

Heat Capacity of Solid He³†

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Exploratory specific-heat measurements have been made on solid He³ for the temperature range from 0.3 to 2°K and to 1800 bars pressure. The data for the relatively high-pressure hcp β He³ phase could not be represented by a Debye function, since anomalous behavior was found at low temperatures for the smaller molar volumes. Similar effects were found for the same phase in solid He⁴. The data for the low-pressure bcc α He³ phase could be described within experimental accuracy by the sum of a Debye function and an Einstein function representing two degrees of freedom. The characteristic temperatures which are associated with the Debye function and the Einstein function, respectively, were found to be functions of the molar volume, and to be linearly related. These data, together with earlier values of the thermodynamic parameters along the melting line given by other workers, were used to calculate the equation of state for α He³, and, hence, the thermal expansion and compressibility as a function of temperature and pressure. Several unusual features were found as a result of this analysis; these include the Einstein anomaly in the specific heat of α He³, the fact that the compressibility of α He³ is appreciably greater than that of the fluid or β He³ at the same molar volume, and the relatively large difference between the Debye θ 's for the α and β phases (about 20%) which differ in molar volume by only 0.5%. These effects do not appear to be due to nuclear ordering. No evidence for a previously predicted negative thermal expansion in α He³ was found.

I. INTRODUCTION

SOLID He³ is of basic interest for several reasons. Calculations by Bernardes and Primakoff¹ have indicated that nuclear antiferromagnetism should occur for this solid at temperatures which are much greater than those which would be calculated from dipole-dipole interactions alone. In addition, since both isotopes of helium can be obtained in quantity in isotopically pure form, a unique opportunity exists for the comparison of the effects on thermodynamic properties of a relatively large difference in isotopic mass. Finally, a low-pressure bcc modification (α He³) exists for solid He³,^{2,3} which most likely is a manifestation of large anharmonic forces between the helium atoms. Anomalous physical properties have been predicted for this solid near the minimum in the melting curve.^{4,5} The transition between α He³ and the higher pressure hcp form β He³ occurs at about 140 atm pressure at the melting line, and has been studied in some detail by Mills and Grilly.² Another phase transition from a hcp to a fcc structure occurs at higher temperatures and pressures.⁶ It is believed that these three phases also occur for He⁴, but the phase corresponding to α He³ (γ He⁴) occupies an almost inaccessible region of the He⁴ phase diagram.^{7,8}

The existing experimental data for solid He³ do not appear to fit into an easily recognizable pattern. Thermal conductivity measurements by Walker and Fairbank show normal behavior for β He³, in contrast with a more complex temperature dependence for α He³.⁹ Nuclear magnetic resonance measurements which have been reported by Adams, Meyer, and Fairbank¹⁰ indicate ordering effects in the solid below 0.3°K, while nuclear relaxation experiments by Goodkind and Fairbank¹¹ and Reich¹² can be interpreted in terms of self-diffusion in the solid. In none of these instances were pressures of more than a few hundred bars utilized. Frank¹³ has reported calorimetric measurements in the region of the α - β -melting line triple point for solid He³.

The objectives of the experiments which will be described below were essentially exploratory and qualitative in nature, and a preliminary discussion of the results has been published.¹⁴ Initially, it was hoped to use specific-heat data to obtain information about possible ordering of the nuclear spins in solid He³ at molar volumes ranging from the minimum in the melting line to 1800 bars pressure. The high temperature tail of a specific-heat anomaly associated with such ordering would be expected to vary as T^{-2} and to be clearly recognizable. We also had hopes of studying the α - β phase transition, and of obtaining data on the thermal properties of both α and β He³. These thermal

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¹ N. Bernardes and H. Primakoff, *Phys. Rev.* **119**, 968 (1960).

² E. R. Grilly and R. L. Mills, *Ann. Phys. (New York)* **8**, 1 (1959).

³ A. F. Schuch, E. R. Grilly, and R. L. Mills, *Phys. Rev.* **110**, 775 (1958).

⁴ R. L. Mills, E. R. Grilly, and S. G. Sydorik, *Ann. Phys. (New York)* **12**, 41 (1961).

⁵ L. Goldstein, *Ann. Phys. (New York)* **16**, 205 (1961).

⁶ A. F. Schuch and R. L. Mills, *Phys. Rev. Letters* **6**, 596 (1961).

⁷ J. H. Vignos and H. A. Fairbank, *Phys. Rev. Letters* **6**, 265 (1961).

⁸ N. Bernardes, Atomic Energy Commission Research and Development Report, Ames Laboratory, IS-285, 1960 (unpublished).

⁹ E. J. Walker and H. A. Fairbank in *Helium Three*, edited by J. G. Daunt (Ohio State University Press, Columbus, Ohio, 1960), p. 103.

¹⁰ E. D. Adams, H. Meyer, and W. M. Fairbank, in *Helium Three*, edited by J. G. Daunt (Ohio State University Press, Columbus, Ohio, 1960), p. 57.

¹¹ J. M. Goodkind and W. M. Fairbank, in *Helium Three*, edited by J. G. Daunt (Ohio State University Press, Columbus, Ohio, 1960), p. 52.

¹² H. A. Reich, in *Helium Three*, edited by J. G. Daunt (Ohio State University Press, Columbus, Ohio, 1960), p. 63.

¹³ J. P. Franck, *Phys. Rev. Letters* **7**, 435 (1961).

