

High-Pressure Phase Diagram and Equation of State of Solid Helium from Single-Crystal X-Ray Diffraction to 23.3 GPa

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Single-crystal x-ray diffraction measurements have been performed on solid ^4He from 15.6 to 23.3 GPa at 300 K with synchrotron radiation. The diffraction patterns demonstrate that the structure of the solid is hexagonal close packed over this pressure-temperature range, contrary to both the interpretation of high-pressure optical studies and to theoretical predictions. The solid is more compressible than is indicated by equations of state calculated with recently determined helium pair potentials. The results suggest that a significant revision of current views of the phase diagram and energetics of dense solid helium is in order.

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The properties of solid helium, as an archetypal quantum solid, are fundamental to our understanding of condensed matter.¹ The crystal structure, phase diagram, and equation of state of this material have thus been the subject of numerous experimental and theoretical investigation for decades. With the refinement of new high-pressure techniques, there has been accelerated interest in the properties of helium at high densities. A maximum static pressure of 61 GPa has been reached in helium.² A variety of experimental methods have been applied, providing observations of phase transformations, pressure-volume relations, and optical properties, primarily at lower pressures.³⁻⁸ These experimental advances have given rise to numerous recent theoretical studies.⁹⁻¹⁵ As a result of its simple charge distribution and tendency toward classical behavior at high pressure, theoretical models for the static and dynamical properties of solid helium are expected to have comparatively high accuracy. In the present study, we show by single-crystal x-ray diffraction that the structure of solid ^4He from 15.6 to 23.3 GPa at 300 K is hexagonal close packed (hcp) in contrast both to the interpretation of indirect experimental observations and to theoretical predictions. These results necessitate a revision of current views of the stability field of the hcp structure for this solid.

Structure determination by diffraction techniques is perhaps the most fundamental measurement to be performed on a material. Such a measurement provides direct and definitive identification of the phase at a given pressure-temperature condition and provides the most accurate means available for determination of the pressure volume relations or equation of state. Despite the continued advancement of high-pressure measurement techniques, there has been no direct measurement of the crystal structure of solid helium at pressures above 0.1

GPa. This problem arises from the extremely low scattering cross section for the helium atom ($Z=2$) and the high compressibility of the material, which gives an exceedingly small volume at high pressure (e.g., of order 10^{-11} l at 10 GPa in a diamond-anvil cell). Recently, we presented a new technique for the measurement of x-ray diffraction from single crystals of low- Z materials in a diamond-anvil cell at high pressure.¹⁶ With use of this technique, the first single-crystal x-ray diffraction measurements on solid hydrogen to 26.5 GPa were obtained. In this Letter, we present the application of this technique to the problem of the crystal structure, equation of state, and phase diagram of solid helium. Crucial for x-ray diffraction studies of these materials is the use of a synchrotron radiation source, which provides high brilliance and narrow collimation of the incident x rays, and the use of a new experimental method involving a combination of single-crystal and energy-dispersive diffraction techniques with polychromatic (white) radiation.

A diamond-anvil high-pressure cell designed for single-crystal x-ray diffraction,^{16,17} with a stainless-steel gasket and containing three 5- μm -size ruby crystals for pressure measurement, was used. The sample was loaded at room temperature.¹⁸ Because of possible stabilization of metastable structures of helium by trace impurities, special attention was given to the purging of the cell of residual air. High-purity (99.995%) ^4He gas at a cylinder pressure of 15 MPa was compressed to 35 MPa in a pressure vessel containing the diamond-anvil cell and the pressure released to 0.1 MPa (1 bar); this cycle was repeated 3 times to purge the cell. For the final loading, the helium was compressed to 200 MPa whereupon the diamond-anvil cell was sealed, giving a pressure of 2 GPa within the cell. The cell was removed from the high-pressure vessel and the pressure first increased to 18 GPa and decreased to 14 GPa. This procedure was re-

peated twice in order to facilitate growth of a single crystal of helium, which had dimensions of approximately $50 \mu\text{m}$ in diameter by $10 \mu\text{m}$ in thickness. The cell was mounted on a two-circle rotation apparatus equivalent to the χ and ω circles of a four-circle diffractometer.¹⁶ Because of the limited opening of the diamond-anvil cell, the access angle of the ω circle was limited to -10° to $+30^\circ$. With a fixed 2θ at 20° , a given reflection was found as a peak in the energy-dispersive x-ray spectrum when the diffraction condition is satisfied for a specific combination of χ and ω . The time required for peak searching with this technique is greatly reduced as only two circles must be scanned as opposed to three circles in conventional diffractometry.

The measurements were performed on the wiggler line (A-3) at the Cornell High-Energy Synchrotron Source (CHESS). The incident synchrotron x-ray beam was collimated by a pair of adjustable slits, which resulted in a beam size of the order of $10 \mu\text{m}$ square. The collimator on the diffracted beam consisted of two slits. A front slit, $50 \mu\text{m}$ wide by $200 \mu\text{m}$ high, was mounted close to the rear diamond anvil to provide the necessary high spatial resolution and to reduce unwanted scattered radiation from the diamonds. The rear slit was close to the detector, 200 mm from the sample, and defined the angular resolution of the diffraction. A resolution of 0.1° for ω and 1° – 2° for χ was obtained with a back slit of $100 \mu\text{m}$ wide by 1 mm high. Single-crystal diffraction of helium could be distinguished from that of the ruby grains and the diamond anvils and from polycrystalline diffraction of the gasket by the spatial resolution of the incident and diffracted beams. Pressures were measured by ruby fluorescence excited by the x-ray beam and the quasihydrostatic ruby pressure scale was used to calculate the pressure from the wavelength shift of the ruby R_1 band.¹⁹ The identical values for the pressure obtained from three ruby crystals at different parts of the sample chamber indicated the homogeneity of pressure at 23 GPa , in agreement with earlier helium studies.² This observation was consistent with the narrow widths of R_1 and R_2 bands indicating quasihydrostatic pressures.^{18,19}

