Specific Heat of Niobium-Tin*

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The specific heat of Nb_3Sn has been measured over the temperature range 1–42°K, and in magnetic fields up to 52.5 kG. The data can be interpreted to give $\gamma=13.1$ mJ/g atom °K², $\Delta C/\gamma T_c=2.4$, $H_0=5350$ G, and $\kappa(T_c)=21.7$. The Debye temperature Θ appears to increase at the rate of 1°K/°K over most of the range of the measurements, with $\Theta(0)=228$°K. Measurements have also been made on a sample of composition Nb_4Sn, and on vapor-grown Nb_3Sn similar to that exhibiting the cubic-tetragonal lattice transformation. The specific heat of Nb_3Sn can be reconciled with elastic-constant data only if it is assumed that the lattice softening implied by the decreasing velocity of sound with decreasing temperatures is limited to frequencies considerably below the Debye frequency.

INTRODUCTION

In spite of a large body of experimental information on the properties of Nb_3Sn, the behavior of this material, as well as other high transition temperature intermetallics of the β-tungsten class, is not well understood. Anomalies have been observed in resistivity, tunneling, elastic-constant, Mössbauer, and low-temperature specific-heat measurements.[1–5] It now appears that much, if not all, of this anomalous behavior is related in some way to the lattice instability seen in the vanishing of the velocity of sound for one of the shear modes at low temperatures. While the cubic to tetragonal transformation has been observed only in selected crystals of V_3Si [6] and Nb_3Sn,[7] the softening of the lattice with decreasing temperature appears to be characteristic of all the high T_c, β-tungsten alloys,[8] so that manifestations of this instability can be expected to be observed quite generally.

Specific-heat studies have given values for $N(0)$, the density of states at the Fermi surface, the Debye temperature Θ,[9] and the specific-heat jump at T_c.[10] The temperature dependence of the specific heat in the superconducting state is obviously of interest, particularly since the energy gap does not appear to be known with certainty. Thermal conductivity,[11] as well as some tunneling measurements,[12] suggests a BCS-like[13] gap of $3.5kT_c$, although the high transition temperature and relatively low Debye temperature of Nb_3Sn imply strong-coupling deviations. More recently, a value of $2\Delta(0)=3.77kT_c$ has been obtained from far-infrared reflectivity studies.[14]

Normal-state measurements in magnetic fields are also of great interest, particularly in view of the implications of the unusual behavior of the elastic constants for the lattice specific heat. Exceedingly high fields (~200 kG) are required to study the normal state near 0°K. In a more modest effort, we have extended the normal-state measurements down to 15°K, providing the means for an unambiguous determination of the temperature dependence of the electronic specific heat in the superconducting state near T_c, and, in addition, useful information on the mixed state.

EXPERIMENTAL METHODS

The bulk of the measurements were made in the calorimeter shown in Fig. 1, which was designed to accommodate a 55-kG, 100-A Nb_3Sn solenoid of $1\frac{1}{8}$-in. bore. Contact to the He bath is made by means of a piston which pushes the sample tray against the brass radiation shield, which in turn presses against the top of the reentrant well. The sample tray, comprising about 5 g of copper, a Ge thermometer, and an 8000-Ω manganin heater, rides on three stainless-steel capillary pins of 3.5-mil wall thickness with a combined thermal conductance of about 15 μW/deg at 4.2°K. The radiation shield heater is controlled manually so as to prevent excessive heat leakage at the higher temperatures. The sample was mounted by spark cutting a well to fit closely over the shaft of the precalibrated addendum. A small, weighed amount of indium was smeared on the sample well to ensure good thermal contact.

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[11] G. D. Cody and R. W. Cohen, Rev. Mod. Phys. **36**, 213 (1964).
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[13] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[14] D. R. Bosomworth and G. W. Cullen, Phys. Rev. **160**, 346 (1967).

Measurements were made by the standard technique of applying a heat pulse and measuring the change in resistance of the Ge thermometer. The resistance was measured on a Leeds and Northrop K-3 potentiometer, and the resistance changes during a data-point run followed by recording the off-balance signal after suitable dc amplification. In general, $\Delta T/T$ was of the order of 1–2%. Thermometer and heater currents were measured potentiometrically across 0.025 and 0.05% standard resistors. Reproducibility was about ±2%, which is outside the combined measurement errors, and is felt to reflect stray rf pickup, random vibration, etc. Because of the relatively small sample size (~15 g), the addendum, the specific heat of which was well represented by the expression $C/T=0.2+0.00555T^2$ mJ/°K² over the range 3–30°K, represented about ¼ of the total specific heat, so that additional uncertainty is introduced in its subtraction. If is felt that the overall accuracy is about ±2%, exclusive of errors in thermometry.

