

We may assume that field inhomogeneity and film curvature make necessary small normal-state strips to carry flux through the film. If the super and normal regions have the shape of narrow lamina lying parallel to the direction of $\mathbf{H}$, then when $\mathbf{H}\perp\dot{\mathbf{q}}$ a large number of interfaces would obstruct the heat flow when a moderate field is applied.[16] Hysteresis would be a result of trapped flux affecting the arrangement of domains. Saturation of the film with trapped flux by application of a large field perpendicular to the film surface before a measurement will ensure that the maximum amount of scattering at S-N boundaries occurs before the measurement field is applied. This procedure does appear to suppress the initial decrease of $K(H)$, as we see in Fig. 9. Following saturation of the film with trapped flux, application of a subcritical field parallel to the plane of the film would sweep out some of the previously trapped flux and partially restore the original behavior, consistent with the results shown in Fig. 10.

H. Search for $p_F \cdot v_{drift}$ Term in the Excitation Spectrum

In view of Bogoliubov's prediction[14] of a $\mathbf{p}_F \cdot \mathbf{v}_{drift}$ term in the excitation spectrum of a current-carrying superconductor, resulting in an anisotropic energy gap, we varied the orientation of the field in the plane of the film between parallel and perpendicular to the direction of heat flow in the film. The directional dependence of $\Delta K(H)$ was studied in several films. In tin II, Fig. 6 ($d=2600$ Å, $T=2.12$°K, $\Lambda_e \approx 600$ Å), no effect was found within the experimental accuracy of about 1%. In indium II, as may be seen in Fig. 5, the result is not so clear-cut. Nevertheless, the apparent deviation of the $\mathbf{H}\perp\dot{\mathbf{q}}$ points from those for $\mathbf{H}\|\dot{\mathbf{q}}$ is not of significant

magnitude, and the deviations may be explained by poor control of the alignment of $\mathbf{H}$ in the plane of the film during the experiments. An experiment was conducted at 2.1°K on film Pb I, which was similar to Pb II (Fig. 11) except for an unexplained initial negative portion of its $\Delta\kappa(H)$ curve. The curves with $\mathbf{H}\perp\hat{\mathbf{q}}$ and $\mathbf{H}\|\hat{\mathbf{q}}$ were identical within the experimental uncertainties, except for a shift in H_c probably arising from a difference in the accuracy of alignment of H in the plane of the film. Since the induced diamagnetic currents are orthogonal to the field, these measurements also show the absence of a dependence on the angle between heat current and diamagnetic current. Thus, if we interpret our results in terms of a decrease of the energy gap with increasing field, the modified gap appears to remain essentially isotropic. Of course, even if there were a $\mathbf{p}\cdot\mathbf{v}$ term, first-order effects would cancel in a transport property such as K, which involves an average of excitations over the entire Fermi surface. However, as the change of ϵ_0 with H approaches 100%, noncancelling second-order effects would be expected to appear, and these would be expected to differ by a factor of several for the parallel and perpendicular cases, because of a different angular average. Thus, another factor must enter to explain the lack of anisotropy. It may well have to do with the fact that in these films, the two equal and opposite surface currents are separated by a distance comparable to ξ_0. Alternately, the short mean free path ($\sim$800 Å) in these samples would be expected to average out anisotropies as in the dirty superconductor theory of Anderson.[28] Both of these characteristics of the experimental situation contrast strongly with the Bogoliubov idealization, which corresponds to a spatially uniform current arising from a displaced sphere of momentum eigenfunctions characteristic of an ideal sample.

The apparent lack of anisotropy is important in evaluating the results of tunnel effect measurements on the magnetic field dependence of the energy gap since, for specular tunneling, this method determines the energy gap normal to the surface of the film, this direction being perpendicular to the directions of both the applied magnetic field and the induced current. This directional aspect of the tunneling experiment would also interfere with any attempt to observe the $\mathbf{v}\cdot\mathbf{p}$ effect in the presence of an externally introduced uniform current flow.

I. Magnetic Fields Not Parallel to the Surface of the Film

We have measured the thermal conductivity of several of our experimental films with field intentionally applied at an angle to the surface. The results were quite striking and unexpected.

