

Thermodynamic Consistency of Critical Field and Specific Heat Data for Superconducting Sn and In†

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The accuracy with which recent experimental data satisfy the thermodynamic relations between the magnetic and calorimetric properties of a superconductor is considered in detail. A convenient and sensitive procedure for calculating the entropy and specific heat differences from critical field data is described. The resulting values are compared with corresponding quantities derived from published calorimetric measurements. Agreement is good over most of the temperature range of the observations. It is concluded that critical field measurements are capable of yielding the changes in the thermodynamic properties at the transition with an accuracy at least equal to that achieved so far in calorimetric work.

INTRODUCTION

EQUILIBRIUM thermodynamic theory gives the following relation between the calorimetric and magnetic properties of a superconductor¹:

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

where S_n and S_s are the molar entropies in the normal and superconducting state, V is the molar volume, H_c is the critical magnetic field, and T is the absolute temperature. A further useful relation derived from Eq. (1) is

$$\Delta C = C_n - C_s = -\frac{VT}{4\pi} \frac{d}{dT} \left(\frac{dH_c}{dT} \right), \quad (2)$$

where C_n and C_s are the molar specific heats in the normal and superconducting states. The validity of these relations depends on the thermodynamic reversibility of the superconducting transition. As a matter of principle at least, this fact has seemed very firmly established since the discovery of the Meissner-Ochsenfeld effect.^{2,3}

The relationship specified by Eqs. (1) and (2) between the results of magnetic and calorimetric measurements can be visualized graphically in a plot of C/T vs T where, since $dS = CdT/T$, areas represent entropies. A plot of this type for the case of tin is given in Fig. 1. The curves C_n/T and C_s/T may be plotted directly from calorimetric data. The shaded area between C_n/T and C_s/T and from 0°K to T gives $\Delta S(T)$, the value computed from H_c data via (1). [For illustration we show the area included between 0 and 2.75°K, i.e., $\Delta S(2.75^\circ\text{K})$.] Thus calorimetric data separately fix the positions of the C/T curves while magnetic data provide a measure of their separation. It is noteworthy that the lower limit of the integral in Fig. 1 is 0°K. This circumstance permits some useful deductions concerning the

behavior of C_s and C_n below the lowest temperature of observation.

The dashed curve in Fig. 1 gives the lattice contribution to the specific heat C_g and is approximately to scale for the case of tin. This contribution is common to both C_n and C_s but its relative magnitude in comparison with ΔC varies greatly among the superconducting elements.⁴ Thus indium, despite its close similarity to tin in electronic properties, has a C_g at T_c which is about six times the magnitude of ΔC . The larger the relative contribution of C_g , the more difficult it becomes to make precise calorimetric measurements of ΔC because of experimental uncertainty in the individual determina-

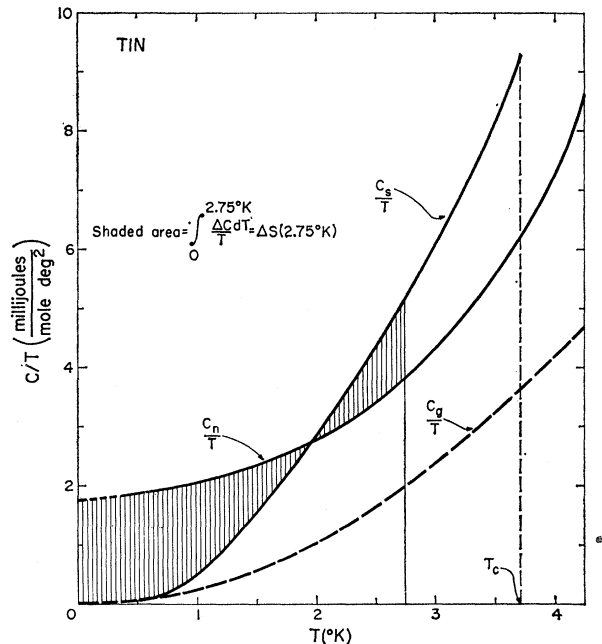


FIG. 1. The relation between the indications of magnetic and calorimetric measurements. Values apply to the case of tin. The lattice contribution, C_g , is calculated assuming a Debye temperature of 195°K.

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¹ D. Shoenberg, *Superconductivity* (Cambridge University Press, New York, 1952), Chap. III.

² W. Meissner and R. Ochsenfeld, *Naturwissenschaften* **21**, 787 (1933).

³ C. J. Gorter and H. B. G. Casimir, *Physica* **1**, 305 (1934).

⁴ A tabulation of 13 superconducting elements is given by W. S. Corak, B. B. Goodman, C. B. Satterthwaite, and A. Wexler, *Phys. Rev.* **102**, 656 (1956).

tions of C_s and C_n . For the extreme (but important) cases of mercury and lead C_g is so large that the error in C_s and C_n is comparable with ΔC itself. Magnetic measurements do not encounter this difficulty since they give ΔC without regard to the relative magnitude of the lattice contribution.

Realization of this theoretical advantage in practice requires demonstration that the H_c values which can be measured with high precision do, in fact, accurately reflect the true thermodynamic H_c for the superconductor. Deviations from Eqs. (1) or (2) in the comparison of independently measured calorimetric and magnetic data have been reported in some cases. However, such deviations must be ascribed to experimental inaccuracy or to departures from conditions of thermodynamic reversibility. Unless the generally accepted interpretation of the Meissner-Ochsenfeld effect is abandoned, observed deviations from Eqs. (1) or (2) cannot be construed as challenging their fundamental validity.