The Ge thermometer was a Minneapolis-Honeywell type-II unit with a resistance of 1800 Ω at 4.2°K. The thermometer was calibrated against a gas thermometer of moderate precision, using a Wallace-Tiernan Bourdon gauge as readout instrument. Interpolation tables were constructed by computer using a fourth-degree polynomial to interpolate between the middle points of each set of four calibration points. Since the calculated specific heat depends on dR/dT, quite small errors in absolute temperature appear as substantial irregularities in specific-heat curves if the calibration grid is small.

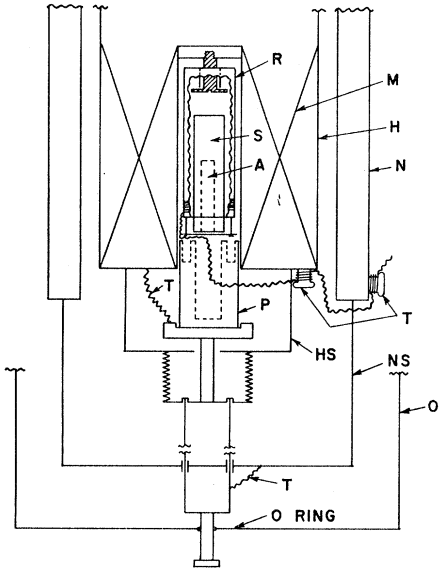

FIG. 1. High-field calorimeter. A, addendum; S, sample; R, radiation shield and thermal contact; M, superconducting solenoid; H, helium Dewar; N, nitrogen Dewar; O, outer Dewar; P, contacting piston; HS, NS, helium and nitrogen shields; T, thermal anchors.

In order to smooth the calibration curve, as well as to check the accuracy of the measurements, we therefore determined the specific heat of a 50-g sample of Asarco copper, presumably identical to the raw material adopted for use as a standard by the Calorimetry Conference.[15] The temperature scale was adjusted to fit the data of Ahlers,[16] and Martin,[17] by the following procedure: The specific heat at temperature T^* on the provisional scale is given by

$$C^*(T^*)=(\delta Q/\delta R)\,(dR/dT^*)=C(T)\,(dT/dT^*),$$

where δQ is the heat input and δR is the measured change in resistance. It follows that

$$T=T_0^*+\int_{T_0^*}^{T^*}\frac{C^*(T^*)/C(T^*)}{\{1-[(T^*-T)/C](dC/dT)\}}\,dT^*.$$

Taking $T_0^*=T_0=4.2$°K, the copper standard scale is obtained by iterative graphical integration. The maximum deviation in T^*-T was 0.07°K, and the maximum error in specific heat was 4%.

For the high-field measurements, a 57-Ω, $\frac{1}{10}$-W Allen-Bradley carbon resistor was attached to the addendum. The carbon thermometer was calibrated against the Ge in the absence of a field, and a three-point interpolation formula used to generate R versus T tables.[18] With calibration points at 4.2, 7.2, and 18.1°K, the carbon scale deviated from the Ge scale by a maximum of −0.025°K, over the range 4.2–18.1°K. The magnetoresistance of the C thermometer at 4.2°K was found to obey the relation $\Delta R/R_0=9.3\times10^{-6}\,H^2$, where H is the field in kG, and the numerical coefficient was assumed to have a $T^{-3/2}$ dependence.[19]

The magnet leads were brought in from room temperature through a neck in the helium Dewar 2 in. wide by 6 in. long. After some experimentation, the scheme shown in Fig. 2 was adopted to prevent excessive helium losses. The leads were thermally anchored to a ¾-in. stainless-steel tube of 10-mil wall thickness extending from the magnet to the top of the Dewar by means of three pairs of sintered copper-alumina-copper sandwich standoffs. Between the bottom standoffs the current was carried by 50-mil Cu wire, folded back on itself several times. A short strip of Cu foil was soldered along the middle of this line to prevent local overheating which was observed at high currents. The current was then brought into the bath with 50-mil wire. With this arrangement, the helium losses were as follows: without solenoid, 60 gaseous liters/h; with solenoid but no current, 240 liters/h; with 100 A, 700 liters/h.

[15] Nineteenth Annual Calorimetry Conference, 1964, Washington, D.C. (unpublished).
[16] G. Ahlers, Rev. Sci. Instr. **37**, 477 (1966).
[17] D. L. Martin, Can. J. Phys. **38**, 17 (1960).
[18] F. E. Hoare, L. C. Jackson, and N. Kurti, *Experimental Cryophysics* (Butterworths Scientific Publication, Ltd., London, 1961), p. 233.
[19] Reference 18, p. 235.