Tin II and indium IV are films thick enough to show first-order transitions in fields parallel to the surface; that is, the energy gap is only slightly depressed from its zero field value even just below the transition. This may be seen by inspection of Fig. 4. Application of a field perpendicular to the film might be expected to produce an intermediate state configuration with the fraction of the material in the normal state approximately given by H/H_c.[29] Thus, we might expect $\Delta\kappa(H)$ to increase linearly from zero at $H=0$ to 1.0 at $H=H_c$, although the curve might "sag" somewhat as a result of both additional scattering of the electrons at S-N boundaries and the partial flux penetration of the superconducting regions.

Our measurements contrast strikingly with the above prediction. As we see in the right-hand portions of Figs. 6–8, $\Delta\kappa(H)$ apparently increases exactly as H^2 up to the normal-state value, which is reached in these samples at a field between 42% and 55% of the bulk critical field. Our results suggest that the transition is essentially complete when $K(H)$ first reaches K_n, as there is no change in K with further increase of H (see Fig. 7).

A possible explanation of the above behavior lies in the fact that for these films d is comparable with λ, ξ_0, and Λ_e, in contrast to the usual case of a thick plate in the intermediate state with a transverse field. In the latter case the superconducting and normal domains are arranged as thin lamina parallel to the field in order to minimize the free energy.[16] This is not possible in our thin film samples, since domains shaped as thin lamina parallel to the field would require adjacent S-N boundaries to be closer together than a coherence length ξ_0, and this would contribute an excessively large positive term to the free energy. We might suppose that, when our films are in a moderate magnetic field, the superconducting domains are blunt lamina whose width is determined so as to minimize the sum of the free energy terms arising from the demagnetizing factor of a blunt superconducting domain and from close spacing of the S-N domain boundaries.[30] On general grounds, one might expect an array of vortices[31] about normal lines to be more favorable energetically than lamina involving normal surfaces. Such a structure would have qualitative properties very similar to the laminar structure.

We have measured $\Delta\kappa(H)$ for Pb II with the field applied at angles θ of 0, 1.3 ($\pm$0.4), 5, 10, 20, and 90° with respect to the plane of the film at $T=2.16°$, as

[28] P. W. Anderson, Phys. Chem. Solids **11**, 26 (1959).

[29] This is expected because the field at a superconducting-normal interface in a bulk sample must be equal to H_c; then H will be close to H_c throughout the small normal domains, while in the interior of the superconducting domains $H\approx 0$ (if the domains are much larger than the penetration depth λ). Thus, the flux HA which passes through area A of the film penetrates normal regions of total area $A_n=HA/H_c$.

[30] Since our domains will have dimensions of the same order as the coherence length, the energy gap may be nonzero nearly everywhere. In this case we may imagine the energy gap to oscillate as a function of position, with the magnetic flux density being greater in the regions where the gap is small. The remainder of the argument is qualitatively unchanged.

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

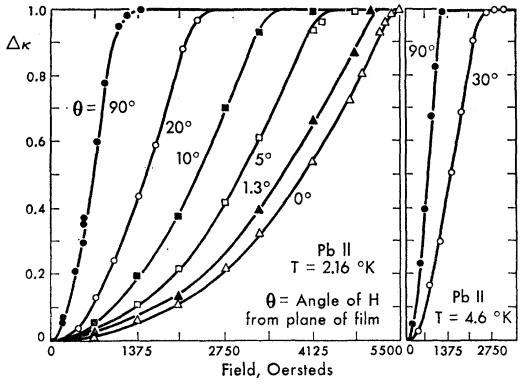

FIG. 11. Change of thermal conductivity of a superconducting lead film with the field applied at various angles with respect to the plane of the film.

well as at 0, 30, and 90° for $T=4.5°$. The results are shown in Fig. 11. We see that as θ is increased from zero the apparent critical field decreases, but the transition appears to remain well defined. The general shape of $\Delta\kappa(H)$ does not change rapidly with θ, but for large θ, $\Delta\kappa(H)$ becomes more nearly linear in H. At $\theta=90°$, the apparent critical field has decreased to a value of the order of H_{cb}.