To date most published comparisons of magnetic and calorimetric data have been restricted to the magnitude of the specific heat discontinuity at T_c . In favorable cases agreement of the order of 10% has been usual, although a puzzling discrepancy of about 20% occurs for Al.⁵ While this is a reasonable confirmation of the fundamental reversibility of the superconducting transition, it is less convincing as a demonstration that calorimetric quantities can be reliably calculated from H_c measurements alone. This consideration is a matter of experimental significance since, for the reason explained above, the differences in thermodynamic properties deduced from critical field measurements are considerably more precise than corresponding values from direct calorimetric measurements, at least in the case of certain important superconductors.

In this article we present the results of a careful comparison between magnetic and calorimetric data for the elements, Sn and In. These elements have been chosen since accurate numerical data from both types of measurement are available. It will be shown that the thermodynamic consistency between the two types of measurement is, in general, of the order of 1% and limited mainly by the precision of the calorimetric data. Certain calculational procedures are described which take advantage of the high precision possible in critical field measurements.

EXPERIMENTAL DATA

The calculations and comparisons to be described here are based on tabulations of published experimental data. The critical field values⁶ are considered accurate over most of the temperature range to about $\pm 0.1\%$ or better. While not in disagreement with other reported

critical field data, both the absolute accuracy and the experimental scatter have been improved.

Calorimetric data from two laboratories have been used.^{7,8} The precision in both cases is reported as about $\pm 1\%$, a value consistent with the scatter of the experimental points in each case. As will be seen later, the absolute precision is somewhat less certain since, above 2°K, differences of several percent occur in comparing the data of the two groups.

The critical field data and also the results of Bryant and Keesom are based on the T_{58} helium vapor pressure scale.⁹ This scale was adopted several years after the work of Corak and Satterthwaite who reported their results in terms of the older T_{48} scale and also a provisional scale designated as T_w . After some examination it was concluded that the T_w scale is sufficiently close to the T_{58} scale that any attempted corrections would give changes smaller than the estimated random uncertainty of the measurements. Thus, the tabulated values of T_w were used without alteration.

The reader concerned with the experimental procedures should consult the original articles and references cited there. The present calculations accept the values of H_c , C_n , and C_s as reported.

THERMODYNAMIC CALCULATIONS

A. Tactical Considerations

In principle Eqs. (1) and (2) permit the comparison of magnetic and calorimetric data in terms of any of the three quantities H_c , ΔS , or ΔC . However, in practice these comparisons are not of equal significance because of the difference in precision of the data and the uncertainties associated with the required analysis. For example, comparison of H_c values obtained by integration of specific heat data with directly measured H_c values is relatively inconclusive. In this case the accuracy of the calculated H_c values cannot exceed the precision of the calorimetric data which is, in general, at least an order of magnitude poorer than the precision of direct H_c measurements.

The most exacting comparisons result from conversion of H_c measurements into ΔS or ΔC values. As will be shown later, the precision of H_c measurements enables them to survive two differentiations and still yield ΔC values of precision comparable with that achieved in direct calorimetric observation. From the standpoint of getting the most physical information from H_c data, ΔS is preferable to ΔC since only one differentiation is involved and the entropy function is

⁷ W. S. Corak and C. B. Satterthwaite, Phys. Rev. **102**, 662 (1956).

⁸ C. A. Bryant and P. H. Keesom, Phys. Rev. **123**, 491 (1961). Indium data of comparable precision have been reported by J. R. Clement and E. H. Quinell, Phys. Rev. **92**, 258 (1953). Good agreement exists between the two measurements down to 1.7°K, the lowest temperature reached in the earlier work.

⁹ F. G. Brickwedde, H. van Dyke, M. Durieux, J. R. Clement, and J. K. Logan, J. Research Natl. Bur. Standards **64A**, 1 (1960).

⁵ J. F. Cochran and D. E. Mapother, Phys. Rev. **121**, 1688 (1961).

⁶ R. W. Shaw, D. E. Mapother, and D. C. Hopkins, Phys. Rev. **120**, 88 (1960).

as suitable an object of theoretical attention as the specific heat.

B. Calculations with Critical Field Data

Taking advantage of the precision possible with H_c measurements, a "perturbation" type calculation has been employed to carry out the differentiation into ΔS and ΔC values. The aim is to display the physically significant variations revealed by the H_c measurements and to extract as much information as is compatible with the limitations of experimental accuracy. The philosophy of the calculation is described as follows.

It will be recalled that all superconducting elements deviate by only a few percent from the so-called "parabolic law,"

$$H_c^p(T) = H_0[1 - (T/T_c)^2], \quad (3)$$

where H_0 and T_c are the intercepts of the H_c vs T curve at $T=0^\circ\text{K}$ and $H=0$, respectively. The entropy and specific heat difference functions derivable from Eq. (3) are well known¹ and they will be denoted hereafter by ΔS^p and ΔC^p .¹⁰ Now just as H_c^p gives the major contribution to the true H_c of a real superconductor, so ΔS^p and ΔC^p approximate the true ΔS and ΔC functions. Thus, we may express a desired property $X(T)$ as

$$X(T) = X^p(T) + \delta X, \quad (4)$$

where $X^p(T)$ is the corresponding property assuming the validity of Eq. (3) and δX is a relatively small perturbation.

The present calculations begin by describing $H_c(T)$ in the form of Eq. (4) so that

$$H_c(T) = H_c^p(T) + \delta H_c, \quad (5a)$$

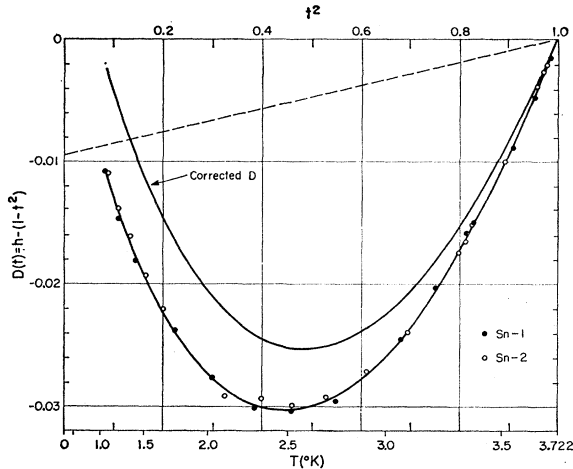


FIG. 2. Deviation function for two tin specimens. Points give data of reference 6 using $H_0=308.6$ gauss, $T_c=3.722^\circ\text{K}$. Derivation of the corrected D curve is discussed in the Appendix. $t \equiv T/T_c$.

