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Thermodynamic Consistency of Magnetic and Calorimetric Measurements on Superconductors

Abstract: Comparison of the entropy and specific heats of normal and superconducting tin and indium as computed from critical field and calorimetric measurements shows excellent consistency. Salient features of the comparison are briefly summarized. Some implications of the recently reported specific heat anomaly for indium are discussed.

From the thermodynamic reversibility of the superconducting transition it follows that the magnetic and calorimetric properties of a superconductor are related by the equation[1]

$$\Delta S = S_n - S_s = -(VH_c/4\pi)(dH_c/dT)\,, \tag{1}$$

where S_n and S_s are the molar entropies in the normal and superconducting states, V is the molar volume, H_c is the critical magnetic field, and T is the absolute temperature. The accuracy with which this equation applies to available experimental data has been examined to establish the conditions of measurement most likely to yield the true thermodynamic properties of a superconductor. Because of the completeness and excellence of the available calorimetric data, primary attention was given to the elements tin and indium. Detailed comparisons were made of entropy and specific heat values from both magnetic[2] and calorimetric data[3,4] in the range from T_c to about 1°K. Preliminary data from measurements extending to about 0.3°K have also been considered.

Calculation of the thermodynamic properties from H_c data has been done in terms of the function[2]

$$D(t) = h - (1 - t^2)\,, \tag{2}$$

where $h = H_c/H_0$ and $t = T/T_c$. This function describes the deviation of the experimental values of H_c from those expected at the same temperature according to the "parabolic law". Values of $D(t)$ are obtained directly from H_c measurements with a precision of about 5%. Since $D(t)$ itself amounts to only about 2 to 3% of H_0, H_c measurements of high precision are required for this type of analysis. Curves giving $D(t)$ values for several superconducting elements are shown in Fig. 1.

A straightforward thermodynamic argument shows that $D(t)$ may be regarded as specifying a small perturbation in the temperature dependence of ΔS^p, where ΔS^p is the entropy difference corresponding to the fiducial parabolic H_c curve assumed in calculating $D(t)$. The relationship is illustrated in Fig. 2, where the dotted curve represents the temperature dependence of ΔS^p. The solid curves show the qualitative variation of ΔS with T for two extreme cases; tin, which shows a negative $D(t)$, and lead, for which $D(t)$ is positive. Detailed analysis shows that, to a good approximation,

$$D(t) \simeq (4\pi/VH_0{}^2)(1 - t^2)^{-1} \times \int_T^{T_c} [\Delta S(T) - \Delta S^p(T)]\, dT\,. \tag{3}$$

The factor which dominates the behavior of $D(t)$ is the integral in (3) whose graphical significance is shown by the shaded area in Fig. 2 (for the case of tin). This is a useful general relation tó invoke in correlating qualitative tendencies of the entropy with the observed behavior of $D(t)$.

Values of the entropy difference are calculated from the relation

$$\Delta S = (VH_0{}^2/2\pi T_c)(1 - D')ht\,, \tag{4}$$

which follows from (1) and (2) and in which $D' = dD(t)/d(t^2)$. Precise values of ΔS are conveniently obtained from (4) by differentiating an experimental plot of $D(t)$ vs t^2. The resulting values are more sensitive and accurate than values deduced from calorimetric data. The specific heat values (which require a second temperature differentiation) appear to be of about the same precision as the best published

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calorimetric data. Details of these calculations will be published later.

In general, the agreement between magnetic and calorimetric measurements on tin and indium is remarkably good. With but few exceptions, the small differences in thermodynamic properties are attributable to the experimental uncertainty in the basic data (about $\pm 1\%$ for the calorimetric data and about $\pm 0.1\%$ for most of the magnetic data). In addition to certifying the precision of the present data for tin and indium, this agreement should raise confidence in the reliability of critical field measurements in cases where calorimetric results of high precision are not available. The following specific points may be of interest.

1. *Properties of tin:* Above about 2°K, the calorimetric values of Bryant and Keesom[4] are appreciably larger than the corresponding results of Corak and Satterthwaite.[3] The difference (as much as 7 to 8% in places) is beyond experimental error and is apparently attributable to real differences in the properties of the measured specimens. In this temperature range our magnetic data[2] are in best agreement with the results of Corak and Satterthwaite.

