Entropy of the Mixed State of Some Low-κ Type-II Superconductors*

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The entropy of the mixed state of type-II superconductors with low $\kappa(\sim 1)$ is studied for the alloys $Pb_{0.96}Tl_{0.04}$ and $In_{0.88}Sn_{0.12}$. The current theories are reviewed for approximations valid near H_{c1} and near H_{c2}. The experiments show for the most reversible sample ($Pb_{0.96}Tl_{0.04}$) that $(\partial S/\partial B)_T$ of the mixed state depends only on temperature, and that $(\partial S/\partial T)_B$ increases linearly with B from its value for the superconducting state until it drops discontinuously to its normal state value at H_{c2}. There is no abrupt increase in the specific heat at constant magnetic induction near H_{c1} as is observed in the specific heat at constant applied magnetic field. A method of determining the thermodynamic critical field of an irreversible sample without assuming a parabolic form is discussed and applied to the data. The thermodynamic critical field determined in this way is used to calculate κ_1 and κ_2. The parameters are very nearly equal for $Pb_{0.96}Tl_{0.04}$ with a temperature dependence of $(1+t^2)^{-1/2}$. Measurements of $(\partial S/\partial B)_T$ are also reported on the type-I superconductors Sn and Pb. The conclusion, as expected, is that $(\partial S/\partial B)_T$ in the intermediate state depends on the temperature only.

I. INTRODUCTION

THE rate of change of entropy S with magnetic induction B at constant temperature for several type-II superconductors has been reported by Otter, Yntema, and Solomon.[1–3] Their result for slab-shaped samples of $Mn_{0.85}Mo_{0.15}$ and $In_{0.60}Pb_{0.40}$ was an initial decrease of $(\partial S/\partial B)_T$ with increasing B followed by a plateau extending to the upper critical field H_{c2}. The results for ellipsoidal samples of $In_{0.60}Pb_{0.40}$ and $Pb_{0.60}Tl_{0.40}$ showed a minimum near H_{c1}, the field at which initial flux penetration occurs, followed by a slow increase extending to H_{c2}. The variation between highest and lowest values was as much as a factor of 2. However, since fluxoid interactions near $B=0$ are small, one would expect the entropy to be a linear function for B for small values of B. Section II shows theoretically that the deviation from linearity depends on the rate of change of the interaction energy with temperature. It is pointed out that S should also vary linearly with B near H_{c2}. Section II also contains a theoretical discussion of the specific heat at constant magnetic induction C_B near H_{c1} and H_{c2}. Sections III and IV present experimental measurements of Q/T versus B and $(1/T)(\delta Q/\delta B)_T$ for ellipsoidal samples of Sn, Pb, $Pb_{0.96}Tl_{0.04}$, and $In_{0.88}Sn_{0.12}$.

The specific heat at constant applied field C_H is another measure of the entropy of the mixed state which has been reported several times.[4–9] However, this approach like the direct isothermal measurement of S versus B is influenced by the irreversibility of the specimen. In both experiments, entropy is produced by irreversible work as well as by adding heat. Section V reports on the measurement of the specific heat at constant B rather than at constant H. The specific heat at constant magnetic induction C_B should directly reveal the influence of the fluxoid interaction and not depend upon whether the fluxoids entered the sample reversibly. Unfortunately, the lattice contribution to the specific heat is very large in the materials chosen for this study so that the precision is low; however, the results do compliment the S-versus-B measurements, and are consistent with the theoretical predictions.

The measurements of S and B were used to calculate the thermodynamic critical field, H_c, H_{c2}, and Maki's[10] parameter κ_1. Values for Maki's[10] parameter κ_2 are also calculated from the magnetization curves and the calorimetric data. Values for all of these parameters are presented in Sec. IV.

II. THEORY

Many authors have calculated the thermodynamic properties of the mixed state of a type-II superconductor near H_{c1}.[11–14] Their results are essentially

$$G_m - G_s = B(H_{c1}-H)/4\pi + f(B,\lambda), \qquad (1)$$

where λ is the penetration depth, the subscripts m and s indicate the mixed and superconducting states, respectively, and $f(B,\lambda)$ is the interaction energy of the fluxoids. At a given H, B is such that G is a minimum.

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[13] B. B. Goodman, in *Reports on Progress in Physics* (The Institute of Physics and The Physical Society, London, 1966), Vol. XXIX, Part II, pp. 463–467.
[14] P. G. de Gennes, *Superconductivity of Metals and Alloys* (W. A. Benjamin, Inc., New York, 1966), p. 67.

This condition results in

$$(H_{c1}-H)/4\pi+\partial f/\partial B+(\partial f/\partial\lambda)(\partial\lambda/\partial B)=0. \quad (2)$$

Since the entropy is given by $-(\partial G/\partial T)_H$, the entropy change upon entering the mixed state can be obtained from Eqs. (1) and (2). The result is

$$S_m-S_s=[-4\pi^{-1}(dH_{c1}/dT)]B-(\partial f/\partial\lambda)(\partial\lambda/\partial T). \quad (3)$$

The interaction energy is exponentially small for small B[14], and the penetration depth λ does not vary rapidly except near T_c. It is expected then that even though the interaction energy of the fluxoids has a large effect on the magnetization curve, it will have a small effect on the entropy. Thus, S should vary linearly with B near H_{c1} with a slight negative curvature developing as B increases.

In Refs. 11–14, the interaction energy of the fluxoids $f(B,\lambda)$ is derived for large κ materials, where λ is much longer than the coherence length. For small κ, the interaction energy will vary with B in a different way, but it will be some function of B and κ. Whatever the functional dependence is, Eq. (3) will not be changed in form, but λ will be replaced by κ. For small B, the general conclusions will be the same since the rate of change of interaction energy with κ must go to zero for small B, and κ changes slowly with temperature.