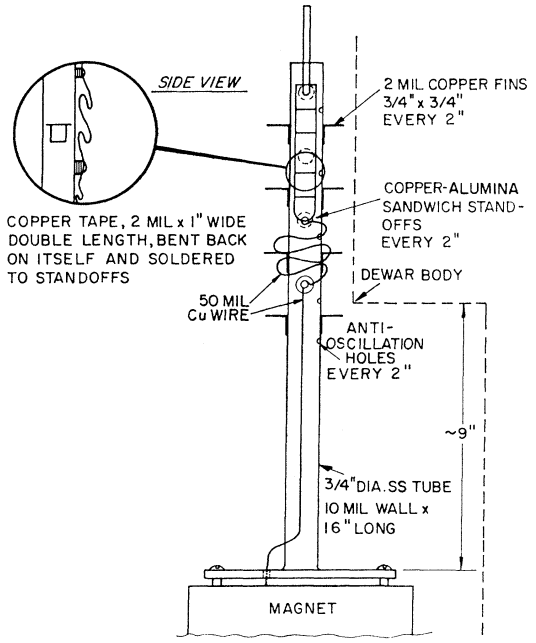

FIG. 2. Magnet lead arrangement.

Additional measurements were made in a more conventional cryostat with working space large enough to accommodate samples of about 1 g-atom, and fitted with an inner liquid He chamber.[20] Exchange gas was used to cool to 4.2°K. It was found that after pumping for about 1 h through a $\frac{1}{4}$-in. tube the can was sufficiently void of He to give reasonable drift rates, and that the measured specific heat was thereafter independent of pumping time. For measurements below 4.2°K, the reflux chamber was filled by condensation, and then pumped through a 20-mil orifice. The chamber, whose volume was 30 cm^3, could be pumped to 0.9°K with a 115 cu ft/min mechanical pump, and held for about 4 h with the outer bath at 4.2°K. Thermal contact between the sample and the reflux chamber was such that the sample achieved the lowest temperature in about 1–2 h. It was convenient to mount the sample by simply resting it on a $\frac{1}{8}$-in. styrofoam pad, which had a thermal conductance of 5 μW/°K cm^2 at 4.2°K. Other mounting (nylon thread) and cooling (carbon resistor)[21] techniques were used for measurements on small samples. For measurements above 4.2°K the reflux chamber was evacuated and heated in order to provide a roughly adiabatic measurement cycle. Data over the range 1–42°K were readily obtained in this apparatus.

Sintered samples were prepared by cold pressing mixtures of -325 mesh Nb and Sn powders and reacting at 1700°C for 8 h in a He atmosphere. The outer Nb-rich layer was then ground off to ensure uniformity. Microscopic examination by the Picklesheimer technique[22] revealed the presence of small amounts of extraneous phases (about 1% by volume) presumed to be oxides and/or nitrides or carbides.

Sample *SH*-3, which had the sharpest transition of several stoichiometric samples, had a sharp x-ray diffraction pattern, with a lattice constant $a_0 = 5.2889$ Å. Measurements were also made on nonstoichiometric material. Sample *SH*-7, of nominal composition Nb_4Sn, had a lattice constant $a_0 = 5.2830$ Å, and a moderately sharp transition near 8°K. Nb_4Sn prepared in this way has been found to be a homogeneous, ordered alloy, with the β-W structure, in which 20% of the tin atoms are replaced by niobium, the niobium sublattice chains remaining intact.[23]

RESULTS

The specific heat of sample *SH*-3 is shown plotted as C/T versus T^2 in Fig. 3. For simplicity, data points for the measurements in magnetic fields are shown for the normal state only. Transition widths are somewhat broader in the presence of fields, although in the case of the measurements made at 52.5 kG the broadening is partially attributable to the use of larger temperature increments ($\sim$0.2°K) near the transition because of noise problems. The nonvanishing of C/T in the superconducting state as $T \to 0$°K is inferred from measurements made down to 1°K on a similar sintered sample, and published elsewhere.[5] This second sample was also used in extending the range of the measurement above 25°K, the results being incorporated into the Debye plot of Fig. 6.

The zero-field specific heat of Nb_4Sn is also shown in Fig. 3 for comparison. Unlike the situation for Nb_3Sn these data present no unusual problems in interpretation, the specific heat closely approximating the predictions of BCS.

The specific-heat jump at T_c for a small (2.61-g) boule of vapor-grown crystal is shown in Fig. 4. This sample consisted of several large crystallites, and, except for its polycrystallinity, is presumed to be identical with the material showing the lattice transformation.[7] The data presented include the addendum, which contributes about one-third of the total specific heat. The dashed line represents the normalized data for sample *SH*-3 in the transition region. The broad transition for the vapor-grown sample is rather unexpected in view of the high degree of chemical and physical perfection of this material, and is probably a manifestation of the lattice transformation. From Fig. 4 we get $\Delta C/T_c = 32 \pm 1.2$ mJ/g at. °K^2.