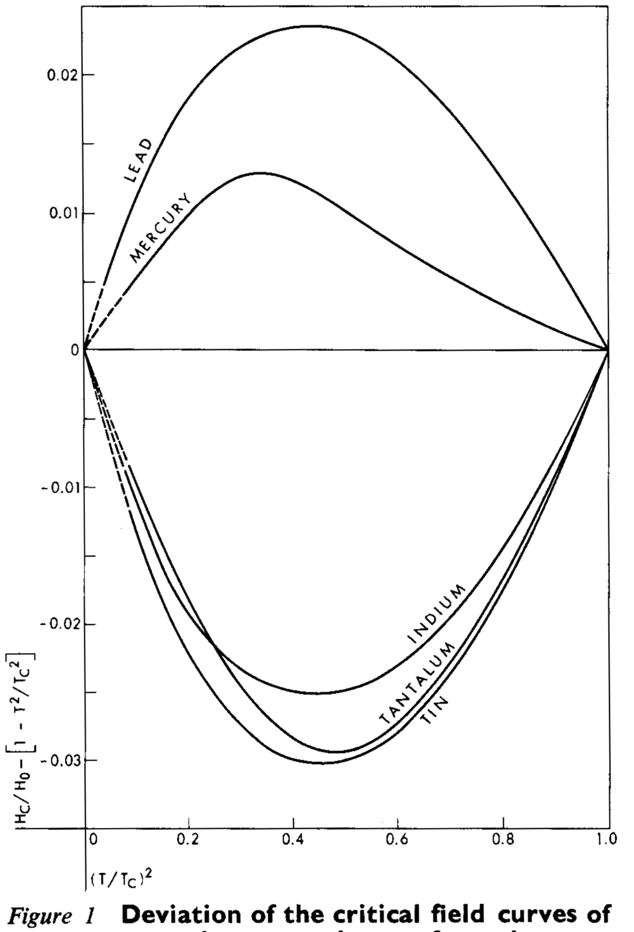

Figure 1 **Deviation of the critical field curves of several superconductors from the parabolic law.** *More recent measurements of H_0 show that the amplitudes of $D(t)$ for Sn and In are somewhat smaller than given here. However, it can be shown that ΔS values computed from Eq. (4) are insensitive to the value of H_0 so long as the analysis is restricted to the temperature range where direct measurements exist.*

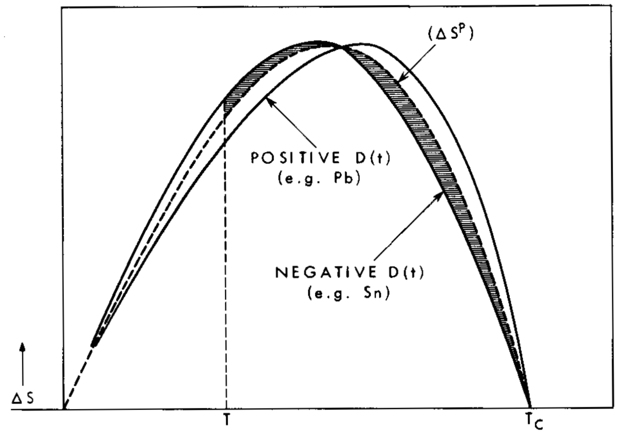

Figure 2 **Effect of $D(t)$ in the temperature dependence of ΔS.** *The dotted curve indicates the temperature dependence of the entropy difference expected for a parabolic critical field curve. The displacement of the solid curves relative to the dotted curve (ΔS^P) has been exaggerated to show the included area more distinctly.*

Below 2°K there are no clearly significant differences between the thermodynamic properties as deduced magnetically or calorimetrically. Comparison of preliminary magnetic data[5] below 1°K with smoothed calorimetric data of Bryant and Keesom is shown in Fig. 3. Despite a small difference in the value of γ (the temperature coefficient of the normal electronic specific heat), agreement is considered satisfactory.

The usual assumption that the lattice specific heat is unaffected by the superconducting transition seems to be valid in tin. Using this assumption, ΔS may be resolved into the normal and superconducting electronic entropies, S_{en} and S_{es}. Values of S_{es} computed from magnetic data show very close agreement with the BCS thermodynamic functions as tabulated by Mühlschlegel.[6]

2. *Properties of indium:* Magnetically calculated values of ΔS are in very good agreement with smoothed calorimetric data of Bryant and Keesom over the range from 1.5 to 3.4°K. The greatest difference amounts to about 1% of the maximum value of ΔS.