¹⁴ E. C. Heltemes and C. A. Swenson, *Phys. Rev. Letters* **7**, 363 (1961).

properties can be combined with data taken along the melting line to obtain considerable information about the equation of state of solid He^3 at both absolute zero and finite temperatures. In particular, the suggestion that solid He^3 exhibits a negative thermal expansion near the minimum in the melting curve could be tested.

II. EXPERIMENTAL DETAILS

A considerably modified ADL magnetic refrigerator was used to obtain temperatures down to 0.3°K . A sketch of the low-temperature experimental apparatus is given in Fig. 1. The arrangement of the thermal valves, reservoir, and magnetic fields in the upper part of the sketch is standard,¹⁵ except for the use of terbium metal as the heat reservoir. The susceptibility of a sphere of powdered potassium chrome alum as measured by a 33-cps Hartshorn bridge was used as the primary temperature standard and was calibrated against the vapor pressure of liquid helium above 1°K . This thermometer was used in turn to calibrate an "Old Speer" carbon resistor which was attached to the calorimeter. The susceptibility thermometer could be isolated from the calorimeter by the lead sample valve at the bottom of the engine. In practice, the susceptibility thermometer was disconnected from the calorimeter during the course of a heat capacity measure-

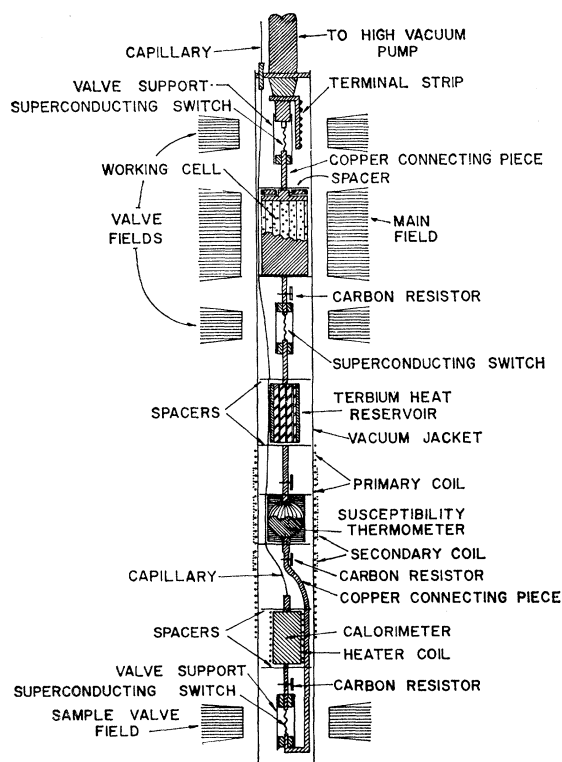


FIG. 1. A sketch of the magnetic refrigerator engine assembly. The surrounding 1°K liquid He^4 bath and associated Dewar system is not shown.

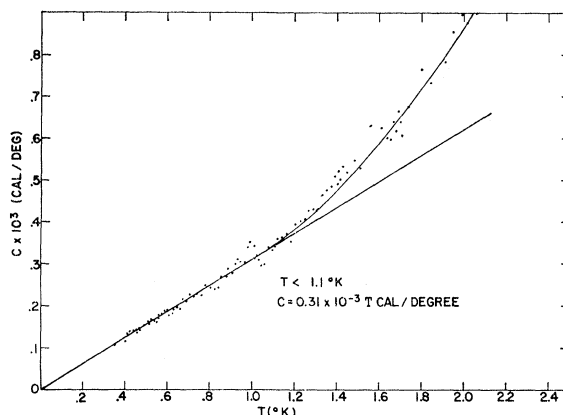


FIG. 2. The heat capacity of the high-pressure bomb and addenda as obtained with a vacuum in the bomb.

ment by reducing the sample valve field to zero. The thermometer currents were chosen to be sufficiently small so as to give a current-independent calibration. This was possible at all except the lowest temperatures. The lower limit of the magnitude of the thermometer current was set by the sensitivity of the 0-1 mV recording potentiometer which was attached to the galvanometer posts of a Rubicon type-B potentiometer and which was used to indicate temperature changes. No attempt will be made to describe the actual experimental procedures in any detail, since many obvious refinements were ruled out by the initial objective of performing a 5% exploratory experiment. In practice, the magnetic refrigerator engine was kept at 77°K or below during the course of a series of runs (6 weeks in one instance) and both the susceptibility and resistance thermometers retained their calibrations over this time.

The calorimeter (or high-pressure bomb) was constructed from hardened beryllium copper (Berylco 25, half hard) since this metal has the necessary yield strength (of up to 10 kbars at 4°K) to withstand the pressures in which we were interested. Stainless steel would have done as well from this standpoint, but a preliminary experiment showed that the electronic specific heats of the transition elements in this metal are so large as to make it unusable. The bomb itself was 1.125 in. long and 0.250 in. i.d. with 0.125-in. walls, weighed 45 g empty and had a volume of 0.78 cm^3 at 4°K . A pair of copper fins, silver soldered at right angles to each other, extended the length of the interior of the bomb, and were silver soldered to a copper rod which in turn came through the bottom of the bomb. These were intended to reduce effects due to thermal boundary resistance, which in practice were never observed. The resistance thermometer and the lead sample valve were attached to this copper rod. A $31\text{-}\Omega$ Manganin heater was varnished onto the outer surface of the bomb. High-pressure He^3 gas was admitted to the bomb through a piece of stainless steel hypodermic tubing (0.018 in. o.d., 0.004 in. wall, plugged with 0.006-in.-diam stainless-steel wire). This tubing was

¹⁵ J. G. Daunt, Proc. Phys. Soc. (London) **B70**, 641 (1957).

