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Specific Heat and Other Thermodynamic Properties of Body-Centered-Cubic He^3†

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The heat capacity of bcc He^3 has been measured between about 0.4°K and the melting curve. The results are in excellent agreement with the recent specific-heat measurements of Sample and Swenson, and the two sets of data have been used to calculate the entropy, the pressure coefficient $(\partial p/\partial T)_V$, and, in conjunction with melting-curve data, the internal energy at melting and at 0°K. The values of $(\partial p/\partial T)_V$ are in excellent agreement with direct measurements except in a small temperature interval close to the melting curve. The internal energy at 0°K, U_0/R, ranges from -1.05 deg K at 24.0 cm^3/mole to $+1.93$ deg K at 20.0 cm^3/mole, and is about 4 deg K below the theoretical values of Koehler and Horner and about 1.0 deg K below those of Hansen and Levesque. Measurements of the discontinuous change in heat capacity on melting have been used to obtain values for the compressibility of the solid which are in good agreement with those from other methods and which range from 4.8×10^{-3} atm^{-1} at $V=23.5$ cm^3/mole to 1.75×10^{-3} atm^{-1} at $V=19.7$ cm^3/mole.

INTRODUCTION

THIS paper reports measurements of the specific heat at constant volume of bcc He^3 in the temperature range from 0.3°K to the melting point. In describing the work we have tried to complement the recent paper by Sample and Swenson[1] on the specific heat of both bcc and hcp He^3. We find that the two sets of experimental data are in excellent agreement and it has, consequently, not been necessary to discuss some questions at length which have been rather thoroughly dealt with by Sample and Swenson. An example is the strong temperature dependence of the Debye Θ of bcc He^3 and its origin in some unusual type of lattice excitation or imperfection. The reader is referred to Sample and Swenson's paper for an excellent introduction to this and other problems connected with solid He^3. The present paper contains extended calculations of the thermodynamic functions including the internal energy at 0°K and, in addition, measurements of the discontinuous change in heat capacity at melting from which values of the compressibility have been obtained.

EXPERIMENTAL

The experimental method was exactly the same as that used in our other work[2,3] on solid He^4 and described in an earlier paper[2] to which we refer the reader for details. The specimens of solid He^3 were held in a sintered copper calorimeter of volume 0.280 cm^3, using the blocked capillary method. The calorimeter was cooled by adiabatic demagnetization via a thin indium thermal switch and the temperature measurements were made with a cerium magnesium nitrate magnetic thermometer. The density of the samples was determined from the freezing and melting points and from the amount of gas evolved on warming to room temperature. The purity of the gas was measured with a mass spectrometer to be 0.03% He^4.

RESULTS

Heat Capacity

The experimental results are shown as Debye Θ's in Fig. 1 for the four molar volumes that we investigated. The continuous lines on this figure represent the measurements of Sample and Swenson[1] (SS) which supersede the earlier, less precise, measurements of Heltemes and Swenson.[4] At higher temperatures, above 0.5°K or so, the data of SS and the present results are in excellent agreement, both in the temperature dependence of Θ and in the volume dependence which is shown more clearly in Fig. 2 and which is discussed below. As SS have observed, the temperature dependence of Θ for bcc He^3 cannot be represented in a simple reduced form like that used[2] for hcp He^3 and He^4.

The low-temperature results in Fig. 1 show the Debye Θ dropping with decreasing temperature, an effect which has been observed in all previous measurements[1,4–6] on bcc He^3 and in some measurements of hcp He^3 and He^4.[1,4–7] The origin of this effect is unknown; its magnitude seems to depend on the experimental arrangement and it is associated with a relaxation of the temperature of the calorimeter just after the heating period. The relaxation effect lasts for a few seconds and appears to be longer in the samples of higher density.

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[1] H. H. Sample and C. A. Swenson, Phys. Rev. **158**, 188 (1967).

[2] D. O. Edwards and R. C. Pandorf, Phys. Rev. **140**, A816 (1965).