The low temperature ΔS values for indium are of special interest at present as a result of the finding of Bryant and Keesom which indicates a lower lattice specific heat in the superconducting than in the normal phase. The present experimental situation is illustrated in Fig. 4, where the calorimetric data for two indium specimens are shown on a plot of C/T vs T.[7] The solid curve through the upper (normal) points of Fig. 4 is of the form

$$C/T = \gamma + (1.944/\theta_D{}^3)T^2 \text{ (millij/mol deg}^2) , \qquad (5)$$

where $\gamma = 1.60$ millij/mol deg^2 and θ_D (the Debye temperature) = 108.5°K, these being averages of the values reported for two specimens. The lower solid curve gives the lattice contribution to (5) (with the same θ_D), and represents the limiting curve to which the superconducting data would ordinarily be expected to converge as $T \rightarrow 0$°K. The Bryant and Keesom anomaly is shown by the tendency of the experimental points to fall beneath the lower solid curve below about 0.8°K.[8]

The ΔS values derived from critical field data give the area between the C_n/T and C_s/T curves from 0°K to the temperature of observation. In Fig. 4, ΔS at $T = 0.5$°K is shown by the shaded area. As drawn in Fig. 4, ΔS(0.5°K) is the value expected if θ_D were unchanged by the superconducting transition, since the shaded area lies between the two solid curves which are parallel parabolas (separated by the "distance", γ). If θ_D is invariant, $\Delta S(T)$ rises from 0°K as a linear function of T with a slope equal to γ. However, the data indicate a small additional contribution to ΔS corresponding to the area between the locus of the experimental C_s/T values and the lower solid curve. Thus the calorimetric data indicate that $\Delta S(T)$ should rise from 0°K with a slope somewhat larger than γ, as shown by the solid curve for indium in Fig. 3.

Depending upon one's theoretical bias as to the origin of this effect[9] it is possible to ascribe various temperature dependences to the presumed lattice contribution. However, the effect itself is so small that attempts to determine its temperature dependence from the present experimental data are probably premature.

Preliminary magnetic data below 1°K do, in fact, yield a somewhat larger value of γ than that reported by Bryant and Keesom. A few tentative points calculated from critical field measurements on indium by Finnemore are shown in Fig. 3. There is reasonable agreement with the solid curve derived by integration of the smoothed calorimetric data. The dotted line gives the entropy contribution of the normal electrons as computed from the calorimetrically determined γ. The difference between the dotted and heavy solid curves for indium in Fig. 3 is another way of displaying the Bryant and Keesom anomaly. It will be recognized that the magnitude of this anomaly depends critically on the determination of γ.

We believe it unjustified at present to regard the agreement for indium shown in Fig. 3 as an unqualified confirmation of the Bryant and Keesom anomaly. While it is gratifying to find that independent measurements in this temperature range show such good thermodynamic consistency, it must be emphasized that evidence of an anomalous lattice contribution is

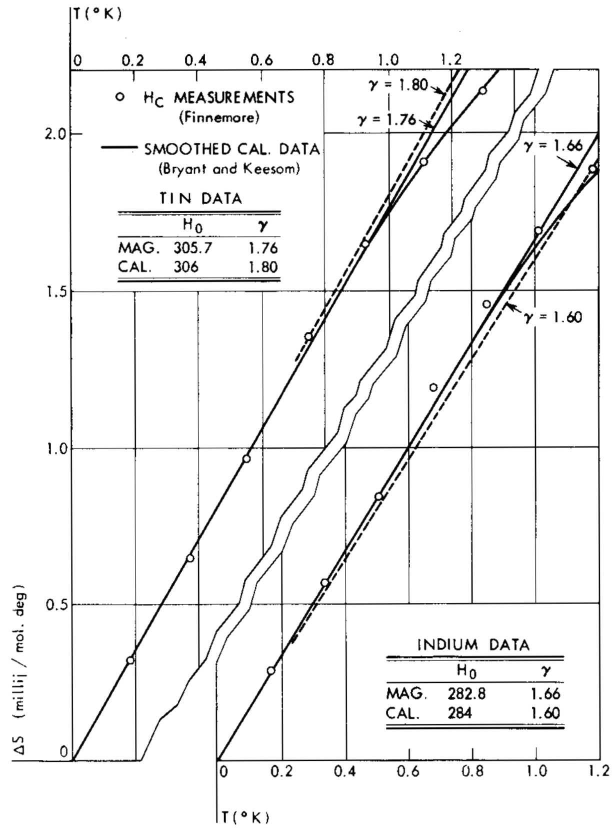

Figure 3 **Comparison of calorimetric and magnetic data for measurements below 1°K.** *Units of numerical entries are H_0 (gauss) and γ (millij/mol deg^2). Points which give magnetic results are preliminary measurements.*