TABLE I. Summary of specific-heat data for He³ and He⁴.^a θ , θ' , and A are as defined in the text, and T_F and T_M are the temperatures at which upon cooling the calorimeter thermometer indicated, respectively, the beginning and the completion of solidification.

T_F (°K)	T_M (°K)	V (cm ³ /mole)	n (moles)	θ (°K)	ϕ (°K)	θ' (°K)	$A \times 10^3$ (cal/mole-deg ²)
αHe^3							
1.077	0.673	24.4	0.0319	17.8±0.4	6.3	17.6± 0.4	0
1.330	0.924	23.7	0.0329	18.8±0.3	7.7	18.8± 0.3	0
1.804	1.402	22.4	0.0348	21.1±0.4	10.4	21.1± 0.4	0
2.149	1.809	21.6	0.0361	23.3±0.3	11.7	23.8± 0.4	1.4
2.640	2.192	20.6	0.0378	26.1±0.3	14.5	26.6± 0.7	1.7
2.724	2.280	20.4	0.0381	26.3±0.3	14.3	27 ± 1	1.5
3.087	2.561	19.8	0.0393	27.8±0.3	15.1	29 ± 1	1.5
βHe^3							
3.192	2.693	19.6	0.0397	33.9±0.5		35.2± 0.5	2.0
3.320	2.814	19.5	0.0401	35.3±0.5		36.8± 0.8	2.1
3.75	3.08	18.9	0.0413	38.2±0.7		39.8± 0.6	2.2
5.12	4.24	17.6	0.0444	45.6±0.8		48.5± 1	2.0
6.70	5.59	16.3	0.0477	53.6±1.6		59 ± 2	1.9
6.97	7.64	15.1	0.0517	63 ±2		71 ± 3	1.8
10.25	8.76	14.5	0.0538	67 ±3		74 ± 3	1.3
13.02	10.85	13.5	0.0578	73 ±3		85 ± 5	1.2
15.27	12.96	12.8	0.0607	79 ±3		91 ± 5	1.2
19.14	16.33	12.0	0.0648	82 ±3		97 ± 8	1.1
He^4							
1.45	2.27	21.04	0.0370	24.2±0.3		24.6± 0.6	1.2
1.79	2.48	20.64	0.0377	26.2±0.6		27.1± 1.2	2.1
2.35	3.12	19.53	0.0399	29.5±1.3		30.3± 2	1.6
2.88	3.78	18.63	0.0418	33.7±0.8		35.4± 2	2.0
4.47	5.60	16.74	0.0465	43.6±1.3		46 ± 3	1.7
6.60	7.98	15.10	0.0516	53.6±1.6		56 ± 3	1.2
6.60	8.14	15.00	0.0519	50 ±3		59 ± 7	1.1
7.54	9.16	14.50	0.0537	58 ±2		61 ± 4	0.8
9.70	11.61	13.57	0.0574	69 ±4		77 ± 8	0.8
11.95	14.35	12.78	0.0610	79 ±5		81 ±11	0.7
14.12	16.85	12.21	0.0638	84 ±5		90 ±12	0.4
...	18.18	11.93	0.0653	88 ±5		101 ±16	0.7

^a See reference 17.

anchored thermally to the reservoir and working salt, and extended through the He⁴ bath to room temperature, where it was connected to a valve at the top of the Dewar system. The dead volume in this line (about 0.1 cm³) was, as will be pointed out below, relatively unimportant.

The specific heat of the calorimeter as determined in a blank run is shown in Fig. 2. The linearity of the data below 1°K indicated that our thermometry was

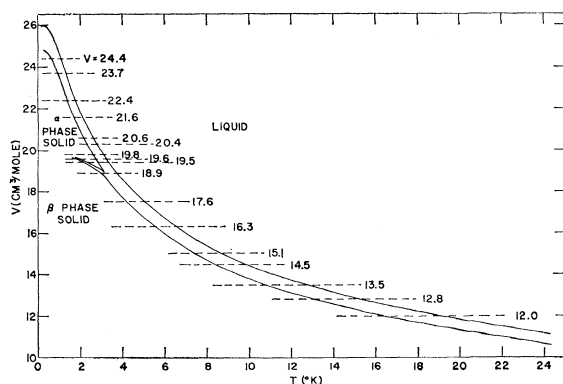


FIG. 3. The temperature-volume relationship for He³ along the melting line (references 2, 4). The dashed lines indicate the molar volumes at which heat-capacity data were taken.

adequate, while the magnitude of the specific heat is roughly that to be expected from a beryllium copper alloy of this composition (12 at. % beryllium). The sharp rise in the apparent specific heat above 1°K is believed to be due to heat leakage through the sample valve. Thus, any of our data which are obtained in this temperature region are suspect. A correction for this effect was applied to data taken above 1°K in the hopes that we could compensate in part for the heat leak and obtain a semiquantitative measurement of the specific heat in this temperature region.