An attempt has been made to fit the experimental values of $H_c(\theta)$ with various analytical interpolation functions. These are based on the assumption that the parallel and perpendicular components of the magnetic field produce additive contributions to the free energy, and that when the sum of these effects reaches a critical value the film is driven normal. Assuming the contributions to the energy to increase as simple powers of the components of the field, this leads to a form

$$\left(\frac{H_c\cos\theta}{H_{c\parallel}}\right)^m+\left(\frac{H_c\sin\theta}{H_{c\perp}}\right)^n=1.$$

Since magnetic field energies normally are proportional to H^2, one might expect that $m=n=2$. However, this gives a very poor fit at small angles. In fact, a considerably better fit was found to result from the choice $m=n=1$. Subsequently, it was shown[31] by detailed consideration of the vortex model for the perpendicular field case that one would expect $n=1$, but $m=2$. A comparison of the degree of fit of these three interpolation formulas to the critical field data on Pb II has been given previously.[31] A similar comparison with data of White on a thin indium film has also been given.[32] Both of these comparisons favor the theoretically based function, with $m=2$ and $n=1$.

J. Behavior of Thin Lead Films

As we have discussed previously, the predictions of the GLG theory fail at low temperatures. The low-temperature limiting behavior of $\epsilon_0(H)/\epsilon_0(0)$ would be of interest in guiding theoretical efforts. Since facilities for producing stabilized temperatures below 1.2°K were not available to us, experiments were undertaken on lead since 1.2°K equals only 0.18 T_c for this metal. Our detailed results are not easy to interpret and may be a reflection of the peculiarities of superconducting lead, rather than characteristic of superconductors in general. However, we may assert with some confidence that the superconducting transition in a field is of second order for thin films ($d<\lambda$) over the range of temperatures from 0.63 T_c at least down to 0.18 T_c. This conclusion follows from the observed absence of any discontinuity in $\Delta\kappa$ at H_c, as was discussed in Sec. IIIC.

Experimental results for Pb II, a lead film about 500 Å thick, are shown in Fig. 12. Another film,[33] Pb I, gave similar results except for an unexplained initial decrease in $\Delta\kappa$ which appeared at 4.2, 2.1, and 1.2°. The initial decrease of $\Delta\kappa$ for Pb I at 2.1°K was the same for $\mathbf{H}\perp\hat{\mathbf{q}}$ and $\mathbf{H}\|\hat{\mathbf{q}}$. Because of this divergence of results between Pb I and Pb II, we have less confidence in the data in the low-field region than we have near H_c. In Fig. 12, the rounded approach of the 4.5° data to the normal-state conductivity may be accounted for quantitatively by the 0.6° temperature drop along the film, and the consequent 15% critical field spread (Table I). In contrast, at 2.16 and 1.27° the critical field spreads are small (see Table I), and the rounding of the curves at the transition results from the form for small ϵ_0/kT of the G function (Fig. 3) connecting K and ϵ_0/kT, as discussed in the analysis of the In III data.

If we naively invert the data of Fig. 12 point-by-point in the usual manner we find the apparent relations between ϵ_0 and H which are given in Fig. 13 for the various temperatures. At each temperature, the upper curve follows from assuming the zero-field gap

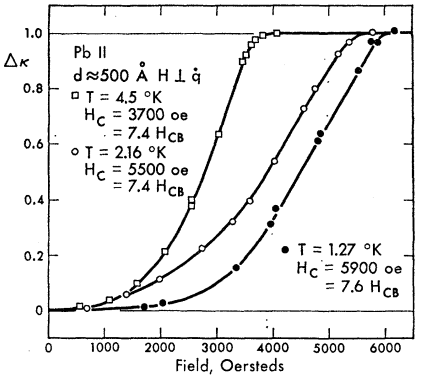

FIG. 12. Change of thermal conductivity of a superconducting film with magnetic field at several temperatures.

[32] M. Tinkham, Rev. Mod. Phys. **36**, 268 (1964).

[33] This film was prepared in a similar manner to Pb II, and has a similar critical field, but it was exposed to the atmosphere for 5 h before mounting, compared to an exposure of ½ h for Pb II. However, we expect that this duration of exposure would have produced negligible oxidation (Sec. IIF).

value based on the BCS result $\epsilon_0=1.75\ kT_c$ at $T=0°K$. If we take instead the value 2.1 kT_c as suggested by several experiments[34–36] the lower curves result.