[3] D. O. Edwards and R. C. Pandorf, Phys. Rev. **144**, 143 (1966).

[4] E. C. Heltemes and C. A. Swenson, Phys. Rev. **128**, 1512 (1962).

[5] A. S. McWilliams, Ph.D. thesis, Ohio State University, 1962 (unpublished).

[6] D. O. Edwards, A. S. McWilliams, and J. G. Daunt, Phys. Rev. Letters **9**, 195 (1962).

[7] J. P. Franck, Phys. Letters **11**, 208 (1964).

Sample and Swenson have suggested that this effect is due to the filling tube; other possibilities are that it is caused by ordering of the nuclear spins, some type of lattice defect which is in thermal equilibrium,[7] or ordering of the small amounts of He^4 impurity which are present.[6] As we discussed in our earlier paper[2] on He^4, and as has been shown in the recent work of Ahlers,[8] the effect does not seem to exist in well-annealed, pure samples of He^4. The possibility that it is due to simple spin ordering seems very unlikely since the results of nuclear resonance and other experiments[9] show that the exchange integral is too small to account for the magnitude of the observed anomalies in the specific heat. There is a possibility that the effect is associated with both the He^3 nuclear spins and He^4 impurity acting together since there is evidence[10] that in the neighborhood of He^4 impurity atoms there is increased exchange coupling between He^3 spins and consequently an enhanced spin heat capacity. Against this hypothesis is the fact that in measurements by Edwards, McWilliams, and Daunt[6] on samples of three different purities, 0.03%, 0.1%, and 0.3%, there were no changes in the anomalous specific heat with purity, at least above 0.3°K. This fact can be used as evidence against the hypothesis of simple isotopic ordering as well, although it must be remembered that in certain circumstances, e.g., below the temperature for phase separation in the solid, the specific heat due to He^4 impurity can become independent of concentration.[6]

The explanation suggested by Sample and Swenson[1] is that, owing to the fairly high thermal conductivity of solid helium, a larger proportion of the specific heat of the metal filling tube is included in the measurements when the calorimeter is full than when it is empty. Unpublished measurements by McWilliams on a few centimeters of stainless steel capillary tubing showed that the heat capacity might be sufficiently large at low temperatures to account for the effect, but quantitative agreement with the observations is poor. What is especially puzzling is the absence of any effect in solid He^4. All that can be said at the present time is

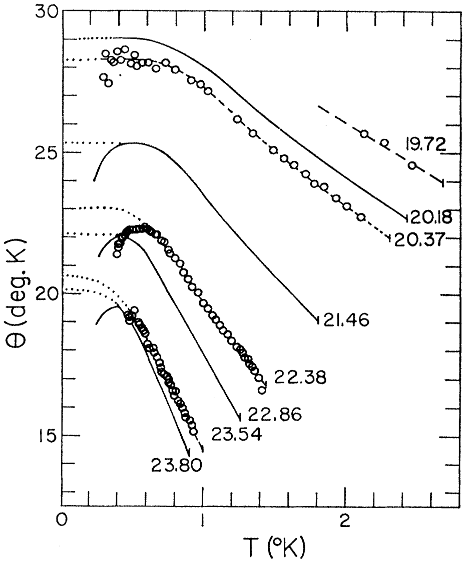

FIG. 1. The Debye Θ of bcc He^3 versus temperature. The solid lines give the results by Sample and Swenson (Ref. 1). The circles with dashed lines drawn through them represent the present data. The short vertical lines give the melting temperature for each volume. The dotted line represents the extrapolation to absolute zero used in the calculation of the lattice entropy, etc., after Sample and Swenson. The sample with volume $V=19.72$ cm³/mole entered the hcp-bcc region at lower temperatures.