¹⁰ The superscript p is used through this work to identify properties derivable from the parabolic temperature dependence of Eq. (3).

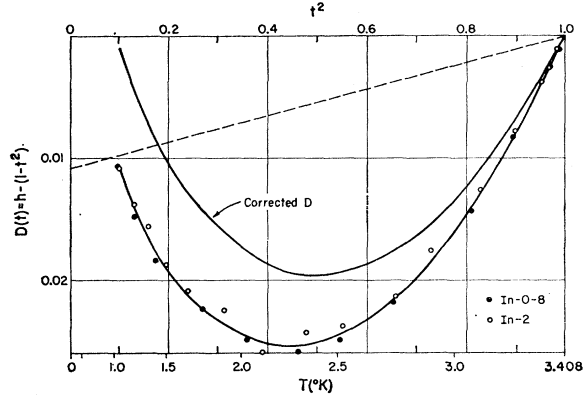


FIG. 3. Deviation function for two indium specimens. Points give data of reference 6 using $H_0=285.7$ gauss, $T_c=3.408^\circ\text{K}$. Derivation of the corrected curve is discussed in the Appendix.

where $H_c(T)$ is the experimental critical field curve and $H_c^p(T)$ is a fiducial parabola having the form of Eq. (3). From Eq. (3) it is seen that $H_c^p(T)$ is defined by the choice of the two constants H_0 and T_c which are determined by extrapolation of the experimental data to the intercepts at $T=0$ and $H=0$, respectively. It is advantageous to express the perturbation term of Eq. (5a) in reduced coordinates, the result being known as the deviation function D where

$$D = (H_c(T)/H_0) - (1 - t^2) = h - (1 - t^2) \quad (5b)$$

and t is the reduced temperature T/T_c .

The separation of Eq. (5a) has a particularly simple interpretation on a plot of H_c vs T^2 since in this case $H_c^p(T)$ appears as a straight line between H_0 and T_c^2 (see Fig. 9). Thus δH in Eq. (5a) or D describe the measured $H_c(T)$ relative to an inclined axis $H_c^p(T)$ whose position is fixed by definition. Since only a subtraction is involved, D provides a highly magnified presentation of the shape of the critical-field curve without distorting or suppressing the experimental scatter in the determination of the individual points. Accordingly, a plot of D values provides a useful initial test of the quality of the data. It proves useful to plot D vs t^2 , and the resulting curve must be smooth enough to permit differentiation in order to justify use of the present analysis. Experimental curves of D vs t^2 for tin and indium are shown in Figs. 2 and 3.¹¹

From Eq. (5b) it is easily shown that

$$dH_c/dT = (2H_0/T_c)(D' - 1)t, \quad (6)$$

where $D' = dD/d(t^2)$ (i.e., the slope of a plot such as Fig. 3 or 4). Substitution of this expression in Eq. (1) gives

$$\Delta S = (VH_0^2/2\pi T_c)(1 - D')ht, \quad (7)$$

¹¹ The "corrected" curves in Figs. 2 and 3 have been shifted to allow for error in the initial estimate of H_0 . Since the procedure for this correction is somewhat involved its discussion will be deferred until the Appendix. There it is shown that error in the initial estimate of H_0 does not affect the accuracy of ΔS and ΔC values derived from D within the range of T where direct measurements are available.

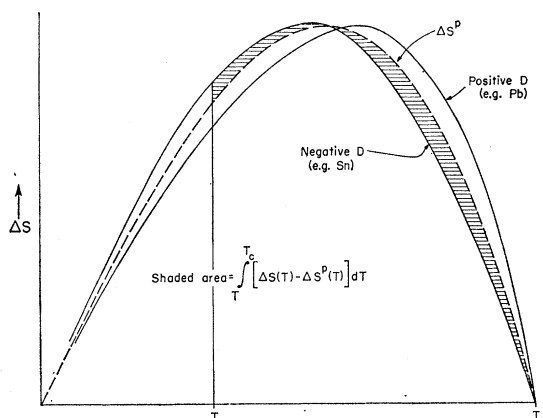


FIG. 4. Graphical interpretation of the significance of the deviation function. Displacement of the ΔS curves relative to ΔS^p is slightly exaggerated for clarity.

which is the relation used in computing the results given here.¹² Values of D' are obtained graphically from large scale versions of Figs. 3 and 4.