Near H_{c2}, the Ginsburg-Landau equations have the approximate solution[10,13,15,16] to lowest order in $H_{c2}-H$

$$-4\pi M=\frac{H_{c2}-H}{\beta(2\kappa_2^2-\eta)}+\cdots, \quad (4)$$

$$G_m-G_n=\frac{-1}{8\pi}\frac{(H_{c2}-H)^2}{\beta(2\kappa_2^2-\eta)}+\cdots, \quad (5)$$

$$S_m-S_n=\frac{1}{4\pi}\frac{H_{c2}-H}{\beta(2\kappa_2^2-\eta)}\frac{dH_{c2}}{dT}+\cdots, \quad (6)$$

where $\beta=1.1596$, η is nearly unity,[16] and the subscripts m and n denote the mixed and normal states, respectively.

Equation (4) can be used to express the entropy difference in terms of B

$$S_m-S_n=\frac{H_{c2}-B}{4\pi[\beta(2\kappa_2^2-\eta)+1]}\frac{dH_{c2}}{dT}+\cdots. \quad (7)$$

Therefore, near H_{c2}, the entropy should vary linearly with B but with possibly a different slope than that at H_{c1}.

The specific heat at constant B in the mixed state near H_{c2} is found from Eq. (7).

$$C_B=C_n+\frac{T(H_{c2}-B)d^2H_{c2}/dT^2}{4\pi[\beta(2\kappa_2^2-\eta)+1]}+\frac{T(dH_{c2}/dT)^2}{4\pi[\beta(2\kappa_2^2-\eta)+1]}-\frac{2T(H_{c2}-B)\beta\kappa_2(d\kappa_2/dT)(dH_{c2}/dT)}{\pi[\beta(2\kappa_2^2-\eta)+1]^2}. \quad (8)$$

[15] G. Lasher, Phys. Rev. **140**, A523 (1965).
[16] Gert Eilenberger, Phys. Rev. **153**, 584 (1967).

Near H_{c2}, C_B should vary linearly with B and have a discontinuous jump of

$$C_B=\frac{T(dH_{c2}/dT)^2}{4\pi[\beta(2\kappa_2^2-\eta)+1]} \quad (9)$$

down to the normal state. This result agrees with that of Zoller and Dillinger, if the demagnetizing factor is taken to be 1 (e.g., $B=H_e$).

Near H_{c1}, C_B can be calculated from Eq. (3)

$$C_B=C_s+\left(\frac{-T}{4\pi}\frac{d^2H_{c1}}{dT^2}\right)B-T\frac{\partial f}{\partial\lambda}\frac{\partial^2\lambda}{\partial T^2}-T\frac{\partial^2 f}{\partial\lambda^2}\left(\frac{\partial\lambda}{\partial T}\right)^2. \quad (10)$$

Therefore, near H_{c1}, C_B should vary linearly with B and approach C_s as B goes to zero. The specific heat at constant B should show no discontinuity nor anomaly at H_{c1} like that seen for the specific heat at constant applied field.[7–9] The details of the magnetization curve are responsible for the anomaly in C_H; whereas, C_B, apart from C_s and the term linear in B, is sensitive to the derivatives of the interaction energy only. Furthermore, C_B has the experimental advantage that it may be measured without performing irreversible work. Since $HdB=0$ at constant B, no work is done at all, whereas, in a measurement at constant H, $HdB\neq 0$, and irreversibility may affect the measured value of C_H. Another experimental bonus is that the more irreversible the sample, the easier it is to maintain B fixed as the sample is heated during the measurement of C_B. On the other hand, the lattice contribution to the specific heat may be so large that it makes measurement of the remaining contributions difficult.

III. EXPERIMENTAL TECHNIQUES

All measurements of the externally supplied entropy along isotherms in the intermediate or mixed states consisted basically of simultaneously monitoring the magnetic induction B, the heat supplied Q, and the temperature of an adiabatically mounted sample. Three different techniques were tried. The first two differed only in the parameter which was used to regulate the temperature. In technique I, constant heater power was supplied to the sample as the applied field was varied manually to regulate the temperature, while in technique II, the applied field was increased at a constant rate as the heater power was varied manually to regulate the temperature. Technique III measured incremental increases in Q and B.

In technique III, the temperature was regulated by turning part of the heater power on and off as B was increased by sweeping the applied field at a constant rate. After B increased the desired increment, the applied field was held fixed until equilibrium was established. This technique was inherently superior because the sample was in equilibrium when the data were recorded; whereas techniques I and II were

TABLE I. Critical field and entropy difference for Sn.

T (K)	ΔS [a] (erg/cm³ K)	ΔS [b] (erg/cm³ K)	H_c [a] (Oe)	H_c [b] (Oe)
3.30	628	655	62.8	61.5
2.65	1255	1289	142.6	143.1
2.24	1474	1509	184.9	187.6

[a] This work.
[b] Reference 19.

dynamic. This technique also allowed for more frequent measurement of the heat leak. However, the results for each technique were the same if appropriate care was taken.