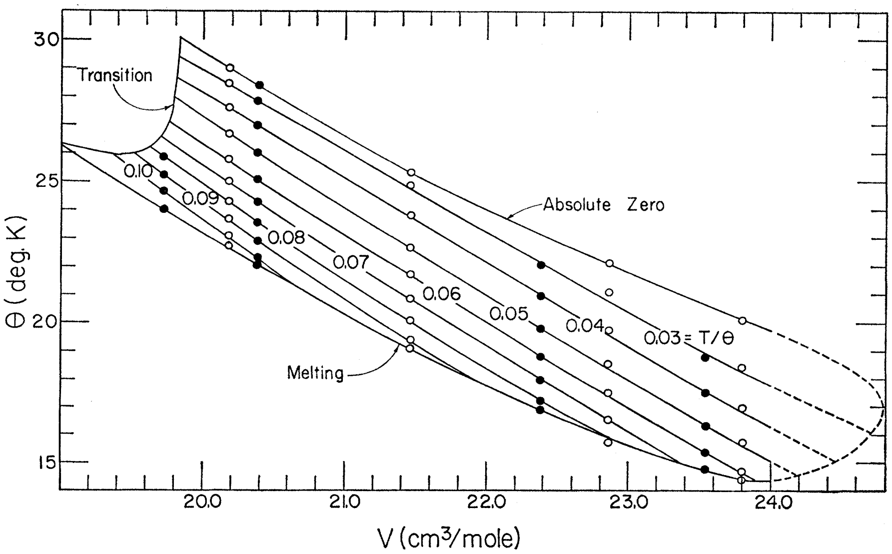

FIG. 2. Smoothed data for the Debye Θ of bcc He^3 at constant T/Θ, at melting and at 0°K versus molar volume. The open circles represent the data by Sample and Swenson (Ref. 1), the closed circles represent the present data.

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[8] G. Ahlers, Phys. Letters **22**, 404 (1966).

[9] See, for example, M. F. Panczyk, R. A. Scribner, G. C. Straty, and E. D. Adams, Phys. Rev. Letters **19**, 1102 (1967).

[10] See, for example, R. P. Giffard and J. Hatton, Phys. Rev. Letters **18**, 1106 (1967); H. D. Cohen and W. M. Fairbank (to be published).

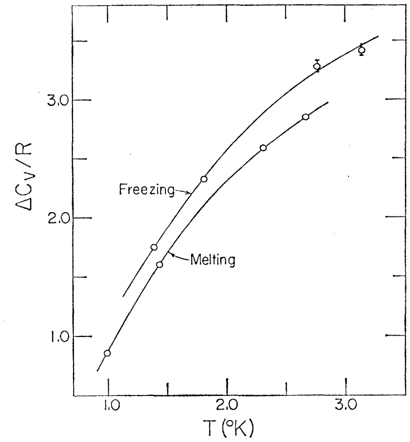

FIG. 3. The discontinuous change in the heat capacity of He^3 at freezing and at melting at constant volume.

that the position is still unclear and that more extensive and systematic study must be made to clear up this point.

In order to make a more direct comparison between the results of Sample and Swenson[1] and our measurements, the Debye Θ for various values of T/Θ is plotted against the molar volume V in Fig. 2. This plot demonstrates the excellent agreement between SS and the present data in all but the very-low-temperature results. The points in Fig. 2 represent interpolations and extrapolations of the results given in Fig. 1. The filled-in points were obtained from the present data, while the open points were obtained from SS. The absolute zero curve was drawn mainly from the extrapolations of SS. The heat capacity at low pressure along the melting line has not been measured, so that the part of the diagram above 24 cm^3/mole is only approximate and is shown dashed. Since helium remains liquid down to absolute zero, the curve of the Debye Θ at absolute zero intersects the curve of Θ at melting. At higher pressure bcc He^3 makes a transition to hcp He^3. The bcc-hcp transition line has been sketched in on the basis of the volume-temperature measurements of Straty and Adams[11] and extrapolations of the specific-heat data.

Some specific-heat measurements were carried out in the liquid phase of He^3 and these are reported elsewhere.[12] In passing through the two-phase, liquid+solid region the discontinuities in the specific heat at melting and freezing were observed. The results are presented in Fig. 3; they are discussed below in connection with the compressibility.