There is an alternate method of describing the relation between D and ΔS which is sometimes useful. This relation is most easily derived from integration of Eq. (1) to obtain the general relation

$$[H_c(T)]^2 = \frac{8\pi}{V} \int_T^{T_c} \Delta S(t) dt. \quad (8)$$

A corresponding equation evidently relates H_{c^p} and ΔS^p and subtracting, we find

$$[H_c(T)]^2 - [H_{c^p}(T)]^2 = \frac{8\pi}{V} \int_T^{T_c} [\Delta S(T) - \Delta S^p(T)] dt = \frac{8\pi}{V} f(T). \quad (9)$$

Factoring the left side yields

$$[H_c(T)]^2 - [H_{c^p}(T)]^2 = DH_0(H_c + H_{c^p}) \approx 2DH_0^2(1 - t^2),$$

which from Eq. (9), gives the good approximation

$$D \approx \frac{4\pi}{VH_0^2} \frac{f(T)}{(1 - t^2)}, \quad (10)$$

where $f(T)$ is the integral in Eq. (9). Thus D is proportional to the area contained between the true ΔS curve and ΔS^p from T to T_c . Figure 4 shows the area described by $f(T)$. Two extreme types of behavior are illustrated corresponding to the opposite cases of lead

¹² The two terms in Eq. (7) correspond closely but not exactly to the separation in the general form of Eq. (4) since the first term, $(VH_0^2/2\pi T_c) \ln t$, is within a few percent of the rigorous expression,

$$S^p = (VH_0^2/2\pi T_c) \ln(1 - t^2).$$

Even though it does not separate exactly in the form of Eq. (4), Eq. (7) is itself an exact relation and no algebraic approximations are involved in its application.

and tin which show, respectively, positive and negative values of D . From this relation the qualitative effect of various observed shapes of D upon ΔS is readily apparent.

Instead of using Eq. (2), ΔC may be evaluated by a reiteration of the procedure described above if we write

$$\Delta C = T(d\Delta S/dT) = T(d\Delta S^p/dT) + T(d\Sigma/dT), \quad (11)$$

where $\Sigma = \Delta S - \Delta S^p$ is an entropy deviation function analogous to D . Values of Σ are obtained from Eq. (7) and the expression for ΔS^p . They must, of course, describe a curve sufficiently smooth to give reasonably accurate values of the temperature derivative. The values of Σ obtained for tin are plotted in Fig. 5. Values of $d\Sigma/dT$ for Eq. (11) were obtained by graphical differentiation of similar large scale plots. The values of $d\Delta S^p/dT$ can be evaluated algebraically as precisely as desired since the temperature dependence of this term is fixed by definition.

For brevity the foregoing presentation has not included any discussion of such matters as sources of error or thermodynamic checks for self consistency of the calculated values. Further discussion of these more detailed questions will be found in the Appendix.

C. Calculations with Calorimetric Data

Tabulated values of C_n and C_s vs T are the basic data used but, because of the nature of the experiments, it is not feasible to measure C_n and C_s at precisely the same

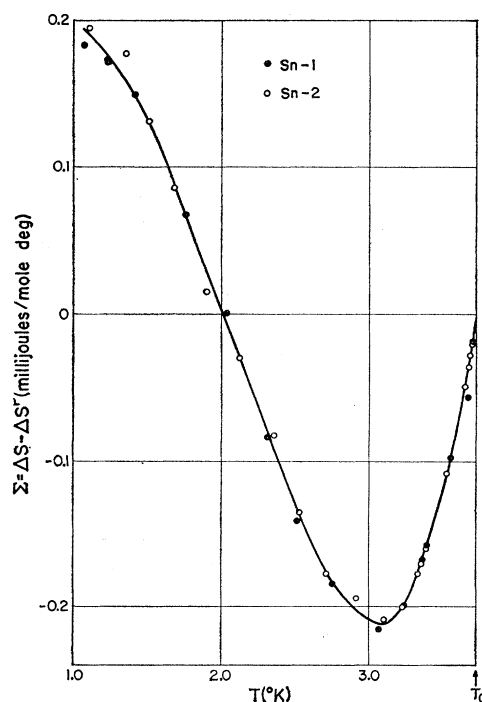


FIG. 5. Experimental values of the entropy perturbation term, Σ . A smooth curve has been drawn through the experimental points for two specimens of tin.

T value. For this reason ΔC values must be obtained from smoothed curves describing the separate temperature variations of C_n and C_s . Values of $\Delta S(T)$ are obtained by numerical integration, the process corresponding to that illustrated in Fig. 1.

RESULTS

Using the procedures outlined in the previous section, ΔS values for tin and indium have been calculated for each critical-field observation. The results are plotted in Figs. 6 and 7 where the points represent the magnetic data and the curves give results derived by integration of calorimetric data. The curve marked ΔS^p (shown only in Fig. 6) gives the entropy difference corresponding to the parabolic critical field curve [i.e., Eq. (3)]. The separation between ΔS^p and the ΔS values (indicated by Σ in Fig. 6) shows the relative magnitude of the perturbation term derived from D' . Since the average contribution of Σ is about 10% of ΔS , differentiation of D with an accuracy of 5% yields ΔS values accurate to 0.5%.

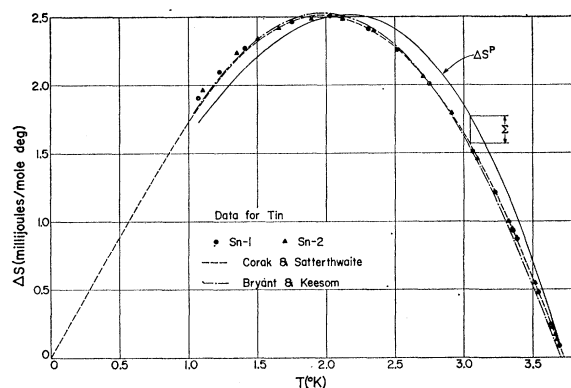


FIG. 6. Entropy difference values for two specimens of tin. Points are computed for each H_c value of reference 6. Broken curves give smoothed values obtained from calorimetric data. Light continuous curve gives the entropy difference corresponding to a parabolic critical field with $H_0=308.6$ gauss, $T_c=3.722^\circ\text{K}$.