A superconducting solenoid provided the applied magnetic field which was uniform to within 0.1% over the volume of the sample. The rate of change of flux through a pick-up coil around the ellipsoidal sample was detected by a nanovoltmeter and recorded on a strip chart recorder. If B in the ellipsoid is uniform, the shape of the pick-up coil is unimportant. However, the irreversibility of some of the samples raises the question of whether or not the pick-up coil actually measured the average of the possibly nonuniform B. If the irreversible behavior of the samples is primarily due to surface effects, the approximation of uniform B is very good because of the small demagnetizing factor (0.043) of the samples. However, if the irreversible behavior is primarily due to flux pinning distributed throughout the volume, B will not be uniform. In this case, the geometry of the sample and pick-up coil becomes important. The pick-up coil was approximately as long as the sample and about twice its diameter. For the coil length to diameter ratio of 3 in this experiment, the volume average of the magnetic coupling of the sample with the pick-up coil is 94% of the coupling at the center of the sample. Therefore, the results are very close to a volume average of B even if B is not uniform. A mutual inductance with its primary in series with the solenoid and its secondary in series opposition to the pick-up coil was adjusted so that with the sample in the superconducting state no change in signal was obtained on the recorder when the current in the solenoid increased or decreased. Thus, any deflection was proportional to dB/dt. As the sample was taken through the intermediate state, B could be determined at any time by integrating the area under the curve swept out on the strip chart recorder. The system was calibrated against a ballistic galvanometer using the fact that $B=H$ in the normal state and $B=0$ in the superconducting state.

The output of the pick-up coil could also be detected by a ballistic galvanometer. To use the galvanometer to find B in the intermediate state, the applied field was slowly increased to the desired value with the temperature held constant. A pulse of heat was then applied to drive the sample well above T_c. The resulting maximum deflection of the galvanometer was taken to be proportional to the magnetization of the sample before the heat pulse. The galvanometer system was calibrated by assuming $B=0$ in the superconducting state.

The heat was applied through an Evan-Ohm wire wrapped bifilarly over the sample and cemented to it with GE-7031 varnish. Corrections were made for the temperature dependence of the resistance,[17] and the resistance of one lead was added to the heater's resistance to account for the heat generated in both leads. The heat leak was determined by a linear interpolation in time of the measured heat leak before and after a transition or part of a transition.

The thermometers were $\frac{1}{2}$-W 48-Ω Allen-Bradley carbon resistors. Their resistance was measured with a 33-Hz bridge designed by Blake, Chase, and Maxwell.[18] The thermometers were calibrated against helium vapor pressure below 4 K. For temperatures above 4 K, the published value for T_c was used as a calibration point. Temperatures were interpolated between T_c and 4 K using the two-constant formula

$$[(\ln R)/T]^{1/2}=A+B\ln R. \tag{11}$$

The experiments were performed on samples which were fabricated into ellipsoids of revolution having major and minor axes of approximately 7.6 cm and 1.27 cm, respectively. The technique was to cast the material into a cylindrical ingot, machine it to the approximate ellipsoidal shape, and then grind and etch it until smooth.

The above dimensions yield a demagnetizing factor N of 0.043. The corrected field ($H=H_{\text{applied}}-4\pi NM$) is obtained for all cases. In this paper, the magnetic field H is always the corrected field unless otherwise specified.

Samples of tin and lead were prepared from 99.999% pure material supplied by Leico Industries, Inc. and Leytess Metal and Chemical Co., respectively. These materials were chosen as representative of type-I superconductors with well documented thermodynamic properties. Tables I and II represent the critical fields and the entropy differences between the superconducting and normal states of tin and lead. The critical fields and total entropy differences measured in this work are

TABLE II. Critical field and entropy difference for Pb.

T (K)	ΔS [a] (erg/cm³ K)	ΔS [b] (erg/cm³ K)	H_c [a] (Oe)	H_c [b] (Oe)
4.76	5927	5727	473.4	468.3
4.18	5769	5665	547.5	549.1
3.51	5501	5256	625.8	626.7
3.01	4746	4744	674.3	675.0
2.04	3481	3401	747.3	745.4

[a] This work.
[b] Reference 20.

[17] R. C. Pandorf, E. Lerner, and J. G. Daunt, Rev. Sci. Instr. **35**, 1070 (1964).
[18] C. Blake, C. E. Chase, and E. Maxwell, Rev. Sci. Instr. **29**, 715 (1958).

compared with published critical field data[19,20] and entropy differences calculated from these published data. The agreement of the entropy differences indicates that very little entropy was produced by irreversible work during the course of making measurements on the intermediate state. This fact lends credibility to our conclusions concerning the entropy in the intermediate state.

The detailed measurements in the intermediate state of both tin and lead show that $(\partial S/\partial B)_T$ is a constant for any part of the intermediate state. This is no surprise since the intermediate state in a type-I superconductor is not finely divided into singly quantized fluxoids as is the mixed state of a type-II superconductor. The interphase surface energy in the intermediate state cannot be nearly so significant in a type-I superconductor as it is in a type-II superconductor.

IV. TYPE-II SUPERCONDUCTORS

A $Pb_{0.96}Tl_{0.04}$ sample was prepared by melting sufficient quantities of 99.999% pure Pb supplied by Leytess Metal and Chemical Co. and 99.98% pure Tl in a Pyrex test tube under a vacuum of about 10^{-5} Torr. The molten alloy, still under vacuum, was thoroughly stirred with a Pyrex rod. The melt was allowed to solidify over a period of about an hour. The ingot was then given to a machinist, who produced an ellipsoid of revolution having a major axis of 7.61 cm and a minor axis of 1.27 cm. The sample was etched and annealed for 24 h at 300°C. The sample was then mounted in the calorimeter and the preliminary measurements were made.

In the hope of improving the reversibility of the transition, the sample was removed from the calorimeter and vacuum annealed for 14 days at 315°C. The surface was then polished using a chemical polish of 70 parts glacial acetic acid and 30 parts 50% hydrogen peroxide. The measurements were repeated with a noticeable improvement in the reversibility. In subsequent attempts to improve the reversibility, the sample was vacuum annealed for 33 days at 315°C, 12% of the volume was etched away, and finally it was manganese plated. None of the last three treatments seemed to improve the reversibility. One simple measure of the reversibility is the amount of the flux trapped in the sample after cycling the applied field above H_{c2} and back to zero. Table III gives the ratio of this remanence to maximum magnetization in an increasing field for the various treatments of the sample.