still very close to the limit of precision of the experiments which show it. However, in view of its fundamental implications it is to be hoped that experimental efforts to confirm the anomaly will match the already manifest zeal of the theoreticians to explain it.

3. *Laws of corresponding states:* The original Bardeen-Cooper-Schrieffer theory[10] (hereafter BCS) predicts a law of corresponding states according to which the H_c vs T curves of all superconductors are described by a universal function of the reduced coordinates, h and t. Accurate measurements of $D(t)$ for various elements reveal substantial departures from this behavior[2] as shown in Fig. 1. It thus seems reasonably certain that a law of corresponding states in terms of only h and t does not apply for real superconductors.

In view of this situation it is noteworthy that experiments which give information about the superconducting energy gap and the density of states are so well described by the BCS theory. The experimental situation has recently been described in an article by Giaever and Megerle[11] where (among other things) it

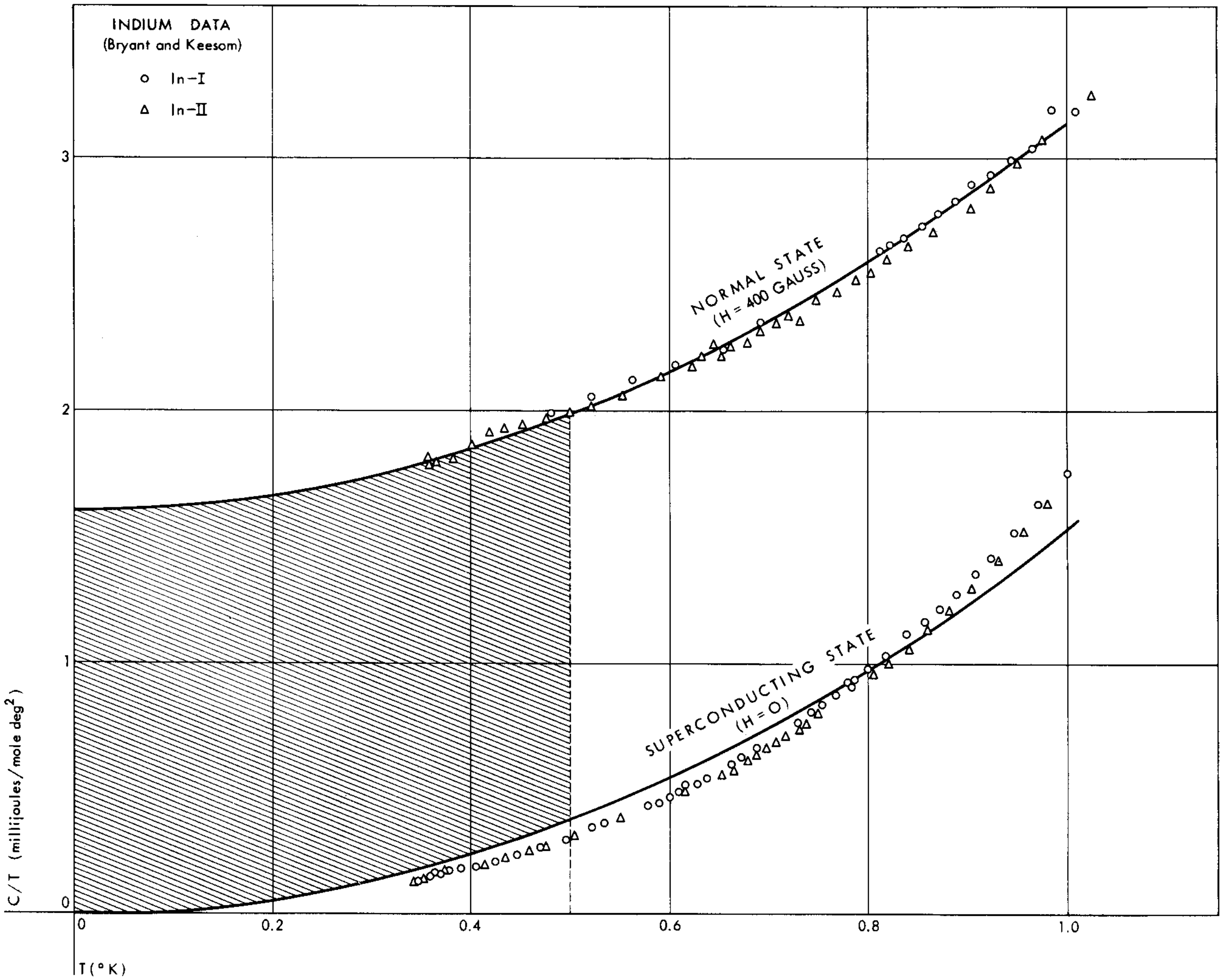

Figure 4 **Calorimetric data of Bryant and Keesom for two indium specimens.** *Upper solid curve gives the best analytic fit to the normal state measurements (i.e., Eq. (5)). Lower solid curve gives the lattice contribution in the* normal *state. Values of H give the applied magnetic field in which the measurements were made.*

is reported that, except for the magnitude, $E_g(0)$, of the energy gap at 0°K, there seem to be no relative differences between tin and lead. (In suitably reduced units both the temperature dependence of E_g and the density of states above the gap follow the BCS predictions for both elements.)

Theoretical calculations by Swihart[12] show reasonable correlation between the strength of the interaction potential and the size of $E_g(0)$. However, the corresponding variation in $D(t)$, while of correct sign, is much smaller than that observed experimentally. The situation may be summarized by saying that presently known deviations from a law of corresponding states applicable to the fundamental electronic properties appear insufficient to account for the deviations in thermodynamic properties revealed by critical field measurements. Two possibilities occur for reconciling this apparent discrepancy.