DISCUSSION

The usual development of the thermodynamic functions by integration of the specific-heat data to obtain

[20] A. C. Rose-Innes, *Low Temperature Physics* (D. Van Nostrand Co., Inc., New York, 1964), p. 40.
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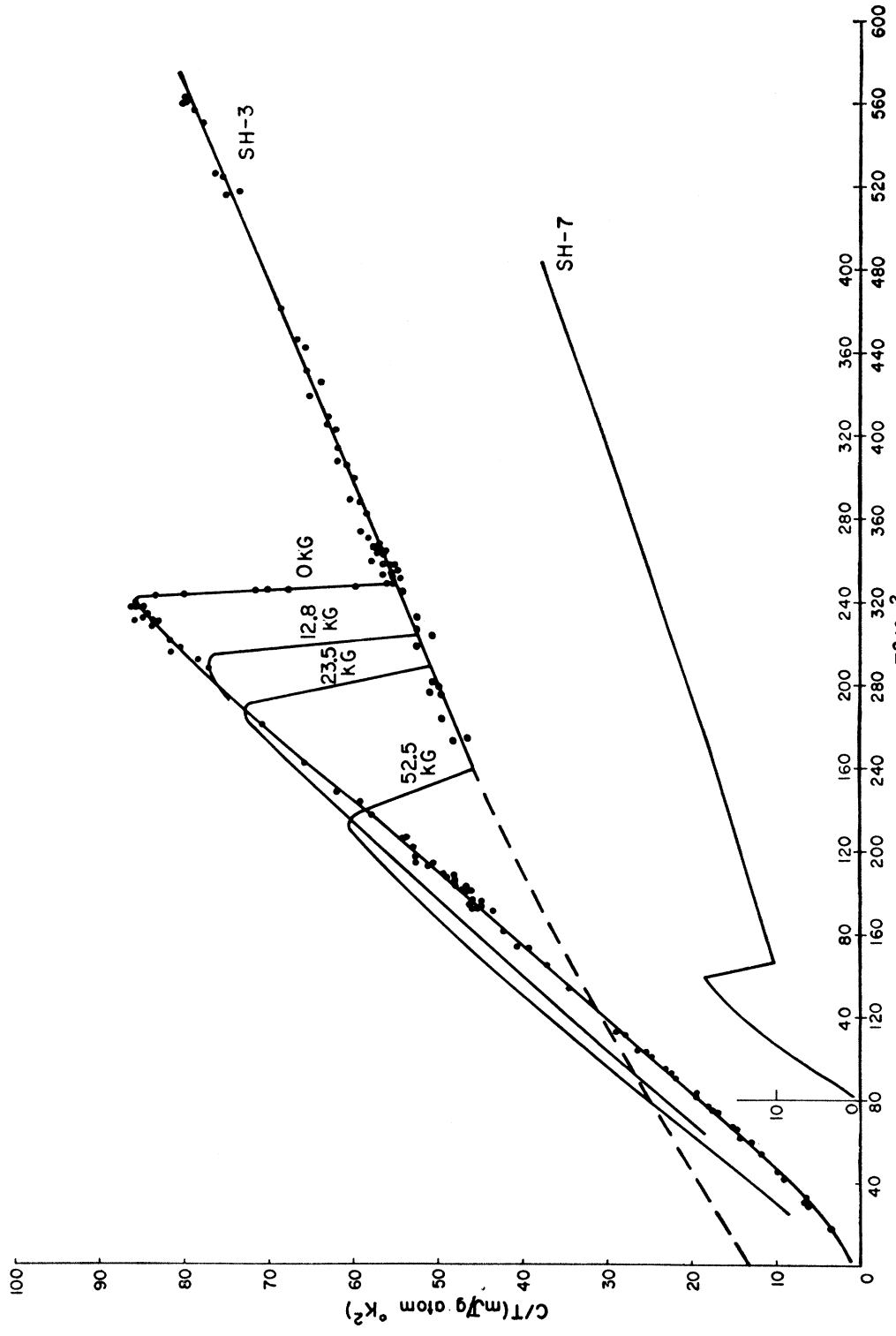

FIG. 3. Specific heat of Nb_3Sn (sample *SH-3*) in various fields, and Nb_4Sn (sample *SH-7*) at zero field. The vertical scale is the same for both samples, as is the gram-atomic volume, 11.1 cm^3. The dashed line is the normal-state behavior of Nb_3Sn inferred by analogy to the behavior of Hg (see text).