TABLE III. Remanence at 4.2°K in the $Pb_{0.96}Tl_{0.04}$ sample.

Treatment	Remanence (%)
Machine, etch, 24-h anneal at 300°C	26.0
Anneal 14 days at 315°C, chemical polish	12.5
Anneal 33 days at 315°C, chemical polish	10.0
Etch off 12% of sample in HNO_3	12.8
Chemical polish, manganese plate	13.4

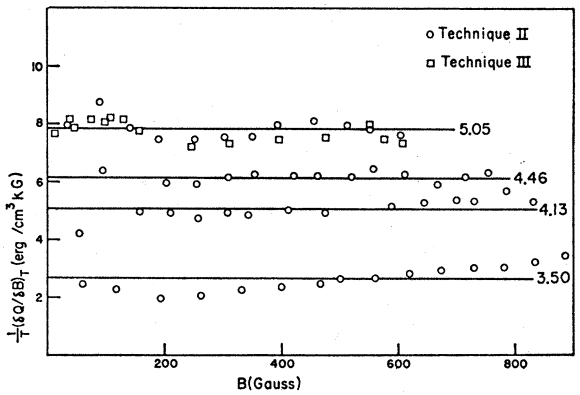

FIG. 1. Rate of change of externally supplied entropy in the mixed state of $Pb_{0.96}Tl_{0.04}$.

There is a sharp increase in the rate with which flux was admitted into the $Pb_{0.96}Tl_{0.04}$ sample near the end of the mixed state following every treatment except the first and the fourth. In these cases, the sample was pitted by the HNO_3 etch so that the grain boundaries were evident. In all the other cases, care was taken to see that the sample was visibly smooth. One might conclude that the pitted surface provided slightly less resistance to flux penetration than did the smooth surface.

The manganese was evaporated onto the chemically polished surface of the sample in vacuum from a graphite boat. A glass slide placed near the sample received an opaque, mirror coating of manganese. The surface of the sample reflected light well and did not oxidize like lead upon exposure to the atmosphere. Therefore, without doubt, manganese was plated on the sample in an amount usually considered to be sufficient to quench the surface superconductivity between H_{c2} and H_{c3}. It failed to do it in this case. A small amount of magnetization as measured by the ballistic galvanometer persisted well above H_{c2}. Furthermore, the manganese plating failed to decrease the remanence or to decrease the sharp rise in the rate of flux admission near H_{c2}.

All three techniques were used to measure the entropy of the mixed state of the $Pb_{0.96}Tl_{0.04}$ sample. Figure 1 shows the rate of increase of externally supplied entropy with increasing magnetic flux in the $Pb_{0.96}Tl_{0.04}$ sample at 5.05 K obtained by techniques II and III. The results obtained by using technique II are also shown in Fig. 1 for some lower temperatures to dramatize what happens as the transition becomes more irreversible. For temperatures below 3 K, the sample actually heats ($\Delta Q/\Delta B<0$) since more entropy is added

[19] R. W. Shaw, D. E. Mapother, and D. C. Hopkins, Phys. Rev. 120, 88 (1960).
[20] D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. 112, 1888 (1958).

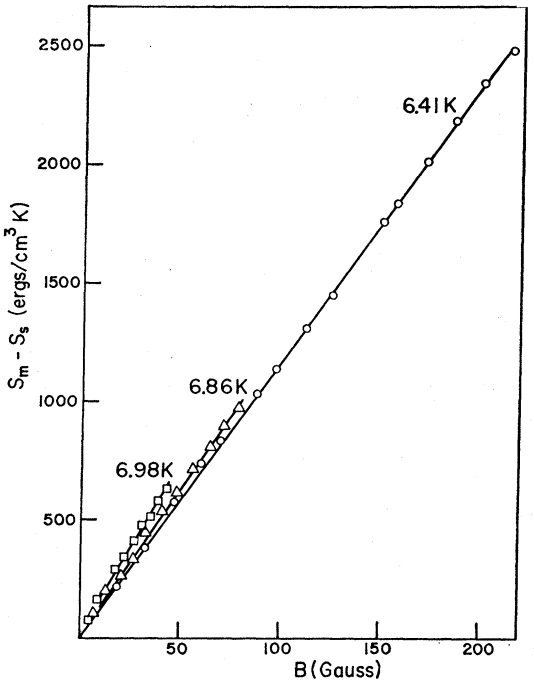

FIG. 2. Entropy in the mixed state of $Pb_{0.96}Tl_{0.04}$ near T_c.

by irreversible work than the actual change of entropy associated with the change of state. The externally supplied entropy in the mixed state as a function of the magnetic induction for several temperatures from within 0.12K of T_c (7.10K) to 3.50K is presented in Figs. 2–4. These results being nearly straight lines above 4.46K vary markedly from those of Otter *et al.*,[1–3] who measured alloys with larger κ.

Since the magnetic transition was so irreversible, it is evident that entropy was added to the sample in going through the mixed state by the performance of irreversible work as well as by adding heat to the sample. However, we have a record of the magnetic induction in the sample and the applied field so that, in principle, the total entropy difference can be calculated even though the transition is through nonequilibrium states. The argument supporting this is given by Otter *et al.*[1] It is based on the fact that the change in internal energy in going from the superconducting state to the normal state is independent of the path.