The He³ gas which was used in these experiments was obtained from the AEC, and a mass spectrometric analysis made in this Laboratory¹⁶ showed it to contain less than 0.1% He⁴. The gas was stored in 1-liter metal containers at essentially one atmosphere pressure. The compression to pressures of the order of 1800 bars involved three steps. First, the He³ was pumped from the storage containers and compressed to roughly one atmosphere overpressure using a mechanical rotary pump. It was then bled into a 1.0 in. i.d. by 10-in. stroke high-pressure cylinder. This cylinder had a metal separator sealed by an "O" ring which isolated the He³ gas from the driving oil. The gas was compressed from

¹⁶ The authors are indebted to Professor H. Svec of the Ames Laboratory for carrying out this analysis.

this cylinder into a second high-pressure cylinder of like design which was 0.50 in. i.d. These cylinders could be isolated from each other by high-pressure valves. About 50 strokes of the larger cylinder plunger were necessary to transfer essentially all the He^3 gas (3 liters) from the storage containers into the high pressure cylinder. An air-driven high-pressure oil pump (30 000 psi maximum pressure) was then used to compress the He^3 to the maximum pressure used. The gas was kept under pressure continuously during the course of these experiments with no sign of leakage. The pressure in the oil driving the high-pressure cylinder was measured with a 40-kbar Heise gauge which was used only as an indicator.

A major problem in experiments of this type involves a knowledge of the amount of solid helium in the bomb. Precise values for the molar volumes of the fluid and solid along the melting line have been published,^{2,4} and it was decided to base our measurements on these data (Fig. 3). The procedure which was used involved first filling the Dewar surrounding the magnetic refrigerator engine with either liquid hydrogen or liquid He^4 , depending on the molar volume in which we were interested. If possible, the temperature of the bath was adjusted so as to be at the temperature at which solidification would start at the desired molar volume, and the pressure on the gas was raised to be at the solidification pressure corresponding to that temperature. For molar volumes where freezing occurred between 4 and 10°K, liquid hydrogen was used as an initial coolant, and the system was adjusted to be at a pressure which was slightly greater than the melting pressure and at a temperature which was as close to the melting temperature as could be obtained by pumping on solid hydrogen. The valve at the top of the capillary leading from the bomb was then closed, and the magnetic refrigerator engine cooled to 1°K

(by first removing the liquid H_2 if it had been used and then adding liquid helium). The capillary blocked with solid helium in the process, isolating the helium in the bomb. The temperature of the bomb was monitored during cooling using the carbon resistor, and the temperatures at which freezing *began* and was *completed* were noted as sharp breaks in the cooling curve. These two temperatures then served to give two independent values of the molar volumes of the He^3 in the calorimeter. The agreement was always within $\pm 0.1 \text{ cm}^3/\text{mole}$. The molar volumes and freezing temperatures are given for each run in Table I and are indicated in Fig. 3. No indication of slippage of the block in the capillary was ever observed.

III. RESULTS

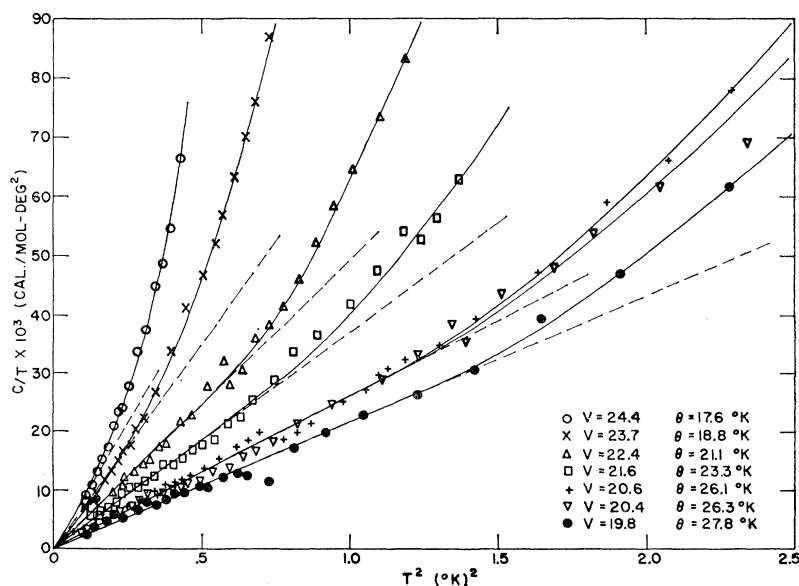
The results of specific-heat measurements which were taken at 17 different molar volumes are given in Figs. 4-6. This specific type of plot (C/T vs T^2) was used in order to emphasize the relative size of the calorimeter correction ($C/T = 3.1 \times 10^{-4} \text{ cal/deg}^2$ below 1°K, Fig. 2) and the data, and to show deviations from T^3 behavior. The different scales on the figures should be noted.

As was mentioned in an earlier report,¹⁴ the heat capacity data for αHe^3 could be interpreted as being of the form

$$C_v/3R = D(\theta/T) + 2E(\phi/T), \quad (1)$$

where $D(\theta/T)$ is the Debye function and $E(\phi/T)$ is the Einstein function, with θ and ϕ both being functions of the volume. The θ values were determined from the low-temperature T^3 regions of the curves in Fig. 4 as is indicated by the dashed lines. The anomalous high-temperature contributions to these data were obtained by subtracting the T^3 contribution from the observed specific heat. The temperature scale was then adjusted by an arbitrary factor for each molar volume until the

FIG. 4. Heat-capacity data for solid αHe^3 . The dashed lines indicate the magnitude of the assumed T^3 contribution.