Entropy

The entropy of the solid was computed by direct integration of smoothed values of the specific-heat data for three of the volumes. The low-temperature anomalies in the specific heat were ignored in all the calculations and we extrapolated the Debye Θ to absolute zero in a way similar to that used by Sample and Swenson. We assume that this extrapolation, shown by dotted lines in Fig. 1, represents the lattice specific heat and does not include contributions from the nuclear spins or He^4 impurity. Above 0.6°K, it may be safely assumed that the total entropy of pure He^3 is $(R \ln 2)+S^l$, where S^l is the lattice entropy. In extrapolating the data, the values of Θ at 0°K have been chosen to agree with those given by SS as shown in Fig. 2. Although the proper method of extrapolation is quite uncertain, it is unlikely that the resulting error in S^l is more than $\pm 3\times 10^{-4}R$.

Values of S^l at melting are presented in Fig. 4 as closed circles for our data and as triangles for extrapolations of the entropy data of SS. To avoid confusion, the points for temperatures lower than melting are not shown but the two sets of data agree with the drawn curves within about 3%. The point represented by the square at 0.8°K was calculated from the entropy of the liquid and the entropy of melting measured by Mills, Grilly, and Sydoriak.[13] The entropy of the liquid at the saturated vapor pressure was taken from the analysis of Roberts, Sherman, and Sydoriak[14] corrected to the melting curve using the measurements of Boghosian, Meyer, and Rives[15] on the entropy of compression of liquid He^3. Of course, Rln2 has been subtracted from this point so as to compare it with the lattice entropy of the solid.

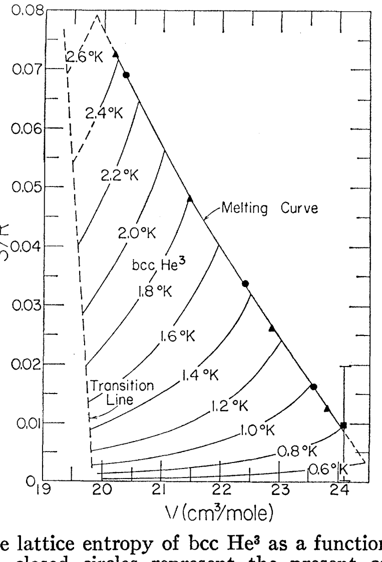

FIG. 4. The lattice entropy of bcc He^3 as a function of molar volume. The closed circles represent the present calculations extrapolated to melting; the triangles represent the data of Ref. 1. For the sake of clarity the points at lower temperatures have been omitted. The square represents the melting entropy of the solid calculated from the freezing entropy of the liquid (see text).

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[11] G. C. Straty and E. D. Adams, Phys. Rev. **150**, 123 (1966).

[12] R. C. Pandorf, E. M. Ifft, and D. O. Edwards, Phys. Rev. **163**, 175 (1967).

[13] R. L. Mills, E. R. Grilly, and S. G. Sydoriak, Ann. Phys. (N. Y.) **12**, 41 (1961).

[14] T. R. Roberts, R. H. Sherman, and S. G. Sydoriak, J. Res. Natl. Bur. Std. **68A**, 567 (1964).

[15] C. Boghosian, H. Meyer, and J. E. Rives, Phys. Rev. **146**, 110 (1966).

The bcc-to-hcp transition line, shown dashed in the entropy diagram, was drawn on the basis of the volume-temperature data of Straty and Adams[11] and extrapolation of the entropy curves to the bcc-hcp phase boundary.