The change in internal energy ΔU in terms of measured quantities is given by the first law of thermodynamics

$$\Delta U=\Delta Q+\int_0^{H_{c2}} HdM=T\Delta S+H_c^2/8\pi. \quad (12)$$

The quantities ΔQ, H, and M are all measured during the course of a transition and the terms on the right-hand side of Eq. (12) are to be determined. Otter and Yntema's Eq. (4)[1] is obtained by performing the integral in Eq. (12) by parts using the fact that $M=0$ in the normal state to obtain

$$\Delta U=\Delta Q-\int_0^{H_{c2}} MdH=T\Delta S+H_c^2/8\pi. \quad (13)$$

At this point, Otter assumed a parabolic temperature dependence for H_c in order to proceed. However, if

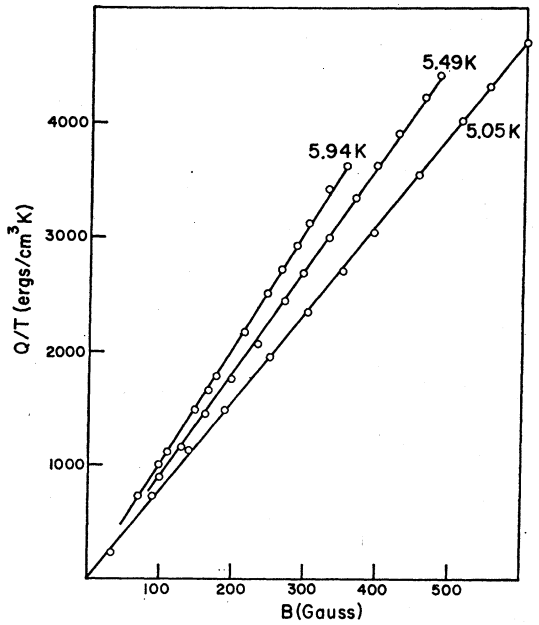

FIG. 3. Externally supplied entropy in the mixed state of $Pb_{0.96}Tl_{0.04}$ for 5.05 K, 5.49 K, and 5.94 K.

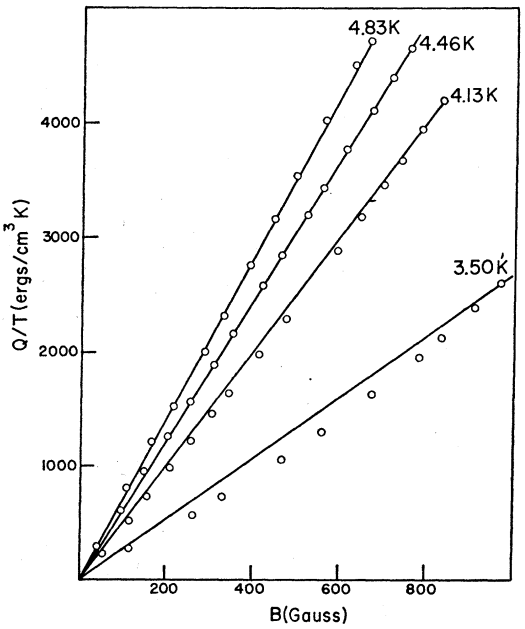

FIG. 4. Externally supplied entropy in the mixed state of $Pb_{0.96}$ $Tl_{0.04}$ for 3.50 K, 4.13 K, 4.46 K, and 4.83 K.

TABLE IV. Thermodynamic parameters of $Pb_{0.96}Tl_{0.04}$.

T (K)	ΔQ (erg/cm³)	ΔW (erg/cm³)	ΔS (erg/cm³ K)	H_c (Oe)	H_{c1} [a] (Oe)	H_{c2} (Oe)	$\Delta S_I/\Delta S(\%)$ (irreversible work)
3.50	9159	21 787	4593.1	611.3	586	1000	42.8
4.13	17 384	16 983	5498.5	540.8	533	860	23.4
4.46	20 959	13 912	5622.2	496.2	497	770	16.3
4.83	22 792	10 868	5363.8	441.4	448	674	11.9
5.05	23 841	9318	5262.6	406.7	413	613	10.7
5.49	24 170	6113	4719.7	331.5	341	491	6.71
5.94	21 503	3399	3780.9	247.8	256	359	4.25
6.41	15 896	1318	2538.5	154.0	159	215	2.31
6.86	6700	198.5	985.7	58.54	57.0	76.7	0.92
6.98	4441	57.1	638.8	31.17	28.5	38.8	0.40

[a] Initial observed flux penetration.

transitions are made at several temperatures, this assumption is not necessary.

To complete the analysis, the thermodynamic relation between the entropy difference and the critical field is substituted into Eq. (13)

$$-T\frac{d(H_c^2/8\pi)}{dT}+\frac{H_c^2}{8\pi}=\Delta U. \tag{14}$$

With some manipulation, Eq. (14) can be integrated to obtain the critical field and the entropy difference

$$\frac{H_c^2}{8\pi}=T\int_T^{T_c}\frac{\Delta U}{T^2}dT, \tag{15}$$

$$\Delta S=\frac{\Delta U}{T}-\int_T^{T_c}\frac{\Delta U}{T^2}dT. \tag{16}$$

The results of this kind of analysis applied to the measurements on the $Pb_{0.96}Tl_{0.04}$ sample are presented in Table IV. The heat added during the transition is ΔQ, ΔW is the magnetic work done on the sample, and ΔU of Eq. (16) is their sum. Once ΔS is calculated by performing the integral indicated in Eq. (16), the entropy added as irreversible work can be calculated by subtracting $\Delta Q/T$ from ΔS. The result of this is shown in the last column of Table IV. This analysis indicated that the results of S versus B in Fig. 2 (data near T_c) are dependable with a small loss of entropy ($<2.3\%$) due to the performance of irreversible work. It is also evident from studying this column that this kind of experiment should be performed near T_c, where the work performed (reversible or not) makes a relatively small contribution to the change in internal energy. This advice also follows from the theoretical expectation that near T_c, the work done in an isothermal transition goes to zero as the second power of $(1-t)$, whereas, the latent heat goes to zero as the first power.