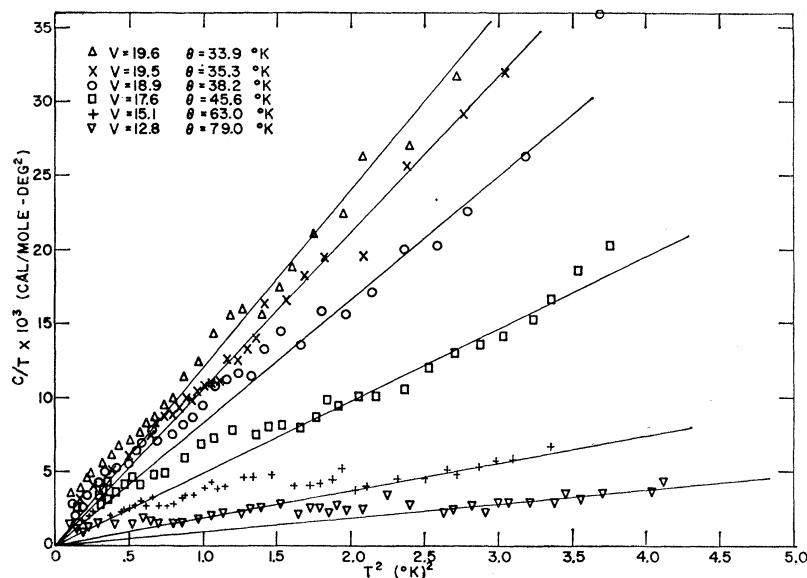


FIG. 5. Heat-capacity data for solid βHe^3 . The solid lines represent the heat-capacity contributions due to the values of θ which are tabulated in Table I.

various anomalous contributions coincided. The resulting curve (Fig. 7) was then found to obey an Einstein specific-heat function, with the values of ϕ that are indicated in the inset. The values of θ and ϕ which were used are given in Table I.

Figures 5 and 6 indicate a low-temperature anomaly which appears to occur in βHe^3 for the smaller molar volumes. This anomaly may also occur in the α phase, but if so, it is obscured by the magnitude of the normal specific heat. Two interpretations of these data are possible. First, one can assume that there is a true T^3 behavior, with an anomaly appearing at low temperatures. That is, in Figs. 5 and 6 a straight line is drawn from the high-temperature points to the origin, with the slope of this line being proportional to θ^{-3} . It is on this basis that the values of ϕ which are given in Table I were obtained. A second possibility involves assuming that there is an additional linear contribution to the specific heat of solid He^3 , and that the specific heat is

of the form

$$C_v = AT + 3RD(\theta'/T). \quad (2)$$

Hence, to obtain θ' , a straight line is drawn which no longer passes through the origin, but intersects the C/T axis at a positive value. This is the basis for the A and θ' values given in Table I. The two different methods of interpreting the data do not influence appreciably the values of ϕ which are given, since the low-temperature anomaly is small for the α phase. This low-temperature anomaly appears to be real, in view of the normal behavior of the runs with the empty calorimeter (Fig. 2). In order to clarify the situation somewhat, a number of similar experiments, analyzed in the same fashion, were done with solid He^4 using the same apparatus.¹⁷ A similar effect was found, and the results of these experiments are given in Table I.

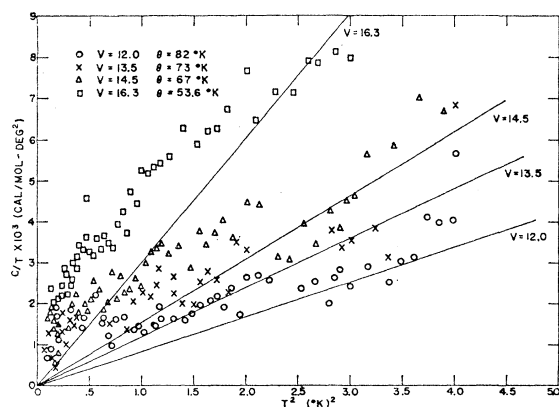


FIG. 6. Heat-capacity data for solid βHe^3 . The solid lines represent the heat-capacity contributions due to the values of θ which are tabulated in Table I.

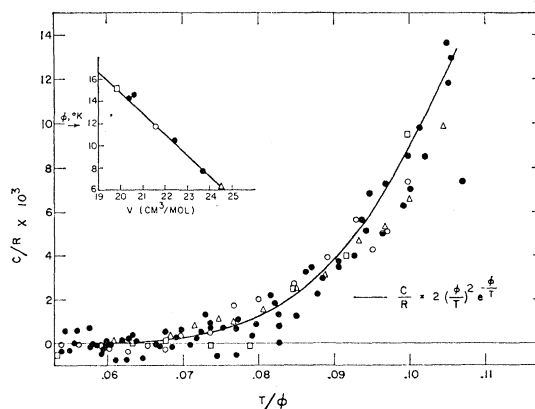


FIG. 7. The anomalous contribution (non- T^3) to the heat capacity of αHe^3 . The solid curve represents an Einstein function as is indicated.

¹⁷ H. H. Sample (unpublished), 1961.