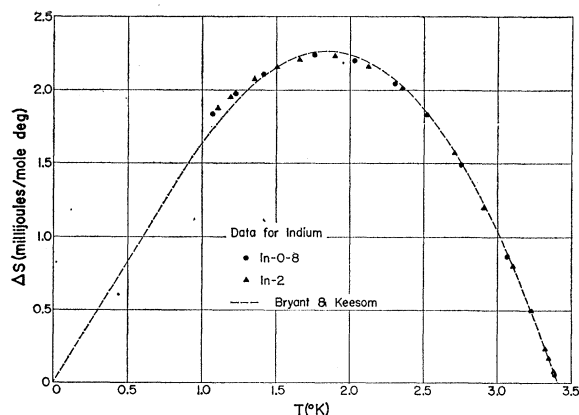


FIG. 7. Entropy difference values for two specimens of indium. Points are computed for each H_c value of reference 6. Broken curve gives smoothed values obtained from reference 8.

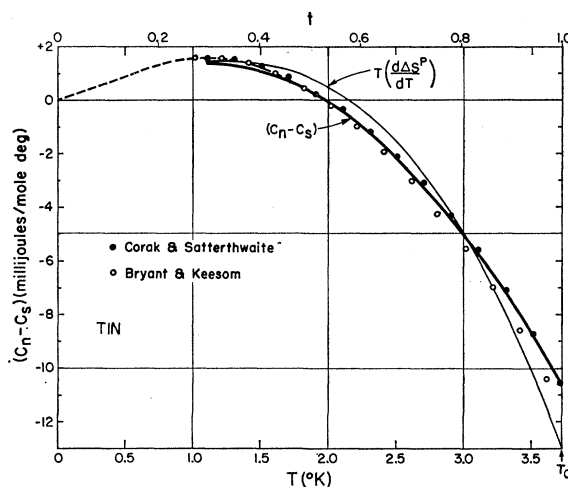


FIG. 8. Specific heat difference for tin. Heavy smooth curve is calculated from H_c data. Points at 0.2°K intervals are obtained from smoothed curves representing the calorimetric data of references 7 and 8. Light smooth curve gives ΔC^p for $H_0=308.6$ gauss, $T_c=3.722^\circ\text{K}$.

Two smoothed curves are available for comparison in the case of tin corresponding to the results of Corak and Satterthwaite⁷ and the more recent work of Bryant and Keesom.⁸ Except for the points below about 1.5°K , the agreement between the two types of measurement is within the limiting experimental precision set by the 1% uncertainty in the calorimetric measurements.¹³ While the disagreement between the two calorimetrically derived curves is not great, it is outside the reported limits of experimental error. The magnetic data are in best agreement with the work of Corak and Satterthwaite.

Another aspect of the same comparison is presented for the case of tin in Fig. 8 where ΔC is plotted vs T . In this figure magnetically derived values are represented by the heavy solid curve while calorimetric values of ΔC (read at 0.2°K intervals from a plot like Fig. 1) are shown by the points. The light curve marked ΔC^p gives the specific heat difference appropriate to the fiducial parabolic H_c^p [i.e., Eq. (3)]. The separation between ΔC^p and the experimental curve shows the relative magnitude of the perturbation term, $T(d\Sigma/dT)$ in Eq. (11).

Except for the region below 1.5°K , where the magnetically derived curve falls below the calorimetric results, agreement between the two types of measurement is very satisfactory.¹³ As in the case of the ΔS plot,

¹³ Subsequent measurements by Finnemore (to be published) have shown that the disagreement between magnetic and calorimetric values below about 1.5°K results from errors in measurement of the vapor pressure of helium at the lowest temperatures reached in the work of Shaw *et al.* (reference 6). The temperature values on which the present calculations were based show a small systematic error which increases from $<10^{-3}^\circ\text{K}$ at 1.6°K and amounts to about $+15 \times 10^{-3}^\circ\text{K}$ near 1.1°K . The low-temperature deviation in Figs. 6, 7, and 8 does not occur in the recent results of Finnemore.

the magnetically derived ΔC values are in best agreement with the calorimetric results of Corak and Satterthwaite.

The comparison for indium is presented only in terms ΔS (Fig. 7). In this case the magnetic data are in good agreement with the calorimetric results of Bryant and Keesom except for temperatures below 1.5°K.¹³

The ΔS vs T results may be analyzed to give the temperature dependence of the superconducting electronic entropy using the same theoretical arguments employed in the analysis of calorimetric data.^{7,8} Critical-field values are particularly advantageous in determining $S_{es}(T)$ at the higher temperatures since the magnetic data are definitely more precise than calorimetric data as the temperature approaches T_c .

The analysis proceeds from the relation

$$\Delta S = S_{en} - S_{es}, \quad (12)$$

which assumes the lattice entropy to change by a negligible amount in the superconducting transition and in which S_{en} and S_{es} represent the electronic entropies in the normal and superconducting states. Since $C_{en} = \gamma T = S_{en}$,

$$S_{es}(T) = \gamma T - \Delta S(T), \quad (13)$$

and Eq. (13) may be solved if γ is known. While, in principle, γ should be determined by the limiting slope of the ΔS curve as $T \rightarrow 0^\circ\text{K}$ the present H_c data do not extend to low enough T values to define this slope. Values of S_{es} for tin were evaluated from Eq. (13) using the calorimetrically determined value $\gamma = 1.76$.⁷ They showed satisfactory agreement with theoretical values tabulated by Mühlischlegel¹⁴ on the basis of the Bardeen-Cooper-Schrieffer (BCS) theory.¹⁵ The maximum difference was 1.5% and it was less than 1% over most of the temperature range of the measurements. Further discussion of this analysis will be given in connection with the forthcoming results of Finnemore¹³ whose measurements extend to 0.3°K and thus permit an accurate magnetic determination of γ .