The thermodynamic critical field H_c calculated from Eq. (15) and tabulated in Table IV is very nearly parabolic in T. The values of H_{c1} were determined from the strip chart recording of dB/dt as the magnetic field at which dB/dt first rose above the zero noise level. These values are not reliable in this case since many of them are higher than the thermodynamic critical field. The values of H_{c2} were determined as the magnetic field at which there was an abrupt decrease of the rate in which flux penetrated the sample. The values of H_{c2} at 4K reported here for 4% Tl in Pb are consistent with previous observations[11,21,22] for Pb-Tl alloys near this concentration.

The parameter κ_1 was determined from $\kappa_1=H_{c2}/(\sqrt{2}H_c)$. The parameter κ_2 was determined in three different ways: (i) from the slope of the magnetization curve near H_{c2} and Eq. (4); (ii) by assuming that the entropy of the mixed state varied linearly with B from

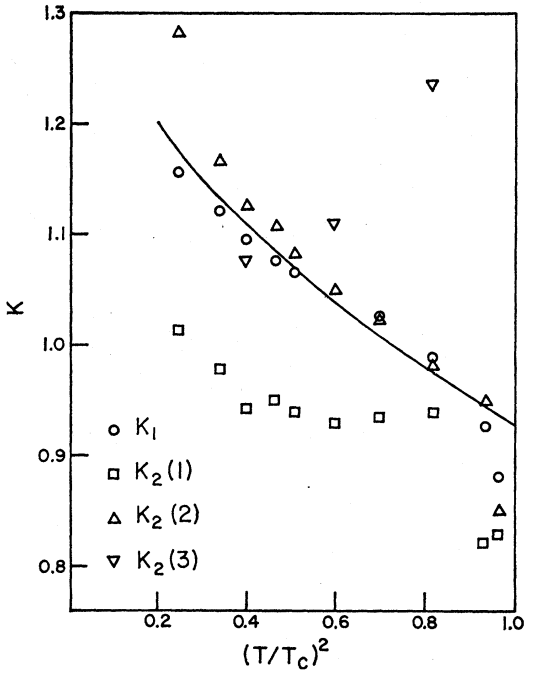

FIG. 5. Temperature dependence of κ_1 and κ_2 determined from (a) slope of the magnetization curve, (b) $(S_n-S_s)/H_{c2}$, (c) ΔC_B at H_{c2}. The solid line shows the temperature dependence $(1+t^2)^{-1/2}$.

[21] J. D. Livingston, Phys. Rev. 129, 1943 (1963).
[22] J. L. Harden and V. Arp, Cryogenics 3, 105 (1963).

TABLE V. Thermodynamic parameters for $In_{0.88}Sn_{0.12}$. $T_c = 5.03$ K.

T (K)	ΔQ (erg/cm³)	ΔW (erg/cm³)	ΔS (erg/cm³ K)	H_c (Oe)	$\Delta S_I/\Delta S(\%)$ (irreversible)	H_{c2} (Oe)	κ_1	κ_2 (magnetization)
3.43	6613	5150	2680	253.0	28.2	562	1.570	1.098
4.19	6562	1541	1742	140.2	10.4	292	1.474	1.086
4.49	4937	680	1177	92.0	6.5	192	1.476	1.076

H_{c1} to H_{c2} in which case $(\partial S/\partial B)_T = \Delta S/H_{c2}$ and Eq. (7); and (iii) from the measured discontinuity in C_B at H_{c2} and Eq. (9). These results are all presented in Fig. 5. Of the three possible methods for determining κ_2, the second one is probably the most accurate. The entropy versus B is observed to be a straight line from H_{c1} to H_{c2} near T_c where very little influence is possible from the irreversibility of the sample. It is also a straight line at temperatures where less than 20% of the entropy is added in the form of irreversible work; therefore, the assumption that $(\partial S/\partial B)_T = \Delta S/H_{c2}$ throughout the mixed state of this sample for any temperature is plausible. At any rate, the second method is certainly the most accurate near T_c.

A temperature dependence of $[2/(1+t^2)]^{1/2}$ given by Bardeen[23] best fit the experimental values of κ_1 and κ_2(2). This was also found to be the case for vanadium as measured by Radebaugh and Keesom.[8] Our values of κ_2 are within about 2% of κ_1 from T_c down to $(T/T_c)^2 = 0.4$. This is consistent with the theoretical prediction[24] that $\kappa_1 \simeq \kappa_2$ in the case of small mean free path of the electrons.

It should be pointed out that the rapid drop of κ_1 near T_c was also observed in vanadium.[8] However, it occurs for both κ_1 and κ_2 here, and it is more pronounced than that observed in vanadium.

The values of κ_2 determined from the slope of the magnetization curve are all too low as can be expected from the irreversibility of the sample.[9] The values of κ_2 determined by the discontinuity in C_B at H_{c2} are not very accurate at high temperatures, but as the lattice contribution decreases at lower temperatures the values approach those determined from the entropy measurements.