IV. DISCUSSION

A. General

The volume dependence of the Debye θ 's for α and β He³ and for He⁴ is given in Fig. 8. The definition of θ for α He³ (and, indeed, for the smaller molar volumes of He⁴) depends on somewhat arbitrary criteria. In our original publication¹⁴ the θ 's were defined essentially by Eq. (1) after a comparison of our He⁴ results with those of Dugdale and Simon.¹⁸ Recently, Franck has measured the heat capacity of solid β He³ at small molar volumes and relatively high (above 4°K) temperatures,¹⁹ and it appears from a comparison of his data with ours that only the definition of θ' as given by Eq. (2) would give consistent results. Hence, it is the values of θ' (Table I) which are plotted in Fig. 8. The falling off of the data for the smaller molar volumes for β He³ is undoubtedly due to experimental errors, since the specific heat is small in this region.

The change in θ at the α - β He³ phase transition is clearly observable in Fig. 8. The difference in the θ 's is so large (29 to 35°K) that it was not difficult to ascertain whether or not a run was taken in the α or in the β phase, and we would estimate that at 0.3°K the transition occurs at a molar volume of roughly 19.7 (± 0.1) cm³ and a pressure of 110 bars. The very large change in θ at the transition implies a very great difference in the lattice properties of the α and the β phases, as has been discussed by Bernardes.²⁰ An attempt was made to investigate the α - β transition directly, but the thermal expansions of the two phases are so small that it did not prove possible to begin a run in the β phase and terminate it in the α phase (see Fig. 3). The ratio of the θ 's for the two isotopes of helium in their common hcp phase is given by $\theta_3/\theta_4 = 1.21$, which appears to be significantly different from that given by the elementary picture, $(4/3)^{0.5} = 1.15$. This is perhaps not surprising since anharmonic effects must play a large role even at the smaller molar volumes. The value of the Grüneisen constant, $\Gamma_\theta = -d \ln \theta / d \ln V = 2.50$, appears to be the same for both isotopes, and for both phases of He³, and to be close to that predicted by Bernardes.²¹ The almost perfect agreement between the θ values for He⁴ and α He³ would appear to be coincidental.

B. Thermodynamic Properties of α He³

Probably the most fruitful application of these data is to combine them with earlier data for the molar volumes and pressures along the melting line^{2,4} to obtain the equation of state of α He³. It is only for this phase that the data are sufficiently unambiguous and

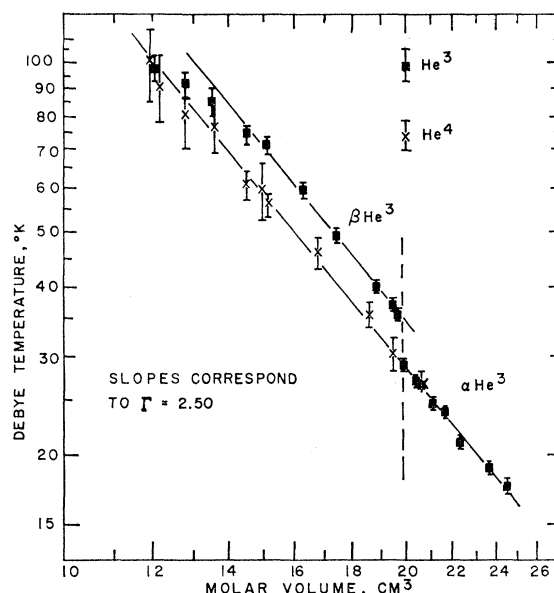


FIG. 8. The volume dependence of the Debye θ 's (θ' in Table I) for He³ and He⁴. The vertical dashed line represents the α - β phase transition in solid He³ at 19.7 cm³/mole.

extend to sufficiently high temperatures to make the analysis useful. A knowledge of the θ 's and ϕ 's as a function of volume [Eq. (1)] can be used to write down the free energy of α He³ as

$$F(T, V) = U_0(V) - T\Phi(\theta/T) - RT \ln[1 + 2 \exp(-\phi/T)]. \quad (3)$$

Here, $T\Phi(\theta/T)$ is the Debye contribution to the free energy, and the second term represents the Einstein contribution. The pressure for a given volume and temperature can be calculated as

$$P(V, T) = -(\partial F / \partial V)_T = -dU_0(V)/dV + \Gamma_\theta U_\theta^*/V - 2R(d\phi/dV) \exp(-\phi/T) \quad (4a)$$

$$= P_0(V) + P^*(V), \quad (4b)$$

where U^* is the Debye thermal energy. Thus, if this relationship [Eq. (4a)] is evaluated for the temperature and volume of the solid at the melting line, the last two terms give the thermal pressure contribution to the observed melting pressure, and $P_0(V)$ is the pressure needed to produce the same volume at absolute zero. These corrections are small (a few percent) and imply that the P - V relationship along the melting line is close to that for the P - V relationship at absolute zero. A similar consideration applies to He⁴.²²

Another quantity which is of theoretical interest is the isothermal compressibility or its reciprocal, the bulk modulus. The molar volume data which exist for the solid along the melting line^{2,4} can be differentiated

¹⁸ J. S. Dugdale and F. E. Simon, Proc. Roy. Soc. (London) A218, 291 (1953).

¹⁹ J. P. Franck (unpublished). The authors are indebted to Dr. Franck for making his results available to us prior to publication.