DISCUSSION

As stated initially, the comparison given above is fundamentally a test of thermodynamic consistency in which the reliability of the experimental procedures is at issue. At least two general factors influence the experimental reliability: (a) technical considerations impose limits on the precision of experimental determinations; and (b) very precise experimental indications can be subject to uncertainty in theoretical interpretation. These two factors summarize the essential distinction between calorimetric and magnetic measurements of the type considered here. The greatest uncertainties in critical field data relate to factor (b) while calorimetric data are generally limited by factor (a).

The H_c data, which can be obtained under rigidly thermostatic conditions, are at present about an order of magnitude more precise than the best calorimetric measurements. This advantage is offset to some degree by uncertainty in the definition of H_c itself. While the progress of the magnetic transition can be followed with great precision, it is seldom practical to observe a transition at constant T which is complete in much less than $0.01H_c$. The principal reason for this is the finite demagnetizing factor of real superconducting specimens although other minor effects may also contribute.

Since from Eq. (1) it follows that any error ϵ in fixing H_c gives an error 2ϵ in ΔS , the absolute accuracy of thermodynamic functions derived from critical-field measurements depends on the accuracy of the interpolation used to fix H_c within the width of the observed transition. The interpolation procedure employed in the present H_c data has been previously described in detail¹⁶ and derives from the analysis of the intermediate state originally given by Peierls.¹⁷ It is generally accepted (though not universally applied). However, the most fundamental experimental test of its validity is its ability to yield values which satisfy the thermodynamic self-consistency requirements applied here. Unfortunately, the precision of the calorimetric measurements is not sufficient to provide a decisive test.

The results shown in Figs. 6, 7, and 8 indicate a reasonably satisfactory state of agreement even though experimentally significant differences occur. As noted in the section on results, more recent measurements show the difference below 1.5°K to be due to a small error in the temperature values of the present H_c data.¹³ It must be kept in mind that the absolute accuracy of both magnetic and calorimetric data is critically dependent on the accuracy of the thermometry and that this remains a difficult technical problem.

Above 1.5°K we feel confident of the absolute accuracy of the temperature values for the magnetic measurements since they have been confirmed in new and more careful observations. At the higher temperatures the agreement between magnetic and calorimetric data is within experimental error for indium but beyond the stated errors for the calorimetric measurements on tin. It is ironic that such disagreement persists for the case of tin which has probably been the subject of more measurements than any other superconducting element.

A closer approximation to the absolute equilibrium values for tin presumably lies somewhere between the following extreme interpretive viewpoints:

1. *Conservative view.* Equilibrium properties are determined only to the extent that the requirements of thermodynamic consistency can be demonstrated. In this view the absolute accuracy of ΔC is no better than

¹⁴ B. Mühlischlegel, Z. Physik **155**, 313 (1959).

¹⁵ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

¹⁶ J. F. Cochran, D. E. Mapother, and R. E. Mould, Phys. Rev. **103**, 1657 (1956).

¹⁷ R. Peierls, Proc. Roy. Soc. (London) **A155**, 613 (1936).

about 7% at T_c because of the disagreement between the two calorimetric measurements.

2. *Liberal view.* From an operational standpoint the H_c measurements are the most precise and they thus provide a decisive test in cases where calorimetric results disagree. In this view the magnetic data confirm the calorimetric results of Corak and Satterthwaite and indicate that the more recent tin data of Bryant and Keesom are incorrect as $T \rightarrow T_c$.

There are both general and specific considerations which suggest that the liberal view should be favored in the present situation.

A specific item of concern is Bryant and Keesom's disclosure⁸ that the calorimetric value for T_c was about 0.02°K lower than their own magnetic determination of T_c using a small piece of the same tin specimen employed in the specific heat measurements. Even though the procedures of adiabatic calorimetry are not ideally suited to the precise determination of T_c , this discrepancy seems large. Moreover their magnetic determination is in satisfactory agreement with the results of Corak and Satterthwaite and with the more extensive magnetic data considered here. This raises the possibility that something was wrong with the large tin specimen used in the calorimetric measurements. The authors suggest that the discrepancy may be due to strains introduced in cooling due to the anisotropic contraction of the large tin polycrystals.⁸

The following general considerations are also pertinent. At T_c the common lattice contribution to the calorimetric values of C_s and C_n (for tin) is about 1.2 times the magnitude of ΔC . This substantially increases the size of the individual terms which must be subtracted to obtain ΔC by the calorimetric method. Moreover, examination of the calorimetric values just above T_c shows that, in addition to discrepancies of about 4% between the two laboratories, values of C_n measured with and without the magnetic field are not in precise agreement for either set of measurements. This experimental situation makes it difficult to substantiate the basic assumption that the magnetic field (which must be applied to get C_n) has no other effect on the specific heat than to suppress the electronic behavior of the superconducting state. On theoretical grounds it seems highly unlikely that any real detectable effect on the specific heat could result from the few hundred gauss fields that are used. However, the possibility of small spurious effects due to a weak magnetic sensitivity in some part of the instrumentation cannot be dismissed without evidence.

Both of these complicating factors are avoided in the magnetic measurements which are made at substantially constant field and which, as previously noted, yield the difference associated with the superconducting transition directly without regard to the relative magnitude of the lattice contribution. These considerations support our opinion that, at least near T_c , experimental conditions for the precise determination of differences in

the thermodynamic properties are more favorable in critical-field measurements than in direct calorimetric experiments by present techniques. The relative advantages of the two methods at the lowest temperatures will be discussed in a subsequent article in connection with more recent measurements extending to 0.3°K. Suffice it to say at this time that the accuracy of the magnetic measurements compares favorably with the best calorimetric results over the entire temperature range.

As a concluding observation we wish to draw attention to the sensitivity with which the deviation function reveals small variations in the thermodynamic properties of different superconducting elements. The point may be illustrated in the following terms. Taking the maximum amplitude of D as a measure of the experimental indication, values at present vary from about -0.025 for tin to about $+0.023$ for lead giving a total range of about 0.05 units for this parameter. With present techniques D is measurable to ± 0.0005 without difficulty and so the range of behavior between the extreme cases of tin and lead can be measured with a precision of about $\pm 1\%$.