If one were to take Fig. 13 at face value, one would be forced to conclude that the variation of ϵ_0 with H is different in lead and indium at the same reduced temperature $t(=T/T_c)$. Although the 4.5° lead curve and 2.1° indium curve (Fig. 4), both with $t\approx\frac{2}{3}$, seem to be consistent with the GLG result $\epsilon_0(H)/\epsilon_0(0)=[1-(H/H_c)^2]^{1/2}$, we see that lead at 2.16° seems to be incompatible with indium at 1.2° even though the reduced temperatures are nearly the same ($t\approx0.35$). It is just possible that the experimental curves for Pb II reflect some spurious effect of the sort that produced the initial negative curve for Pb I, although the deviation would have to be of opposite sign from that observed in Pb I in order to make the Pb II and In III results compatible. Inversion of the Pb I data produces an $\epsilon_0(H)/\epsilon_0(0)$ versus H^2 curve with the same qualitative deviation from the indium curve, once the field is greater than about $(H/H_c)^2=0.3$, [so that we are well above the region where $K(H)$ decreases from the zero-field value].

An alternative, and probably more sound, explanation of the discrepancy is that the relation derived from BRT which we have used to connect the thermal conductivity variations with changes in the energy gap is not completely valid, at least in the case of lead.

It is well known that the thermal and electrodynamic properties of lead and mercury deviate considerably from the law of corresponding states. It has not been possible to accurately test the applicability of Sec. 3 of the BRT theory to these metals, because phonon scattering contributes to the thermal resistance as a result of the low values of θ_{Debye}. But, since $K_e=\frac{1}{3}C_e v_F \Lambda_e$ and the experimentally determined[37] $C_e(T)$ is different from that predicted by BCS, on which the BRT theory is based, we may expect that the BRT calculation will not account satisfactorily for the thermal conductivity of lead and mercury.

Upon comparison of Figs. 4 and 13, we note that if the effective value of the energy gap of lead were to decrease from the usual value at 4.5° to about 1.4 kT_c at 2.16° and about 1.0 kT_c at 1.27°, both of the low curves for lead could be made to coincide with the 1.3° indium III curve. This suggests that we might combine the $\Delta\kappa(H)$ curves of Pb II with the $\epsilon_0(H)/\epsilon_0(0)$ result found for In III at 1.3°, and find the function $G_1(x)$ which would be necessary to connect them. If we now subtract $G(x)$ from $G_1(x)$, we find that the difference, $\Delta G(x)$, is a function which is zero at $x=0$, increases to a maximum of about 0.35 for x between 4 and 6, and then decreases with further increase of x. Let us generalize $G(x)$ to include an "effective density of states"

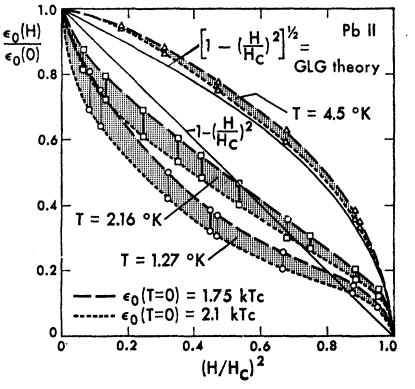

FIG. 13. Dependence of energy gap of a lead film on field as calculated from the data of Fig. 12 using the $G(\epsilon_0/kT)$ function from Fig. 3. For each experimental point, two gaps are computed as shown: one assuming the gap ($2\epsilon_0$) approaches 3.5 kT_c at $T=0$ as found by BCS; and one assuming the gap goes to 4.2 kT_c as found experimentally.

$\rho[E/\epsilon_0(H)]$. Note that this brings us completely outside the BRT theory, and thus we can have no confidence in the result except as a phenomenological description. Let

$$G_1(x)=\int_0^\infty \rho(E/\epsilon_0)E^2(\partial f/\partial E)dE \Big/ \int_0^\infty E^2(\partial f/\partial E)dE$$

and take $\rho(E/\epsilon_0)=1$ for $E\geq\epsilon_0$ (the usual BRT form). Then

$$\Delta G(x)=\int_0^{\epsilon_0} \rho(E/\epsilon_0)E^2(\partial f/\partial E)dE \Big/ \int_0^\infty E^2(\partial f/\partial E)dE.$$

We have attempted to fit $\Delta G(x)$ with several simple forms of $\rho(E/\epsilon_0)$. Within our very limited accuracy of ΔG, we find a satisfactory fit for the delta function $\rho(E/\epsilon_0)=\frac{2}{3}\delta[(E/\epsilon_0)-\frac{1}{2}]$, or for the parabolic function $\rho(E/\epsilon_0)=\frac{3}{2}(E/\epsilon_0)^2$. We emphasize that we do not take the above to be conclusive evidence for the existence of "states in the gap" of lead, or for the location of any such hypothetical states. Rather, these considerations are intended to indicate the major scale of the departure of the data on lead from that on indium at low reduced temperatures. We conclude that lead behaves in some respects differently from other superconductors even at the same reduced temperatures, but the cause is not at present fully understood.