At the present time the sensitivity of ΔS to the form of $E_g(T)$ and the density of states function has not been thoroughly examined. Therefore, it is not entirely clear that present experimental determinations of these electronic parameters are of sufficient accuracy to rule out changes in the superconducting electronic entropy of the magnitude indicated by critical field measurements. Thus subsequent theoretical work may reveal the variation of $D(t)$ to be of entirely electronic origin.

A somewhat conjectural alternative is suggested by the Bryant and Keesom anomaly in indium discussed above. Assuming the authenticity of this effect, it appears that, for some superconductors, the lattice entropy gives a *positive* contribution to $\Delta S(= S_n - S_s)$ resulting in distortion of the temperature dependence from that predicted by the BCS theory (and approximately obeyed by tin). Analysis of the thermodynamic significance of the $D(t)$ curves for In, Hg and Pb shows[2] that the possibility of a positive lattice contribution to ΔS is consistent with the observed behavior. To show this we assume that

$$\Delta S = \Delta S_e + \Delta S_g \,, \tag{6}$$

where ΔS_e and ΔS_g represent independent electronic and lattice contributions. It is further assumed that ΔS_e has the BCS theoretical temperature dependence.[13] Under these assumptions, analysis of the experimental ΔS curves shows that the ΔS_g contribution must be positive. It may be further shown that, for the sequence In, Hg and Pb (arranged in order of increasing values of T_c/θ_D or, equivalently, in order of increasingly positive $D(t)$ with respect to tin), the relative size of the contribution of ΔS_g to ΔS increases systematically.

It should be emphasized that the foregoing argument shows only that the hypothesis of a positive lattice contribution to ΔS is consistent with present information. Experimental confirmation by calorimetric measurements will be difficult for the cases of Hg and Pb. Although the relative size of ΔS_g should (in this interpretation) be largest for Hg and Pb, it is never more than a fraction of ΔS. Unfortunately both Hg and Pb have very small values of θ_D and, therefore, very large lattice specific heats over most of the superconducting temperature range. As a result only small apparent changes in θ_D for these elements would suffice to explain the $D(t)$ data. A rough quantitative calculation based on the assumptions of the previous paragraph indicates that a 1% increase in θ_D for Pb in the superconducting transition would explain its positive $D(t)$. A change of this magnitude is about the limit of precision of the best calorimetric data reported thus far.

Acknowledgments

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