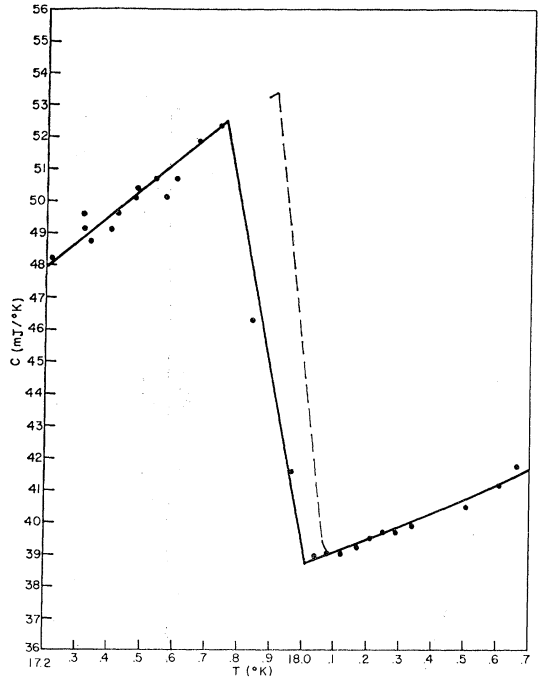

FIG. 4. Specific-heat jump at T_c for annealed vapor-grown crystal. The data include the contribution of the addendum. The dashed line shows the transition for *SH*-3, normalized above T_c.

the entropy and free-energy differences between the superconducting and normal states is here frustrated by the lack of data for the normal state of Nb_3Sn at temperatures much below T_c. This is not ordinarily a serious problem, since the normal-state specific heat is given to a good approximation by $C_n=\gamma T+aT^3$, where γ and a are constants proportional to the density of states at the Fermi surface and Debye temperature, respectively. However, the normal-state entropy at T_c obtained by integration of the extrapolated specific heat is 14% larger than $S_s(T_c)$ obtained from the measured specific heat below T_c. Straight-line extrapolation of the normal-state data of Fig. 3 is therefore not satisfactory if we are to maintain the assumptions that the superconducting to normal transition is second order, $\Delta S(T_c)=0$, and that $S_s(0)=0$. [The dashed curve of Fig. 3 represents a possible normal-state temperature dependence which meets these requirements (see below)]. Although alternative approaches are possible, it seems desirable, in view of the length of the necessary extrapolation and the known peculiarity of the elastic constants, to abandon the Debye extrapolation. There is one term which cannot be handled by the usual separation of lattice and electronic contributions, and which must be considered in the case of Nb_3Sn; that is the temperature-dependent contribution to the electronic specific heat in the normal state arising from the electron-phonon interaction.[24] This additional term is given at low temperatures by

$$\frac{C}{T}=\gamma\left[\frac{12\pi^2}{5}\frac{\lambda}{\pi+\lambda}\left(\frac{T}{\Theta}\right)^2\ln\frac{\Theta}{T}\right],$$

where λ is the coupling constant, the renormalized density of states being given by

$$N(0)'=N(0)[1+\lambda/\pi]\sim 2N(0)$$

for Nb_3Sn. This contribution amounts to about 3% of the total specific heat at T_c, and is therefore not entirely negligible. Moreover, since the calculation has been made only for a simple Debye model, and using a spherical Fermi surface, we cannot rule out the possibility that the correction is even more substantial. However, we will proceed without further explicit consideration of this term.

REGION ABOVE 15°K

Equating the entropies at T_c, the entropy and free-energy differences between the normal and superconducting states are given by

$$S_s-S_n=\int_{T_c}^{T}\frac{C_s-C_n}{T}\,dT$$

and

$$G_n-G_c=\frac{VH_c^2}{8\pi}=\int_{T_c}^{T}(S_s-S_n)\,dT,$$

where V is the volume per gram atom [11.1 cm^3], and H_c the thermodynamic critical field. H_c is given to within 3% over the range $0.7<t^2<1$ by $H_c=5400(1-t^2)$, while the limiting slope of the critical field as a function of temperature, obtained from the relation

$$\Delta C/T_c=(V/4\pi)\,(dH_c/dT)^2=31.5\pm 0.6\ \text{mJ/g at. °K}^2,$$

is found to be

$$(dH_c/dT)_{T_c}=-597\ \text{G/°K}.$$

A specific-heat jump of $\Delta C/T_c=31$ mJ/g at. $°K^2$ has been reported by other workers.[10] The normalized jump, $\Delta C/\gamma T_c$, is close to the BCS prediction of 1.43 if the value of γ obtained by linear extrapolation of the normal-state data ($\gamma=21$) is used. However, the temperature dependence of the specific heat is quite unlike BCS. This is shown in Fig. 5, where the electronic specific heat of Nb_3Sn is compared with that of other superconductors, and with the BCS model. The BCS line was taken from the tabulation of Muhlschlegel.[25] The line for Nb was obtained from specific-heat data,[26] while that for Hg was derived from magnetization data[27] by differentiation of the critical-field curve. The two sets of points for Nb_3Sn show the relative insensitivity

[24] S. Maitra and R. E. Prange, University of Maryland Technical Report No. 266, 1965 (unpublished).

[25] B. Muhlschlegel, Z. Physik **155**, 313 (1959).

[26] A. T. Hirshfeld, H. A. Leupold, and H. A. Boorse, Phys. Rev. **127**, 1501 (1962).