IV. CONCLUSIONS

From the results of the preceeding sections we may draw several conclusions: First, the thermodynamic transition in a field may be quite sharp and well-defined even for films sufficiently thin (700 Å) that $H_c>7\,H_{cb}$. The thermodynamic transition appears to be reversible and without hysteresis for typical films up to 2500 Å thick. Our experiments give direct evidence that the superconducting transition is of second order in

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films which are thin (compared with the penetration depth) for temperatures ranging from T_c down to 0.18 T_c, the lowest available temperature, in disagreement with the theory of Bardeen[8] but in agreement with that of Nambu and Tuan.[9]

We have applied the theory of BRT,[13] which is based on BCS, to our data on thin films of Pb, Sn, and In, on the assumption that their theory is valid for $H \neq 0$ with a suitable field-dependent gap parameter $\epsilon_0(H)$. At $T=0.65\ T_c$, the function $\epsilon_0(H)$ which results from our analysis is essentially identical to that predicted by GLG and experimentally found in tunnel measurements. At lower temperatures ($0.36\ T_c$), our $\epsilon_0(H)$ computed with the aid of BRT is different, indicating a breakdown of the GLG theory for $T \ll T_c$, or possibly a failure of the method of data analysis via BRT.

By varying the relative orientation of the direction of heat flow and the applied magnetic field in the plane of the experimental films, we unsuccessfully sought evidence for vestiges of the $\mathbf{p}_F \cdot \mathbf{v}$ term in the excitation spectrum of a current-carrying superconductor, predicted by Bogoliubov.[14] Since the experimental conditions differed radically from those envisioned by Bogoliubov, this negative result is not surprising.

Application of magnetic fields at various angles up to 90° with respect to the film plane still produced surprisingly well defined thermodynamic transitions, although H_c was reduced considerably below the parallel field value. The transition in a perpendicular field appeared to be second-order even for films of thickness up to 4000 Å, whose parallel field transition was definitely first order. The perpendicular critical field values and the angular dependence of H_c seem to be explained satisfactorily by the theory of Tinkham.[31]

Lead films gave results qualitatively similar to indium and tin films, but quantitatively the form of the derived $\epsilon_0(H)$ at low temperatures was different from that of tin and indium. We suspect that this is connected with the well-known peculiarities in the thermal properties of superconducting lead.

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Higher Order Coherent Raman Effects*

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With the recently available very intense coherent maser light, interesting higher order coherent Raman effects have been observed in solids, liquids, and gases. Garmire, Pandarese, and Townes have given a phenomenological theory of these higher order coherent Raman effects. In this paper a somewhat more detailed theory of these effects is given. The analysis is based on a perturbation solution of the Boltzmann equation for the density matrix of the Raman active medium. General expressions for all the relevant induced dipole moments and absorbed or emitted Stokes and anti-Stokes radiations in the ordinary or higher order coherent Raman processes are given. These cover a great variety of possible experimental situations. Several specific simple examples are studied in some detail and the results of the phenomenological theory are reproduced from the general results given here.

I. INTRODUCTION

THE first-order Raman effects have been investigated extensively in the past both experimentally and theoretically. With the recently available very intense maser light, interesting higher order coherent Raman effects in solids,[1] liquids,[2] and gases[3] have also been observed. Garmire, Pandarese, and Townes[4] give a detailed macroscopic theory of these higher order coherent Raman effects, particularly those through excitation of intense coherent molecular oscillations at infrared frequencies. Many interesting conclusions were drawn from the theory and some of these have already been observed experimentally. In this paper an attempt is made to give a somewhat more detailed analysis of the same effects on the basis of the quantum-mechanical Boltzmann equation for the density matrix characterizing the Raman-active medium and to include in the theory the effects of various relaxation processes.

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