Pressure Coefficient, $(\partial p/\partial T)_V$

Figure 2, which summarizes both our data and those of SS, was found to be a convenient diagram from which to work in computing the other thermodynamic functions. First the "pressure coefficient" which is the ratio of expansion coefficient to compressibility α/κ was determined by integrating the volume coefficient of the specific heat:

$$\alpha/\kappa=(\partial p/\partial T)_V=(\partial S/\partial V)_T=\int_0^T T^{-1}(\partial C_v/\partial V)_T dT$$

$$\approx\int_0^T T^{-1}(\delta C_v/\delta V)_T dT. \quad (1)$$

From Fig. 2, Θ-versus-T curves were obtained at volume intervals δV of 0.4 cm³/mole. From these curves, values of $(\delta C_v/\delta V)_T$ as a function of temperature were obtained at average volumes in the range 20 to 24 cm³/mole. Integrating $(\delta C_v/\delta V)_T$ with respect to T then gave the values of $(\partial p/\partial T)_V$ shown in Fig. 5.

Adams, Straty, and Wall[16–18] have made direct measurements of $(\partial p/\partial T)_V$ for bcc He³ using a capacitor pressure gauge. Some of these measurements, taken from Straty's thesis,[18] are given as the circles in Fig. 6 together with appropriate interpolated curves from the present data. It may be seen that the agreement is excellent except in an interval of about 0.08°K next to the melting curve. Here the direct measurements rise much more slowly with temperature with the result that there is a serious discrepancy in the values at melting, shown by the dashed line (direct measurements) and the dash-dotted line (deduced from the specific heat). At least part of this discrepancy is due to a systematic effect in the direct measurements, since more recent data, quoted in Straty and Adams's paper,[17] made in an apparatus with a narrower filling tube, are in much better agreement with the specific-heat results. We should also point out that the specific-heat measurements were not usually taken within 0.08°K of melting and in those cases in which they were, we observed a slightly more rapid rise in the specific heat which was attributed to "premelting," i.e., premature melting of small parts of the sample due to pressure inhomogeneities. Similar but much larger effects were observed in our work on solid He⁴.[2,3] In the calculation of $(\partial p/\partial T)_V$, the almost linear dependence of Θ on T seen in Fig. 1 was assumed to continue into the region of the melting curve.

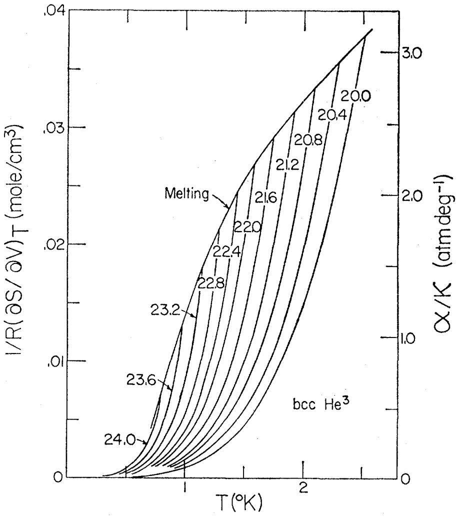

FIG. 5. The pressure coefficient $\alpha/\kappa=(\partial p/\partial T)_V=(\partial S/\partial V)_T$ for bcc He³, calculated from the heat capacity. The numbers give the volumes for each curve in cm³/mole.

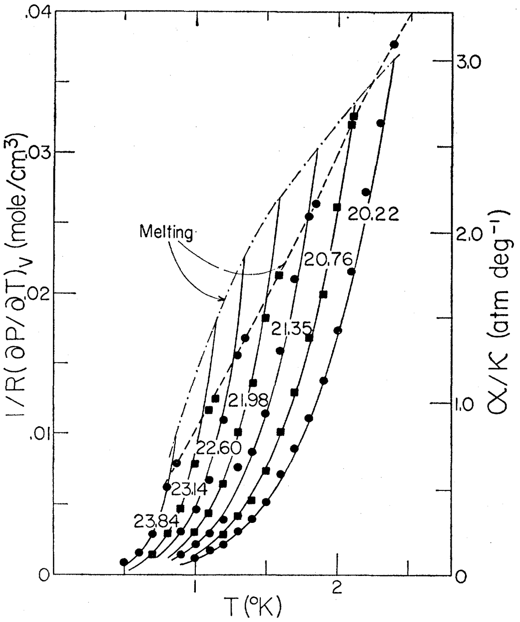

FIG. 6. The pressure coefficient $(\partial p/\partial T)_V=\alpha/\kappa$, calculated from the heat capacity and represented by the continuous curves, compared with the direct measurements of Straty and Adams (Ref. 17) represented by the points. The numbers give the volumes for each curve in cm³/mole. The dashed curve has been drawn through the direct measurements at melting, the dot-dash line represents the melting curve calculated from the heat capacity.