[27] D. K. Finnemore and D. E. Mapother, Phys. Rev. **140**, A507 (1965).

of the temperature dependence of C_{es} to the assumed value for γ. On the basis of correspondence, as well as entropy considerations, it appears that the density of states is substantially smaller than inferred from the simplest interpretation of the normal-state data. If this is so, then the T^3 dependence of the normal state from 15 to 23°K is fortuitous, since extrapolation to 0°K should give the proper value for γ as long as the Debye temperature is constant over this range.

LOW-TEMPERATURE REGION

For $T_c/T>5$ the electronic specific heat in the superconducting state might be expected to vanish exponentially, permitting a direct measurement of the lattice term. Instead, it is found that while a T^3 term is observed over the range $3.2<T_c/T<16$, there is in addition a term linear in T. The simplest assumption that can be made is that the T^3 term is due to the lattice contribution alone, and that the anomalous linear term may be subtracted out from the total specific heat to be dealt with separately. In this case, the Debye temperature is found to be $\Theta(0)=228$°K, and assuming Θ to be constant at temperatures not too far above 5°K, we can obtain the electronic specific heat in this region. A BCS-like (exponential) specific heat is inferred, but with a gap of $2\Delta(0)=4.8kT_c$. The high value of Δ is apparent from the fact that the electronic contribution is observed only at relatively high temperatures, i.e., $T_c/T<3.2$ (cf. Ref. 5).

This procedure finds justification in the two-gap model of Suhl *et al.*,[28] and precedent in the behavior of high-purity Nb and Ta,[29] and V.[30] Only V shows a sufficiently small gap associated with the s band so that a strictly linear region is observed, the low-temperature

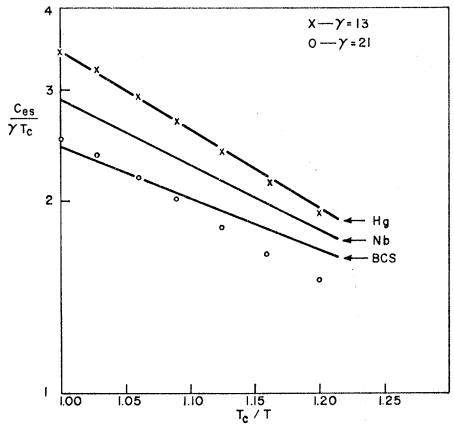

FIG. 5. Temperature dependence of the electronic specific heat near T_c for various superconductors and the BCS result. The points are for Nb_3Sn, using two assumed values for γ.

[28] H. Suhl, B. T. Matthias, and L. R. Walker, Phys. Rev. Letters **3**, 552 (1959).

[29] L. Yunlung Shen, N. M. Senozan, and N. E. Phillips, Phys. Rev. Letters **14**, 1025 (1965).

[30] R. Radebaugh and P. H. Keesom, Phys. Rev. **149**, 209 (1966).

TABLE I. Results of measurements in magnetic fields.

H (kG)	$T_c(H)$ (°K)	κ_1	Calc. $\Delta C/T_c(H)$ mJ/g at. °K²	Meas. $\Delta C/T_c(H)$ mJ/g at. °K²
0	18.00	21.7[a]		
12.8	17.30	22.2	25.9	25
23.5	16.70	22.1	24.9	24
52.5	15.15	23.1	21.7	19

[a] Extrapolated.

electronic specific heat being given by $C_e \propto N_s T$, where N_s is the density of states at the Fermi level in the s band. Two aspects of the behavior of Nb_3Sn are particularly noteworthy when interpreted in this way: First, the smaller gap, if indeed a gap is present at all, must be exceedingly small, of the order $\lesssim 80$ μV; and second, the density of states in the s band is typical of nontransition metals, the intercept at 0°K indicating a density of states per tin atom of about twice that of metallic tin.

The principal difficulty lies in the very high value of the gap. Reversing the procedure, we could assume a gap of $2\Delta(0)\sim 4kT_c$, compute the electronic specific heat on the BCS model, and subtract this from the measured value to obtain the lattice term. However, the T^3 dependence observed below 5°K would have to be fortuitous, a significant contribution arising from electronic excitations above 4°K.

MERCURY AS A MODEL FOR Nb_3Sn

It is of interest to use similarity arguments to estimate the electronic contribution to the specific heat, and thereby infer the normal-state behavior over the entire range. While the principle of corresponding states has been extended empirically to strong-coupling superconductors with some success,[31] it is clear that for very-strong-coupling superconductors the details of the thermodynamic behavior will depend on the phonon density of states. Thus Pb, which has a slightly higher temperature dependence of $C_{es}/\gamma T_c$, and a higher specific-heat jump, has a lower gap than Hg. Nevertheless, the general behavior of the specific heat is similar for the two elements, and quite different than that for weak-coupling superconductors.[32] Taking Hg as the model, and normalizing to the reduced critical

[31] T. P. Sheahen, Phys. Rev. **149**, 368 (1966).