It now seems that the differences shown by the variation of D can be largely explained in terms of variations in the relative magnitude of $\Delta(0)$, the superconducting electronic energy gap of the Bardeen-Cooper-Schrieffer theory. Several methods which give $\Delta(0)$ in a relatively direct manner have been devised in recent years, and the resolution of such methods may be compared with that possible in critical field data. The highest precision is claimed for electron tunneling experiments for which Giaever and Megerle¹⁸ give the following values for tin and lead, respectively, $\Delta(0)_{\text{Sn}} = 3.46 \pm 0.10$; $\Delta(0)_{\text{Pb}} = 4.33 \pm 0.10$ (in units of KT_c). Thus differences between these elements are resolvable by these direct measurements with a precision of about 12%.

The tunneling experiments, together with infrared and microwave techniques, provide data which, from the standpoint of directness and intimacy of detail, cannot be matched by the thermodynamic measurements. However, from the standpoint of experimental precision, critical-field determinations of D possess a resolving capacity which is at least an order of magnitude greater than any other method in current use.

ACKNOWLEDGMENTS

The writer has profited from many discussions with D. K. Finnemore who was making further H_c vs T measurements below 1°K while the present work was in progress. Finnemore's results, which will be published soon, were of great value in clarifying or confirming certain aspects of the present discussion. C. A. Bryant and P. H. Keesom kindly provided an advance copy of their article and also supplementary data and comments pertaining to their measurements. Most of the work

¹⁸ I. Giaever and K. Megerle, Phys. Rev. 122, 1101 (1961).

reported here was done while on sabbatical leave at Cornell University. The cordial hospitality of the Cornell Physics Department and support from the J. S. Guggenheim Foundation which made this arrangement possible are gratefully acknowledged.

APPENDIX

From the definition of Eq. (5b) it is seen that D is sensitive to the value of H_0 . In the foregoing treatment we have based our calculations on a value of H_0 determined by extrapolation of the H_c data to 0°K . The temperature interval bridged by the extrapolation is appreciable and so, also, is the possibility of error in H_0 . In the discussion below it will be shown that the accuracy of the D analysis is insensitive to error in H_0 within the temperature range of the measurements. Thermodynamic calculations to correct the extrapolated value of H_0 and check the self consistency of the ΔS and ΔC values are also described.

Effect of Error in H_0

The situation confronting the experimenter is shown in exaggerated detail in the plot of H_c vs t^2 of Fig. 9. The curve $H_c(t^2)$ represents a *measured* critical-field curve for which data extend only to t_{\min}^2 . Faulty extrapolation of $H_c(t^2)$ to 0°K yields the erroneous value H_0^* and D is constructed relative to an incorrect parabola which on this diagram appears as the straight line $H_e^p(t^2)$. The dashed line A represents the correct (but initially unknown) extrapolation to the true value, H_0 .¹⁹

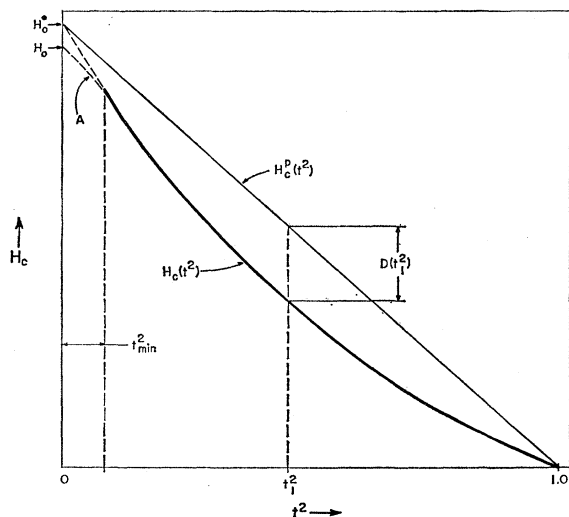


FIG. 9. Diagram of a critical-field curve vs t^2 for the case of a negative deviation function. The amplitude of D is greatly magnified.

¹⁹ Various theoretical considerations may be invoked to improve the extrapolation procedure and thus yield a more accurate initial estimate of H_0 . We will not digress to treat such possibilities since it is our intention to show that an accurate initial estimate of H_0 is unnecessary.

Inspection of Eq. (6) shows that dH_c/dT has been expressed as the sum of the slopes of D and H_e^p , both plotted vs t^2 (and multiplied by appropriate scaling factors). Any error in H_0 will change the slope of H_e^p but an exactly opposite compensating change also occurs in the slope of D because of the way it has been defined. [To prove this Eq. (6) may be partially differentiated with respect to H_0 with the result that each term yields the same value, $(D' - 1)(2t/T_c)$, but with opposite algebraic signs.] Thus computation of ΔS from Eq. (7) is independent of any uncertainty involved in fixing H_0 *within the range of T where measurements exist to specify $H_c(t^2)$* .²⁰ In terms of Fig. 9 this result has the obvious interpretation that a known curve such as H_c (and its derivatives) can be described as the sum of a line of arbitrary slope such as H_e^p and a deviation function, D .

The situation is different below t_{\min} since the true curve, indicated by A , is experimentally undetermined. An extrapolation of D into this region will be erroneous if the initial value of H_0 is wrong. The errors can be substantial owing to the magnification implicit in the use of D . For this reason we have not tried to extrapolate the present D curves below 1°K .