Internal Energy

The curves of $(\partial p/\partial T)_V$ deduced from the specific heat have been integrated with respect to T to give the change in pressure between absolute zero and melting, p_m-p_0, as a function of volume. From the melting curve data of Grilly and Mills[19] and Mills, Grilly, and

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[16] E. D. Adams, G. C. Straty, and E. L. Wall, Phys. Rev. Letters **15**, 549 (1965).

[17] G. C. Straty and E. D. Adams (to be published).

[18] G. C. Straty, thesis, University of Florida, Gainesville, Fla., 1966 (unpublished).

[19] E. R. Grilly and R. L. Mills, Ann. Phys. (N. Y.) **8**, 1 (1959).

TABLE I. Properties of bcc He^3 at melting and at 0°K. S^l is the lattice entropy, α and κ are the expansion coefficient and the compressibility. The suffix m refers to the melting curve; the suffix 0 refers to 0°K.

V (cm^3/mole)	T_m (°K)	p_0 (atm)	p_m-p_0 (atm)	U_0/R (deg K)	$(U_m-U_0)/R$ (deg K)	$S_m{}^l/R$	α_m/κ_m (atm/deg)
19.5	2.80	115.0	1.84[a]	2.53[a]	0.195[a]	···	3.3_4[a]
20.0	2.51	99.2	1.53	1.93	0.150	0.076_3	3.3_1
20.5	2.24	86.8	1.23	1.35	0.117	0.066_2	2.8_8
21.0	2.00	75.9	0.99	0.86	0.089	0.056_6	2.6_6
21.5	1.78	66.3	0.78	0.43	0.067_5	0.047_8	2.4_5
22.0	1.58	58.2	0.59	0.05	0.050	0.039_8	2.2_1
22.5	1.39	51.5	0.44	−0.28	0.036	0.032_2	1.9_4
23.0	1.20	44.9	0.30	−0.57	0.024_5	0.024_6	1.5_8
23.5	1.00	39.4	0.19	−0.83	0.014_5	0.017_2	1.1_3
24.0	0.80	34.7	0.08	−1.05	0.004_8	0.010_0	0.6_2

[a] Extrapolation.

Sydoriak,[13] we then determined p_0, the pressure at absolute zero, as a function of volume. Since the calculations were made using the *lattice* specific heat only, we have ignored all effects that the low-temperature ordering of the nuclear spins have upon the pressure. Since the ordering presumably takes place at an extremely low temperature, the effect on p_0 will be very small.

The internal energies at 0°K, U_0, and at melting, U_m, were estimated in the following way: First a "reference" value of U_m on the melting curve at 1°K was calculated. Starting with the internal energy of the vapor at zero density, $\frac{3}{2}RT$ at 1°K, we obtained the energy of the liquid at the saturated vapor using the virial coefficients of the vapor and the latent heat of vaporization given by Roberts, Sherman, and Sydoriak.[14] The energy of compression from the liquid at the saturated vapor pressure to the freezing liquid at 1°K was computed using the data of Sherman and Edeskuty[20] with the correction given by Grilly and Hammel.[21] This calculation gives $U_m(1°\text{K})/R=-0.826$ deg K. Integration of C_v with respect to T then gave (U_m-U_0) as a function of V from which, with $U_m(1°\text{K})$, one obtains $U_0/R=-0.830$ deg K at $V=23.50$ cm^3 per mole. The variation of U_0 with V was obtained by integration of p_0 with respect to V.