²⁰ N. Bernardes, Phys. Rev. Letters 8, 164 (1962).

²¹ N. Bernardes, Phys. Rev. 120, 1927 (1960).

²² See, for instance, J. S. Dugdale, Suppl. Nuovo cimento 9, 27 (1958).

to give

$$(dV^s/dP)_M = (\partial V^s/\partial P)_T + (\partial V^s/\partial T)_P dT/dP, \quad (5a)$$

or

$$k^s = -V^{s-1}(dV^s/dP)_M + \beta^s(dT/dP)_M, \quad (5b)$$

where $k^s = -(\partial \ln V^s/\partial P)_T$ and $\beta^s = (\partial \ln V^s/\partial T)_P$. The first term on the right-hand side and $(dT/dP)_M$ can be evaluated from the published melting parameter data.^{2,4} The isobaric thermal expansion β^s can be calculated directly from our data using the Mie-Grüneisen equation of state [Eq. (3)],

$$\beta^s = (k^s/V^s)(\Gamma_\theta C_\theta + \Gamma_\phi C_\phi), \quad (6)$$

where Γ_θ is as defined before, $\Gamma_\phi = -d \ln \phi/d \ln V$, and C_θ and C_ϕ are the contributions to the heat capacity due to the first and second terms, respectively, in Eq. (1). Hence, k^s can be evaluated along the melting line. The results of this calculation are shown in Fig. 9. In principle, Eqs. (5b) and (6) can be used only by making successive approximations for k^s . In practice, the correction term to Eq. (5b) is so small that this is unnecessary.

Equation (4) can be differentiated with respect to volume to give the contribution to the compressibility due to thermal vibrations. Here, Γ_θ and $d\phi/dV$, respectively, were assumed to be independent of volume. The values of k^s at absolute zero for αHe^3 and βHe^3 (obtained in much the same manner), as well as for the fluid,⁴ are given in Fig. 9 also.

The analyses which are outlined above emphasize the unusual properties of αHe^3 . Figure 9 shows that the compressibility of this phase is considerably greater than that of the fluid (or the β phase) for a given molar

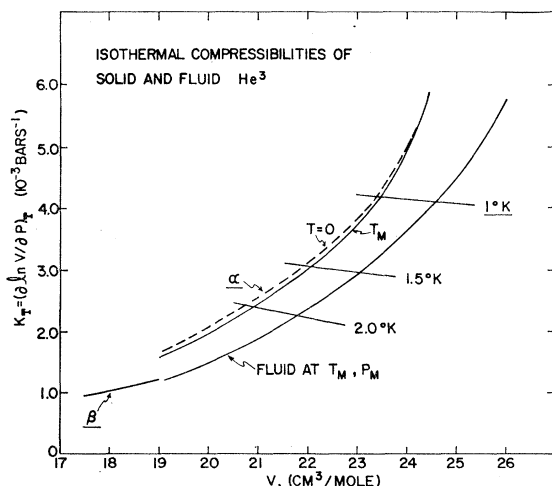


FIG. 9. The isothermal compressibilities of solid and fluid He^3 . The solid curves labeled T_M are evaluated along the melting line, where both the temperature and pressure are changing. The dashed curve refers to the k_T vs V relationship for the solid at absolute zero. The approximately horizontal solid lines join the molar volumes of the fluid and the solid which are in equilibrium with each other at the indicated temperature.

volume. This is undoubtedly associated in some manner with the same effects that produce the anomalously large difference in θ between the two phases, and the specific heat anomaly of Fig. 7. The thermal expansion would appear to be positive at all temperatures [Eq. (6)], and not to show the negative values which were predicted earlier from an analysis of the melting curve data.^{4,5} In part, the analysis which predicted this behavior relied on the postulate that at a given temperature the isothermal compressibility of the solid along the melting line should not be greater than that of the liquid in equilibrium with it. Figure 9 clearly shows that this is incorrect. We believe that all the existing thermodynamic data for solid He^3 can be made consistent (within experimental error) by the use of our data, and the resulting expression for the thermal expansion as given by Eq. (6). In particular, the thermal expansion for the solid never need become negative, although it approaches zero rapidly as T^3 near the minimum in the melting curve.

The thermodynamic consistency between our results and the earlier melting line data^{2,4} can be shown as follows: The temperature dependence of the difference in molar volume between the liquid and solid along the melting curve is given by

$$\frac{d(V^L - V^s)}{dT} = \frac{d\Delta V}{dT} = (V^L \beta^L - V^s \beta^s) - (V^L k_T^L - V^s k_T^s) dP/dT. \quad (7)$$

The earlier work gives $d\Delta V/dT = -0.2 \text{ cm}^3/\text{mole} - ^\circ\text{K}$ at 1°K .⁴ These data also give at 1°K $V^L = 24.63 \text{ cm}^3/\text{mole}$, $V^s = 23.52 \text{ cm}^3/\text{mole}$, $\beta^L = -3 \times 10^{-3} \text{ } ^\circ\text{K}^{-1}$, $k_T^L = 4.12 \times 10^{-3} \text{ bar}^{-1}$ and $dP/dT = 26.8 \text{ bar}/^\circ\text{K}$. If our data are used to give $k_T^s = 4.2 \times 10^{-3} \text{ bar}^{-1}$ and $\beta^s = 4.5 \times 10^{-3}$, and it is recognized that neither of the compressibility values is accurate to more than 5% or so, Eq. (7) can be used to calculate $d\Delta V/dT = -0.23 (\pm 0.20)$, to be compared with the directly measured value of -0.20 . The greatest problem in an analysis of this type involves the second term on the right-hand side of Eq. (7) which depends on the small difference between two very large numbers. This was, indeed, recognized earlier.⁴ The major suggestion given by the present work is that the anomalous behavior of He^3 along the melting line should be characterized by an abnormally large compressibility, not a negative thermal expansion.