Thermodynamic Tests for Consistency

As has just been shown, the calculational procedures used here yield accurate values of ΔS vs T without precise knowledge of H_0 . However, they also provide opportunity for numerical error. It is therefore desirable to check the internal consistency of the values obtained. This is conveniently done by using the integral equations which relate ΔS and ΔC to the critical-field values.

The calculated ΔS values must satisfy Eq. (8), where the integral on the right is evaluated numerically. The ΔC values are even more susceptible to error since two differentiations of the H_c data are involved. Numerical integration of the ΔC values must satisfy the following relation [obtained by integration of Eq. (2)]:

$$\int_T^{T_c} \Delta C dt = -[T\Delta S(T) + (V/8\pi)H_c^2(T)]. \quad (\text{A1})$$

It is apparent that these checks on ΔS and ΔC involve no new principles but the numbers which enter are different from those occurring in the differential analysis. They thus provide independent assurance that the ΔS and ΔC values are consistent with the observed H_c and T data.

Correction of H_0 and D

The integral relation for ΔS also provides a means of correcting the initial estimate of H_0 . If Eq. (8) is

²⁰ The temperature range near T_c is completely accessible to experiment and thus the accuracy of T_c is limited only by the inherent precision of the measuring method. For this reason error in T_c is generally negligible in comparison with that involved in extrapolation of H_0 .

evaluated between 0°K and T_c we have

$$(8\pi/V) \int_0^{T_c} \Delta S dT = H_0^2.$$

To obtain H_0 it is necessary to extrapolate ΔS to 0°K but this can be done rather accurately using specific heat data. The extrapolation depends on two considerations:

(a) because of the third law of thermodynamics, $\Delta S=0$ at $T=0^\circ\text{K}$, and

(b) near 0°K, ΔS is dominated by S_{en} , the entropy of the normal electrons.

For the case of tin it turns out that the gap between 0 and 1.1°K on the ΔS plot of Fig. 6 can be closed by erecting a straight line from the origin having a slope γ , since $S_{en}=\gamma T$ as noted earlier. Numerical integration under the resulting ΔS curve gives $H_0=306.7$ gauss, or about 2 gauss less than the value estimated from a parabolic extrapolation of the measured critical field curve.

A more accurate approximation to H_0 requires consideration of the superconducting electronic entropy S_{es} . This may be done by making use of calorimetric measurements which show

$$C_{es}(T) = a\gamma T_c \exp(-bT_c/T). \quad (\text{A2})$$

and thus

$$\begin{aligned} S_{es}(T) &= a\gamma T_c \int_{x=bT_c/T}^{\infty} \frac{e^{-x}}{x} dx \\ &= a\gamma T_c [-\text{Ei}(-bT_c/T)]. \end{aligned} \quad (\text{A3})$$

Tabulated values of the function $[-\text{Ei}(-x)]$ are available²¹ and experimental values of the constants a , b , and γ , from calorimetric measurements are used. For both tin and indium the curves $\Delta S=\gamma T-S_{es}$ join the magnetically derived ΔS values near 1.5°K as shown in Figs. 6 and 7. The area under the ΔS curve is not very sensitive to the S_{es} contribution near 1°K and so the accuracy requirements on the constants a and b are not stringent. Integration under the resulting ΔS curves gives the values: for tin, $H_0=305.7$ gauss (using data of Corak and Satterthwaite)²²; and for indium, $H_0=282.6$ gauss (using data of Bryant and Keesom).

²¹ E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, Inc., New York, 1945), p. 6.

²² Although not visible in Fig. 6, there is a small difference in the ΔS extrapolation for tin depending on which set of calorimetric

For both elements these values are about 1% lower than those initially estimated on the basis of parabolic extrapolations of the H_c data. An error of this magnitude does have a significant effect on D as shown by the corrected curves of Figs. 3 and 4. These corrections were not applied to the H_0 values in Table II of the article by Shaw, Mapother, and Hopkins.⁶ Most of the discrepancy between the magnetic and calorimetric deviation functions shown by Bryant and Keesom (their Figs. 5 and 9) is removed by this correction.

It may be of interest to point out a graphical construction which corrects D for the error in H_0 in a simple way. In the case of tin, for example, the corrected H_0 is 0.94% less than the H_0 used to define the initial D . Thus a true extrapolation of D to 0°K would reach the ordinate at -0.0094 rather than at 0.00. Therefore, on Fig. 3 the dashed line, between the corrected intercept at $\ell^2=0$ and the point $D=0$; $\ell^2=1$, corresponds to the new ℓ^2 axis which would result if D were entirely recalculated using the corrected H_0 to define a new H_c^p . However, instead of recalculating D algebraically, the same result is obtained graphically (and with an accuracy at least equal to that of the experimental data) by measuring the vertical separation between the points as plotted on the original uncorrected D curve and the dashed line of Fig. 3. The validity of the graphical procedure follows from the linearity of H_c^p when plotted vs ℓ^2 .

The trend of the corrected D curves at the lowest temperatures suggests that they will cross the ℓ^2 axis. In part this appearance in the present case is a complementary aspect of the deviation of the ΔS points below 1.5°K in Figs. 6 and 7. (If D' is too large, as is the case below 1.5°K in Figs. 2 and 3, Σ will be too large and the ΔS values will be erroneously high.) However, even a correct D does not extrapolate linearly to the origin since the exponential T dependence of C_{es} results in a reversal of curvature in D below $\ell^2=0.10$ (for both tin and indium). The present H_c measurements do not extend to low enough T values to show this reversal of curvature although it shows up clearly when measurements are extended to 0.3°K.¹³ This effect explains the inadequacy of the initial parabolic extrapolation to obtain H_0 .

constants are used. The Corak and Satterthwaite constants are preferred since they yield an H_0 value in better agreement with the recent measurements of Finnemore (reference 13). The difference is slight (about 0.2% of H_0) but it is resolvable in H_c measurements.