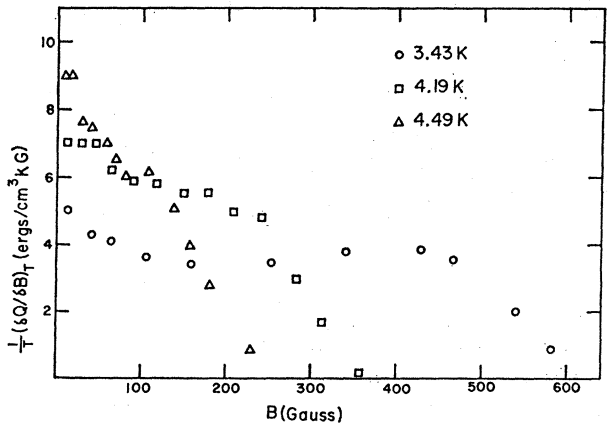

FIG. 6. Rate of change of externally supplied entropy in the mixed state of $In_{0.88}Sn_{0.12}$.

Another type-II sample was prepared and measured. This was $In_{0.88}Sn_{0.12}$. Its reversibility as judged by the remanence was about a factor of 4 worse than the $Pb_{0.96}Tl_{0.04}$ sample. The remanence of the $In_{0.88}Sn_{0.12}$ sample at 4.19K was 0.47. The entropy changes and flux changes in the mixed state were measured by using technique II, described previously. Figure 6 shows $(1/T)(\delta Q/\delta B)_T$ plotted versus B for three temperatures. The only curve which approximates the results obtained for $Pb_{0.96}Tl_{0.04}$ is at the lowest temperature (3.43K). These data are very difficult to understand and are presented primarily for comparison with the heat-capacity data which appear in Sec. V. However, the thermodynamic analysis of Eqs. (15) and (16) can be applied to the $In_{0.88}Sn_{0.12}$ data. Table V contains the results of this effort. H_{c2} in Table V was determined by extrapolating a straight line portion of the magnetization curve to zero magnetization.

V. SPECIFIC HEAT AT CONSTANT B

An entirely different method was tried to obtain information on the entropy of the mixed state of a type-II superconductor. This was to measure the specific heat at constant magnetic induction C_B. This has the potential of being a very powerful method because there is no production of entropy due to irreversible motion of flux. In fact, the flux in the sample is stationary during this measurement.

In the measurement of C_B, the irreversibility of the sample was used to advantage. The applied field was increased isothermally until the desired value of B, as determined from a previously measured magnetization curve, was obtained. The magnetization could be reproduced to within about 0.5% as measured by the ballistic galvanometer so that for the purposes of this measurement the uncertainty in B was negligible. The applied field was then decreased while the output of the pick-up coil was monitored to verify that B did not change. The heat leak at the set tempreature was measured. Additional heat was applied and the rate of change of temperature was measured. After the sample had warmed by about 0.04 K, the heat leak was again

[23] J. Bardeen, Phys. Rev. 94, 554 (1954).
[24] C. Caroli, M. Cyrot, and P. G. de Gennes, Solid State Commun. 4, 17 (1966).

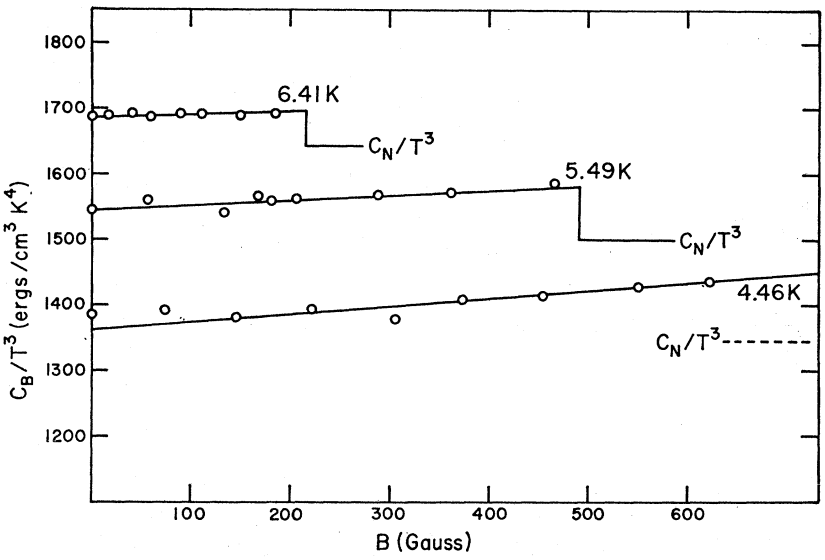

FIG. 7. Specific heat at constant magnetic induction in the mixed state of $Pb_{0.96}Tl_{0.04}$. The solid lines were calculated from the isothermal entropy data.

measured. It was assumed that the heat leak changed linearly with temperature between the lower and higher temperatures. The output of the pick-up coil was monitored while the sample was heated and if any evidence of flux motion appeared the data were discarded. If the applied field was decreased enough after establishing the desired B in the sample, there was never any detectable motion of flux as the sample was heated the few hundredths of a degree necessary to measure C_B.

The results of these measurements for $Pb_{0.96}Tl_{0.04}$ are the data points shown in Fig. 7. The specific heat increases nearly linearly as B increases in the mixed state, and then it drops to the normal state value. There are no spectacular effects in the mixed state due to the interaction of fluxoids. The magnitude of the heat capacity is consistent with the heat capacity of lead.[25]

The results of the measurements of C_B and the entropy of the mixed state for $Pb_{0.96}Tl_{0.04}$ can be shown to be consistent with one another. The derivative $(\partial S/\partial B)_T$ was found to be independent of B for temperatures near T_c where negligible irreversible work was performed. The further observation that $(\delta Q/\delta B)_T$ was independent of B at temperatures down to 4.46 K encourages the assumption that $(\partial S/\partial B)_T$ is independent of B over this same range of T. This is a profitable assumption because $(\partial S/\partial B)_T$ is then simply $\Delta S/H_{c2}$ where ΔS is the total entropy difference between the superconducting and the normal states. This entropy difference has been extracted from the data in spite of the production of entropy through irreversible work and is presented in Table IV. The empirical expression for $\Delta S/H_{c2}$ for temperatures above 4.46 K is $-3.27+2.35T$ in Gaussian units. Thus, $S_m-S_s=(\Delta S/H_{c2})B=(-3.27+2.35T)B$; and $(C_B-C_s)/T=2.35B$. The solid lines of Fig. 7 represent this expression, and the agreement with the specific-heat data is gratifying.