[32] There is some uncertainty over the behavior of Pb, many authors having taken the specific heat calculated from critical-field data [D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. **112**, 1888 (1958)] to indicate a departure from exponential behavior at low temperatures. However, this departure probably arises from the fact that the specific heat is obtained by differentiation of the critical-field polynomial in the region where the critical field is very nearly constant (H_0). When analyzed in the same way that Finnemore and Mapother treated the case of Hg, the Pb data are entirely consistent with an exponential dependence.

field at $t^2=0.7$ gives, by correspondence [$H_c/H_0=U(T/T_c)$ where U is a universal function] $H_0=5350$ G and $\gamma=13.1$ mJ/g at. °K^2. The inferred normal-state behavior is shown as the dashed line in Fig. 3. Similar results would be obtained by normalizing to the specific heat of Pb, with $\gamma=11.8$ mJ/g at. °K^2. However, as discussed above, the low-temperature data for Nb_3Sn are most readily interpreted in terms of a high-energy gap, consistent with that of Hg.

MAGNETIC FIELD MEASUREMENTS

The results are summarized in Table I, where $\kappa_1\equiv H_{c2}/\sqrt{2}H_c$. The specific-heat jump is related to the critical field in the Abrikosov theory as extended by Maki[33] by

$$\Delta C/T_c(H)=(\partial M/\partial H)\,(dH_{c2}/dT)^2$$
$$=[V/4\pi(1.16)\,(2\kappa_2^2-1)](dH_{c2}/dT)^2.$$

Values for the jump in Table I were obtained by taking $\kappa_1=\kappa_2$. H_{c2} is given closely by $H_{c2}=\sqrt{2}\kappa(t)5400(1-t^2)$, assuming the Gor'kov[34] temperature dependence for κ. The deviations at high fields are partially attributable to the broad transitions. The peak heights were obtained by taking the transition midpoints as $T_c(H)$ and idealizing the data so as to conserve entropy. The entropy at 18°K is found to be the same to 1.5% by integration of the zero-field data or the 52.5-kG data, an uncertainty of this order being introduced by the extrapolation of the high-field data to 0°K.

Assuming the Gor'kov dependence to hold down to 0°K, we get $\kappa_1(0)=27.2$, and $H_{c2}(0)=206$kG. Since the measured upper critical field is somewhat higher than this, (221kG),[35] Nb_3Sn does not appear to exhibit a paramagnetic limit, justifying the assumption that $\kappa_1=\kappa_2$.

The extrapolated intercept for the 52.5-kG data can be used to estimate γ, the specific heat being given by[36]

$$C_s(0,H)/T$$
$$=(\gamma/1.16)[0.16+h+h(1-h)\,T_c^2(\kappa''/\kappa)]+0.8=4.0,$$

where $h=H/H_{c2}(0)$. Taking $H_{c2}(0)=221$ kG, and assuming $\kappa=\kappa(0)\,(1+0.34t^2)^{-1}$, gives $\gamma=13.5$ mJ/g at. °K^2.

LATTICE SPECTRUM OF Nb_3Sn

The availability of low-temperature sound velocity data for single-crystal Nb_3Sn makes possible the calculation of the lattice specific heat near 0°K by means of the continuum model. The crystal measured by Keller and Hanak did not show the lattice transformation,[7] although the elastic constant for the soft shear mode, $(C_{11}-C_{12})/2$, was found to approach zero at 32°K with a linear temperature dependence, and it is assumed that the vanishing of this constant, at least to within experimental error, is a general characteristic of Nb_3Sn. However, it seems likely that the characteristic temperature is somewhat higher, since the transformation has been observed to occur at 43°K in similar crystal with a more typical lattice constant.[7]

The Debye temperature calculated from the elastic constants of Nb_3Sn is shown in Fig. 6 as a function of temperature, together with Θ calculated from the specific heat for both Nb_3Sn and Nb_4Sn. Since the Debye approximation is unrealistic for highly anisotropic materials, (cf. Fuchs),[37] we have investigated the consequences of using the more appropriate Born–von Karman procedure which cuts off the distribution of states in wave vector rather than in frequency. Treating the solid as monatomic, and taking the Brillouin zone to be a sphere of radius $Q=(6\pi^2N/V)^{1/3}$, where N/V is the number of atoms/unit volume, the density of states is given by

$$N(\omega)\,d\omega=\frac{V}{2\pi^2}\,\omega^2 d\omega\sum_{i=1}^{3}(4\pi)^{-1}\int\frac{d\Omega}{c_i^3(\Omega)}.$$

