

Compression of Solid He³ and He⁴ to 20 000 Bars*

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For purposes of comparison, we have measured the compression of both solid He³ and He⁴ at 4.2°K up to 20 000 bars pressure. The relative volume changes of the solid samples were measured in a direct piston displacement apparatus. It was found that both isotopes fit a Murnaghan finite strain relation. From this compressibilities were computed. Within experimental error, the two isotopes have the same compressibility throughout the range. As might be expected from its larger zero-point energy, He³ has the slightly greater molar volume at all pressures.

WE have measured the compression of solid He³ and He⁴ at 4.2°K up to 20 000 bars pressure. This is of potential interest in connection with possible isotopic differences. The piston displacement method originally suggested by Bridgman¹ was used. Details of the apparatus including its previous application to He⁴ and other solidified gases have been published previously.²⁻⁵

Preparation of solid He samples was not so straightforward as for the solidified gases previously investigated. It was not possible to seal liquid helium in the pressure cylinder with the potassium packing on the moving piston. The samples, therefore, were pressurized through the filling capillary by means of an auxiliary hydraulic system before the copper sealing disk on the top of the sample holder was penetrated by the moving piston. The helium gas in the filling capillary was compressed by low vapor pressure oil to pressures somewhat above the freezing pressure at 4.2°K (He⁴, 2500 psi; He³, 3500 psi). When the seal subsequently was broken and the pressure on the main piston raised very rapidly, the latter pressed on solid rather than liquid, and the packing invariably held. A liquid nitrogen trap in the capillary prevented oil contamination of the samples. To insure sample purity, the system was monitored for leaks before and during the pressurization.

On account of both the large and rapidly changing compressibilities of both solid helium isotopes and the friction in the solid samples (which are assumed² to transmit the uniaxially applied compressive stress as approximate hydrostatic pressure), our direct measurements cannot be extended below about 2000 bars pressure. The relative volume changes above 2000 bars ($\Delta V/V_{2000}$ in the second and third columns of Table II) were calculated as described previously.² Several runs for each isotope were made in each of two different sized sample holders: $\frac{1}{4}$ in. i.d. and $\frac{5}{16}$ in. i.d. The results in the two holders were always consistent.

Dugdale and Simon⁶ have published isochores for solid He⁴ up to roughly 3000 bars. From these the 4.2°K isotherm between the melting pressure and 2000 bars can be calculated. The present data can then be used to extend the molar volumes up to 20 000 bars pressure.

No corresponding low pressure data appear to exist for solid He³.⁷ However, Grilly and Mills⁸ have measured molar volumes for both isotopes along the melting curves to 3500 bars. If we assume that solid He³ has the same coefficient of thermal expansion between 4.2°K and the melting curve as does He⁴, we can combine the data of Dugdale and Simon⁶ with those of Grilly and Mills,⁸ and obtain the 4.2°K isotherm for He³ at low pressure (Table I).

Since the total expansion at 2000 bars is only 1.1% for He⁴, a 20% difference in the thermal expansion coefficients for He³ and He⁴ would result in an error in V_{2000} for the former of only 0.2%. The over-all accuracy of the $\Delta V/V_{2000}$ data in Table II is estimated as 2 to 3%.

After the observed $\Delta V/V_{2000}$ data had been converted into molar volumes, a fit of the results was made to a Murnaghan finite strain relation, such as that used by Birch⁹ and in the previous solidified gas work.²⁻⁵

$$P - P_0 = \frac{3}{2} K_0 (y^7 - y^5) [1 - \xi (y^2 - 1)], \quad (1)$$

where $y^3 = V_0/V$, with V_0 the molar volume at pressure $P = P_0$; K_0 is the bulk modulus at $P = P_0$, and ξ is an adjustable constant. The parameters K_0 and ξ were determined by a least squares fit of $(P - P_0) / (y^7 - y^5)$ vs $y^2 - 1$ to a straight line. The relative root mean square deviation of the points along the PV curve from this straight line was 2.5% for He⁴ and 2.1% for He³. The values of K_0 and ξ were: He⁴, $K_0 = 0.979 \times 10^8$ bars, $\xi = -2.00$; He³, $K_0 = 0.958 \times 10^8$ bars, $\xi = -1.91$.

In order to obtain values of the "instantaneous" compressibilities β_i , such as are given in the last two columns of Table II, one may differentiate the

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TABLE I. Low-pressure molar volumes for solid He⁴ and He³.