The discontinuity of C_B at H_{c2} can be compared with the theoretical prediction of Eq. (9). Figure 7 has three points which were obtained from Eq. (9)—the points $\kappa_2(3)$. While this is not an accurate method for evaluating κ_2, the results do have the correct magnitude. Unfortunately, the discontinuity in the specific heat at H_{c2} is only about 3% of the total specific heat at the highest temperature so that the precision is low.

The specific heat at constant magnetic induction was also measured for the $In_{0.88}Sn_{0.12}$ sample. These results are shown in Fig. 8. The specific heat and $(\partial S/\partial B)_T$ are related thermodynamically, but the observed behavior is irregular and data were taken at too few temperatures to make a meaningful analysis. However, it can be qualitatively observed that C_B/T^3 increases gradually as B increases and then begins to decrease to the normal state value beginning near the B value where $(1/T)(\delta Q/\delta B)_T$ drops sharply.

The general behavior of C_B is consistent with the expectations of the theory and is similar to that of the $Pb_{0.96}Tl_{0.04}$.

VI. SUMMARY

The entropy of the mixed state of type-II superconductors has been investigated by two different methods. The first was a direct calorimetric measurement of the heat added to hold the sample at a constant temperature as the magnetic induction was increased. From this experiment, $(\delta Q/\delta B)_T$ was obtained. The second measurement was the specific heat at constant magnetic induction $T(\partial S/\partial T)_B$. For a $Pb_{0.96}Tl_{0.04}$ sample the conclusion was that $(\partial S/\partial B)_T$ in the mixed state is constant from H_{c1} to H_{c2} for any given temperature above 4.46 K. This means that the interaction

[25] M. Horowitz, A. A. Silvidi, S. F. Malaker, and J. G. Daunt, Phys. Rev. 88, 1182 (1952).

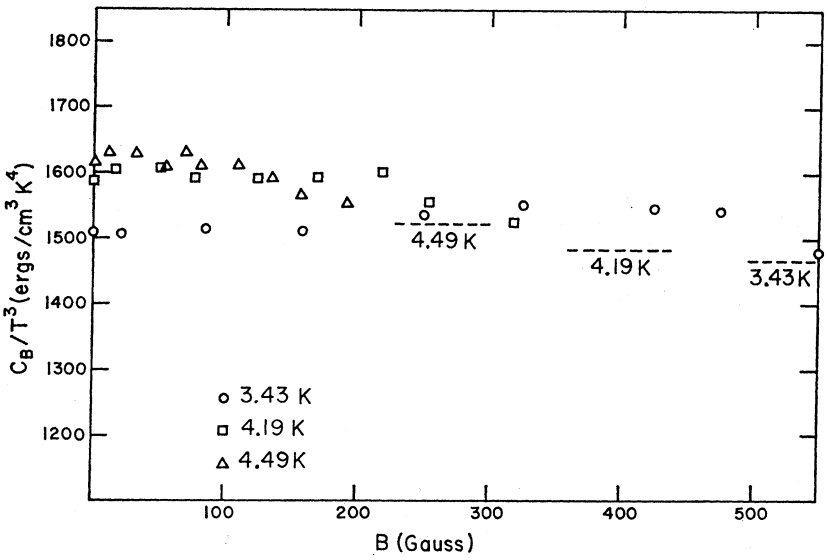

FIG. 8. Specific heat at constant magnetic induction in the mixed state of $In_{0.88}Sn_{0.12}$. The dashed lines are normal state values.

energy of the fluxoids does not change rapidly enough with temperature in this sample to influence the entropy significantly. The measurement of $(\partial S/\partial T)_B$, though free of any influence from the irreversibility of the sample was not as definitive as the first measurement, but the two measurements were consistent. This measurement of $(\partial S/\partial T)_B$ did prove, however, that there is nothing anomalous about the specific heat of the mixed state of this type-II superconductor if it is measured at constant magnetic induction rather than at constant applied field. The specific heat at constant magnetic induction plotted as a function of B at a given temperature rises linearly from the superconducting value until it drops discontinuously to the normal state value at H_{c2}.

Another type-II sample was investigated, but it was of such poor quality (reversibility) that no general conclusions should be drawn from it. Pure Sn and Pb samples were also studied with the expected conclusion that $(\partial S/\partial B)_T$ is a constant for a given temperature throughout the intermediate state.

Another contribution of this paper is a technique for determining the thermodynamic critical field for an irreversible sample which avoids reliance on any assumed temperature dependence of H_c (i.e., parabolic). It requires a simultaneous measurement of the heat added to the sample and the magnetic work done on the sample in making an isothermal transition from the superconducting to the normal state. This information was obtained in the course of our measurement of $(\delta Q/\delta B)_T$.

The thermodynamic critical field determined in this way was used with the directly measured H_{c2} to calculate the parameter κ_1. The most accurate determination of κ_2 was from $(\partial S/\partial B)_T$ as determined from $(S_n-S_s)/H_{c2}$. These two parameters are nearly equal for $Pb_{0.96}Tl_{0.04}$ with a temperature dependence of $[2/(1+t^2)]^{1/2}$. The value of κ_2 was slightly higher than κ_1, and they both dropped sharply near T_c. This drop could be caused by a nonhomogeneous sample; however, such a drop in κ_1 has also been observed independently in pure vanadium.

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