The origin of the specific-heat anomaly shown in Fig. 7 is open to speculation. The values of ϕ which we obtain are very close to the activation energies for self-diffusion which were obtained by Reich in nuclear relaxation time experiments.¹² This suggests that the specific-heat anomaly could be due to the creation of vacancies.²³ This postulate is plausible, and also could

²³ See reference 12. The authors are indebted to Dr. H. A. Reich for pointing out the relationship between our data and his, and for suggesting this interpretation of the heat-capacity data.

possibly offer an explanation for the anomalous thermal conductivity of α He³.⁹ An empirical relationship usually appears to exist between the melting temperature T_m and the activation energies in the case of diffusion. A plot of ϕ vs the melting temperature is shown in Fig. 10. The curve is not linear since ϕ is a function of volume only, and the volume of the solid is practically independent of the temperature along the melting curve below 0.5°K. A similar plot of θ vs the melting temperature is given also. Outside of an additive constant, both θ and ϕ appear to be given by the same function of the melting temperature, implying that roughly

$$\phi(V) = [\theta(V) - 11]^\circ\text{K}. \quad (8)$$

V. CONCLUSIONS

The present data for the heat capacity of the hcp β He³ phase are sufficiently imprecise so as to preclude any definite conclusions as to its thermodynamic properties, other than to give a rough idea as to the volume dependence of the Debye θ . The ratio of the θ 's for the same crystallographic modifications of He³ and He⁴ is significantly different from the value which would be predicted from the elementary theory. In addition, a low-temperature anomaly appears to exist in the heat capacities of both He³ and He⁴ which is not understood at present, and which must be investigated further. No evidence was found for a nuclear contribution to the specific heat of He³ at any of the molar volumes which were investigated.

The properties of the bcc α He³ phase appear to be extremely interesting. It is fortunate that our data are more reliable in this temperature and pressure range due to a more favorable ratio of sample to sample holder heat capacity. Bernardes has shown that a bcc structure cannot be stable for a harmonic inert gas solid,²¹ and, indeed, anharmonic effects must be extremely important for this solid because of its low density. These effects appear to manifest themselves in a very high compressibility (as compared with the fluid or hcp phase at the same molar volume), in the specific-heat anomaly of Fig. 7, in an unusual temperature dependence of the thermal conductivity,⁹ in the nuclear relaxation time measurements,¹² and in the very large difference in the θ 's for the α and β He³ phases. Nuclear susceptibility measurements¹⁰ indicate that α He³ obeys Curie's Law above 0.3°K, so these effects most likely are not nuclear in origin. Thus, one would expect similar behavior for the corresponding (γ) phase of He⁴. The two characteristic temperatures which describe the

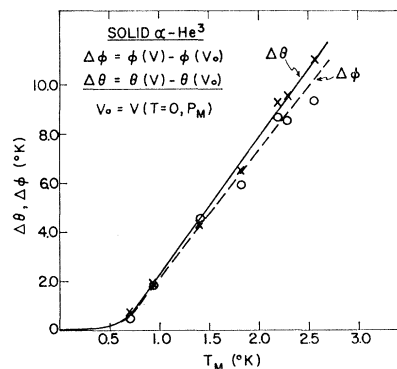


FIG. 10. The dependence of the parameters θ and ϕ on melting temperature for α He³. V_0 is the molar volume of the solid at the melting line at absolute zero, so $\Delta\theta$ and $\Delta\phi$ represent the increase in these parameters as the molar volume of the solid is increased from this value.

properties of α He³ appear to be closely related to each other as well as to the melting temperature. No real understanding of the basis for these various phenomena exists at present.

The experiments which have been reported here are capable of considerable refinement, and the results are such that these refinements should produce much more interesting information. In particular, α He³ would seem to offer an unusually good opportunity for the theoretical study of anharmonic effects. An investigation also should be made of the possibility that the low-temperature anomaly which was observed for β He³ will appear for other inert gas solids below 1°K.²⁴

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²⁴ Note added in proof. The existence of the specific-heat anomaly in α He³ has been confirmed by D. O. Edwards, A. S. McWilliams, and J. G. Daunt [Physics Letters 1, 218 (1962)]. The "anomalous" behavior suggested for β He³ in Figs. 5 and 6 can be represented roughly as a large (20 to 30%) decrease in the Debye temperature at 0.3°K from the high-temperature value θ given in Table I. F. J. Webb, K. R. Wilkinson, and J. Wilks [Proc. Roy. Soc. London A214, 546 (1952)] have reported heat-capacity measurements on He⁴ down to 0.6°K at three molar volumes near 19 cm³/mole. An analysis of these data in terms of θ_D vs temperature at constant volume as given in Wilkinson's thesis [J. Wilks (private communication)] suggests strongly that θ_D passes through a maximum and then decreases below 1°K. The magnitudes and temperature dependences of the θ 's which they report agree well with our data.