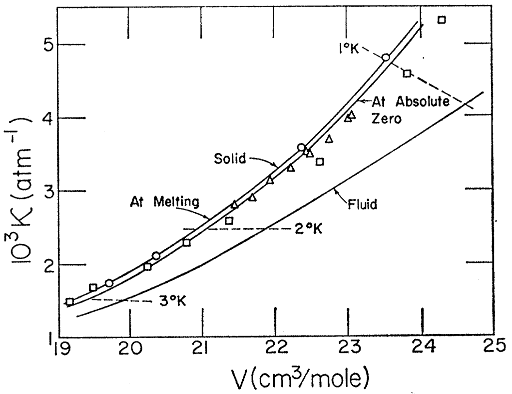

FIG. 7. The compressibility of He^3 as a function of molar volume. The circles represent the compressibility at melting as computed from the discontinuity in the heat capacity at melting using Eq. (2). A curve marked "at melting" has been drawn through these points. The curve marked "at absolute zero" was calculated from the melting values using Eq. (3). The other points represent values near melting; the triangles are from Grilly (Ref. 22), the squares from Straty and Adams (Refs. 17 and 18). For comparison the compressibility of the fluid at freezing is also shown (Refs. 13, 20, and 22). The dashed lines link the compressibility for the fluid and solid in equilibrium at 1, 2, and 3°K.

The results of all these calculations are given in Table I which also gives some other melting properties of bcc He^3. The uncertainties in the melting values of $(\partial p/\partial T)_V$ mentioned in the discussion of Fig. 6 produce only small uncertainties in the derived quantities in Table I, e.g., about ±0.001 deg K in U_0/R.

Compressibility and Expansion Coefficient

The compressibility of the solid at melting has been calculated from the discontinuous change in heat capacity at melting using the relation[2]

$$\kappa_m=\Delta C_v/VT[(\partial p/\partial T)_{V,\text{melt}}-dp/dT]^2, \tag{2}$$

where V, T, and dp/dT were taken from Grilly and Mills,[19] $(\partial p/\partial T)_{V,\text{melt}}$ from Fig. 5, and ΔC_v from Fig. 3. The term in $(\partial p/\partial T)_{V,\text{melt}}$ is only a small correction compared to dp/dT in Eq. (2). The resulting values of κ_m are presented as open circles in Fig. 7, with a continuous line drawn through the points. The compressibility at absolute zero, κ_0, was computed from κ_m and the equation

$$\frac{1}{\kappa}-\frac{1}{\kappa_0}=-V\left[\left(\frac{\partial p}{\partial V}\right)_T-\frac{dp_0}{dV}\right]=-V\left[\frac{\partial}{\partial V}(p-p_0)\right]_T. \tag{3}$$

The right-hand side of this equation was computed from our values of $p-p_0$. The compressibility at absolute zero is shown as a solid line in Fig. 7.

Some direct measurements of the compressibility near melting are also presented in Fig. 7. The values shown by the squares are those of Straty and Adams[17,18]

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[20] R. H. Sherman and F. J. Edeskuty, Ann. Phys. (N. Y.) 9, 522 (1960).

[21] E. R. Grilly and E. F. Hammel, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1961), Vol. II, p. 122.

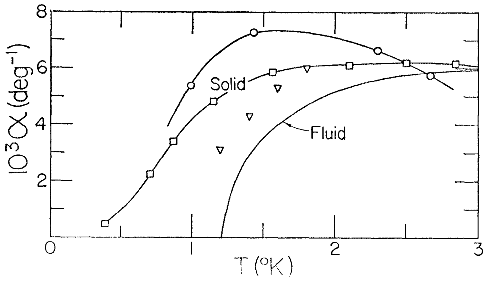

FIG. 8. The expansion coefficient of bcc He^3 at melting. The circles represent the present results determined from the ratio α/κ at melting, Fig. 5, and from the compressibility at melting, given in Fig. 7. The squares are from Ref. 17 and the triangles from Ref. 22. The expansion coefficient of the fluid at freezing is also shown (Ref. 19).

and the triangles are measurements by Grilly.[22] The direct measurements are lower than our values but for the most part are within 5% of them which can be considered as fairly good agreement. Earlier values of κ and κ_0 from specific-heat data by Heltemes and Swenson[4] (not shown in the figure) are also somewhat lower than the present results.