P (bars)	He ⁴				P (bars)	He ³		
	Melting temp. ^a (°K)	Melting volume ^a (cm ³ /mole)	Volume ^b at 4.2°K (cm ³ /mole)	% expansion		Melting temp. ^a (°K)	Melting volume ^a (cm ³ /mole)	Calculated volume at 4.2°K (cm ³ /mole)
143 (melt)	4.20	17.00	17.00	0.0	201 (melt)	4.205	17.56	17.56
1099	14.746	12.14	12.08	0.5	1185	14.689	12.49	12.42
2000	21.60	10.84	10.72	1.1	2000	20.88	11.19	11.07

^a See reference 8.
^b See reference 6.

Murnaghan relation (1) to give

$$K = -V_0(\partial P/\partial V)_T = \frac{1}{2}K_0y^8[-9\xi y^4 + (7+14\xi)y^2 - (5+5\xi)] \quad (2)$$

from which

$$\beta_i = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{V_0}{VK}$$

The present results for He⁴ are in good agreement with those reported earlier.² The greatest discrepancy in $\Delta V/V_{2000}$ is 0.009, which is within experimental error. The initial compressibility of He⁴ at the melting curve (Table II) is (probably fortuitously) within 1% of that reported by Dugdale and Simon⁶ at molar volume 17.00 cm³. There is also good agreement for the

initial compressibility of solid He³ at 4.2°K with a value recently reported by Heltemes and Swenson.¹⁰

It is known that both solid helium isotopes have three polymorphs with bcc, hcp, and fcc structures.^{6,11,12} It is not certain whether the 4.2°K isotherm intersects the hcp-fcc transition in either isotope below 20 000 bars. The suspicion of a phase transition at 10 000 bars noted in the earlier He⁴ work² is not confirmed here. On account of the sample friction the volume changes to be expected at these transitions are too small to be observed with the present apparatus. Neither isotope showed any sign of a transition at 4.2°K in this pressure range.

There appears to be no significant difference in either the relative volume changes or the compressibilities of the two solid helium isotopes. At all pressures He³ has the slightly greater molar volume, as might be expected on the basis of its larger zero point energy. In the case of solid hydrogen and deuterium² at 4.2°K, the difference in the molar volumes at atmospheric pressure is about 14% and at 20 000 bars still 6%. In 20 000 bars the over-all compression of solid hydrogen is 56% and deuterium 52%. One might expect the ratio of the zero point energies to be roughly $\sqrt{2}:1$ or 1.41 for hydrogen and deuterium but only $2:\sqrt{3}$ or 1.15 for He³ and He⁴. On account of the weaker interatomic forces, the over-all effect of zero point energy on compressibility is greater for the helium isotopes than for the hydrogen isotopes. This is demonstrated by the fact that β for He (at the elevated pressure of the melting curve) is more than twice that of H₂ at atmospheric pressure. Evidently, however, the helium compressibilities are not sensitive to isotopic differences in zero point energy.

TABLE II. Compression of solid He⁴ and He³ at 4.2°K.

Pressure (bars)	Observed relative volume change, $-\Delta V/V_{2000}$		Molar volumes (cm ³ /mole)		Instantaneous compressibilities $\beta_i = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ (bar ⁻¹ × 10 ⁻⁵)	
	He ⁴	He ³	He ⁴	He ³	He ⁴	He ³
Melting	17.00	17.56	102	104
1000	12.25	12.86	17.6	19.7
2000	0	0	10.72	11.07	9.72	10.18
3000	0.074	0.082	9.93	10.16	7.05	7.12
4000	0.125	0.133	9.38	9.60	5.60	5.65
5000	0.164	0.173	8.96	9.15	4.67	4.68
6000	0.199	0.206	8.59	8.79	3.94	4.00
8000	0.253	0.258	8.01	8.21	3.01	3.07
10 000	0.293	0.299	7.58	7.76	2.44	2.47
12 000	0.327	0.331	7.21	7.41	2.01	2.08
14 000	0.353	0.357	6.94	7.12	1.75	1.80
16 000	0.373	0.380	6.72	6.86	1.55	1.57
18 000	0.391	0.398	6.53	6.66	1.40	1.41
20 000	0.406	0.415	6.37	6.48	1.27	1.27

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