The cutoff is introduced by evaluating the integral

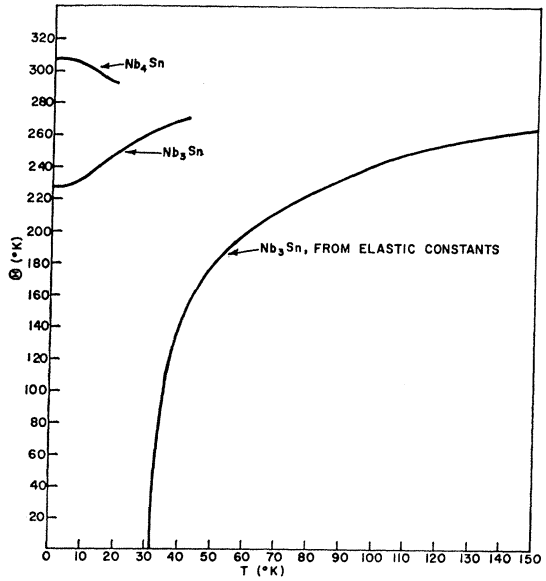

FIG. 6. Debye Θ versus temperature for Nb_3Sn from elastic constants and specific heat, and for Nb_4Sn from specific heat.

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over solid angle for

$$c_i(\Omega) \geq \omega/Q, \qquad Q = 1.47 \times 10^8 \text{ cm}^{-1},$$

all angular regions contributing the same total number of states, $3Nd\Omega/4\pi$. Solution of the equations of motion in terms of the elastic constants and direction cosines of the propagation vector[38] gives for the velocity of the soft shear mode near the [110] direction, for $C_{11} = C_{12}$,

$$\rho c^2 = [C_{44}/(C_{11}+C_{44})][(C_{11}+C_{44})\Delta\theta^2 + 4C_{11}\Delta\phi^2],$$

where ρ is the density, and $\Delta\theta$ and $\Delta\phi$ the azimuthal and polar deviations from the [110]$(\pi/2, \pi/4)$ direction. This linear angular dependence of the velocity gives $\Theta(T) = 0°\text{K}$ in the Debye model as long as $C_{11} = C_{12}$. Substituting into the density-of-states expression and integrating over angle, the frequency dependence is found to be

$$N(\omega) = 9 \times 10^{-3}\omega, \qquad (\hbar\omega/k < \sim 25°\text{K}),$$

differing from the usual result, which gives a quadratic dependence for a finite sound velocity. The two higher velocity modes will of course contribute a small quadratic term, but the low-frequency behavior will be dominated by this contribution from the soft mode. The specific heat should therefore vanish as T^2, rather than the usual T^3, suggesting a possible source of the low-temperature anomaly. However, the calculated specific heat, given closely by $C = 13T^2$ mJ/g at. °K below 5°K, is more than an order of magnitude too large at 1°K. This situation can be remedied in principle by choosing an appropriate dispersion relation, the lattice apparently being stiffer for high-frequency phonons, as suggested by Testardi and Bateman for the case of V_3Si.[39]

It is of interest to compare the lattice behavior of Nb_4Sn. This alloy is found to be a well-behaved, moderately-strong-coupling superconductor, with a specific-heat jump and temperature dependence below T_c close to the BCS values. The Debye temperature at 0°K is $\Theta = 307°\text{K}$, and the behavior above 9°K exhibits the deviations from the Debye limiting law usually observed as the result of normal dispersion, as shown in Fig. 6.

The major contribution to the change in elastic properties with change in stoichiometry arises from the renormalization of the sound velocity with the change in the density of states, which for the longitudinal mode at least, can be approximated by[40]

$$C/C' \approx [N'(0)/N(0)]^{1/2} \approx 1.4.$$

This implies $\Theta \sim 220°\text{K}$ for Nb_3Sn, in *qualitative* agreement with the low-temperature data, since the effect on the transverse modes is not taken into account.

The room-temperature elastic constants, which for typical metals provide a reasonable measure of $\Theta(0)$, indicate a value of $\Theta = 300°\text{K}$ for Nb_3Sn, with a slight upward trend in the elastic constants with temperature persisting to the highest experimental temperature. In terms of renormalization arguments, this implies a density of states similar to Nb_4Sn. This is not unreasonable in view of the strong temperature dependence of the magnetic susceptibility of the high T_c, β-W superconductors,[41,42] this dependence probably being related through extreme fine structure in the electronic density of states to the strong dependence of $N(0)$ on the Nb concentration in the Nb–Sn system.

However, the renormalization must be confined to low-frequency phonons. This is because the contribution to the specific heat arising from a change in zero-point energy with temperature, given by

$$C = \frac{d}{dT}\int_0^{\omega_m} N(\omega)\tfrac{1}{2}\hbar\omega d\omega,$$

which in the Debye approximation is

$$C = (9/8)\,Rd\Theta/dT,$$

is not observed.

In fact, it is reasonable to suppose that the bulk of the phonon spectrum, i.e., near the Debye frequency, is entirely unaffected by whatever mechanism is responsible for the lattice softening, strongly suggesting that the motivation for the lattice softening arises from the interaction of the acoustic mode with a temperature-dependent optical mode at $q = 0$, as first suggested by Anderson and Blount.[43]

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