The expansion coefficient α has been computed from the compressibility and the values of α/κ at melting given in Fig. 5. The results are presented as open circles in Fig. 8. Direct measurements by Straty and Adams[17] are given as squares and measurements by Grilly[22] as triangles. The difference between our results and the direct measurements of Straty and Adams is due partly to the discrepancy in the values of κ used (Fig. 7), and partly to the discrepancy in the values of $\alpha/\kappa = (\partial p/\partial T)_V$ at melting which we discussed in connection with Fig. 6. As we pointed out before, the discrepancy between our values of $(\partial p/\partial T)_V$ and those of Straty and Adams only appears in a narrow region close to the melting curve.

COMPARISON WITH THEORY

The theory of quantum crystals as it has been applied to bcc He^3 (see, for example, Refs. 23 to 27) is in fairly good agreement with experimental data as far as the pressure and compressibility, the velocities of sound and the Debye Θ at 0°K are concerned. A comparison between theory and experiment for these properties has been made in several papers by other authors[23–27] and it would be superfluous to include a detailed discussion here. Recently de Wette, Nosanow, and Werthamer[27] have calculated the temperature-dependent Debye Θ for bcc He^3 from theory and have compared it with the results of SS which, as we have seen, are in agreement with the present data. The theoretical values of Θ at 0°K are some 15–20% higher than the estimated experimental values, although this may not be significant in view of the uncertainty in extrapolating the data to 0°K. A more serious difference is that the theoretical Debye Θ's have a much weaker temperature dependence which can be expressed in reduced form, $\Theta = f(T/\Theta_0)$, where Θ_0 is the value at 0°K. The experimental data cannot be reduced in this way. A similar discrepancy exists for He^4: The theoretical[27] Θ for bcc He^4 at $V = 21$ cm^3/mole, $T = 1.62$ °K is 23.5 deg K compared to the experimental[3] value 16.9 deg K. Finally we consider the problem of the energy at absolute zero, for which we gave experimental values in Table I and which we have compared with the most recent theoretical results in Fig. 9. All the theories except that of Iwamoto and Namaizawa[28] are variational calculations and give upper limits for the energy. The accuracy of the approximations made by Iwamoto and Namaizawa is not yet known, and they have remarked that their agreement with experiment may be partly a coincidence. In any case it is clear that neither their calculation nor that of Hansen and Levesque[29] is in good agreement as far as the pressure, that is, $-dU_0/dV$, is concerned.

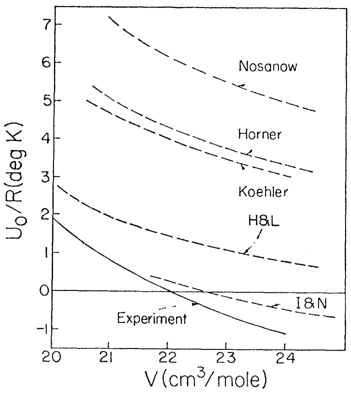

FIG. 9. The energy of bcc He^3 at 0°K as a function of molar volume. The curve labelled "experiment" is the present data. The theoretical curves are: Nosanow (Ref. 23); Koehler (Ref. 25); Horner (Ref. 26); I&N, Iwamoto and Namaizawa (Ref. 28); and H&L, Hansen and Levesque (Ref. 29).

ACKNOWLEDGMENTS

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[23] L. H. Nosanow, Phys. Rev. **146**, 120 (1966).

[24] L. H. Nosanow and N. R. Werthamer, Phys. Rev. Letters **15**, 618 (1965).

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[26] H. Horner, Z. Physik **205**, 72 (1967).

[27] F. W. de Wette, L. H. Nosanow, and N. R. Werthamer, Phys. Rev. **162**, 824 (1967).

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