The measurements were begun at 15.6 GPa , and diffraction patterns at four pressures to 23.3 GPa at 300 K were obtained. A representative energy-dispersive diffraction pattern at 23.3 GPa from single-crystal helium is shown in Fig. 1. Excellent signal-to-noise ratio was observed. Six diffraction peaks from helium were detected. They can be indexed as 101 , $0\bar{1}1$, 102 , $1\bar{1}2$, 110 , and 112 of the hexagonal-close-packed (hcp) structure (space group $P6_3/mmc$) with the ideal c/a value of 1.633 , and definitely cannot be indexed as face-centered cubic (fcc) or body-centered cubic (bcc) as predicted by theory. The calculated d spacings from different diffractions are consistent with hcp within the 0.1% error expected from the slit widths of the detector. The calcu-

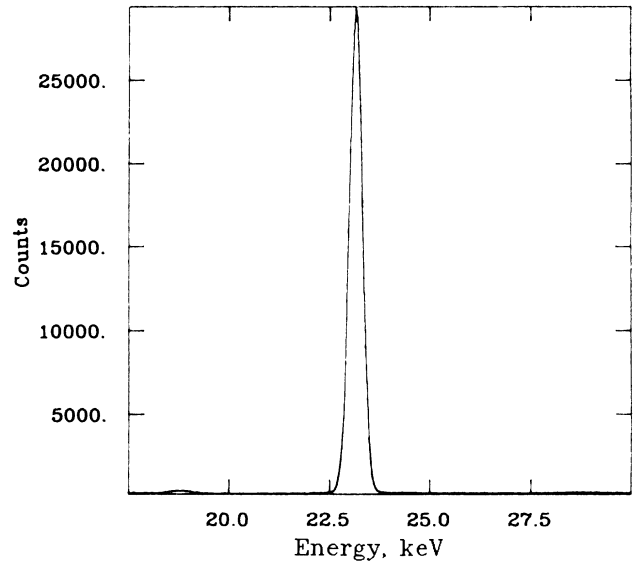


FIG. 1. Representative energy-dispersive x-ray diffraction spectrum for solid helium (101 reflection) at 23.3 GPa .

lated angles among reflections agree with the angles of hcp within the uncertainty of the values of ω and χ . The crystal was oriented approximately with the $(\bar{1}12)$ plane parallel to the diamond surface. Reflections from the $\{100\}$ and $\{002\}$ classes were inaccessible because of the limited opening of the diamond-anvil cell and the crystal orientation. Although the only observed diffraction peaks were consistent with the hcp structure, our measurements would fail to observe any weak supercell reflections corresponding to slight distortions from the ideal structure. There is no reason, however, to expect such behavior.

With increasing pressures to 23.3 GPa , the helium remained as a hcp single crystal and maintained its orientation within 3° while the gasket and sample chamber deformed extensively. The helium crystal was observed to deform with the sample chamber, apparently annealing and releasing the strain at each increment of pressure. This phenomenon has also been observed in hydrogen, neon, and argon at lower pressures.^{16,20} Above 20 GPa for hydrogen, 10 GPa for neon, and 5 GPa for argon, the single crystals begin to break up to form smaller crystals, and the annealing process at a given temperature slows down. In the present study, however, not all the strain in the helium crystal is annealed at 23.3 GPa (and 300 K). At 15.6 GPa , the range of "rocking angle" (uncertainty in ω for a diffraction peak) of helium was small, only 0.1° . At 23.3 GPa , it broadened to 0.5° , whereas the rocking angle of the ruby crystals in helium was still 0.1° . Nevertheless, helium is still the most closely hydrostatic pressure medium of any material yet studied in this pressure range, as previously concluded.²

The x-ray diffraction data are summarized in Table I. With increasing pressure helium compresses from 3.944

TABLE I. Lattice parameters and molar volume of solid helium to 23.3 GPa (300 K).

P (GPa)	a (Å)	c (Å)	V (cm ³ /mol)
15.6(1)	2.100(2)	3.430(3)	3.944(9)
16.2(1)	2.087(1)	3.408(2)	3.871(5)
17.4(1)	2.069(1)	3.379(2)	3.772(4)
23.3(1)	2.003(2)	3.271(3)	3.422(8)

cm³/mol at 15.6 GPa to 3.422 cm³/mol at 23.3 GPa, which is an extraordinarily high degree of compression in this pressure range. The new pressure-volume data are compared with the results of theoretical calculations performed for the hcp structure with recently developed pair potentials for helium. The Ceperley-Partridge potential is a fit to recent quantum Monte Carlo calculations and is presumably an accurate representation of the pure two-body interactions at small interatomic separations.²¹ The Aziz-McCourt-Wong potential (HFD-B) was obtained from a fit to low-pressure data and to the Ceperley-Partridge potential at 1 bohr on the repulsive wall.²² Finally, the Ross-Young potential is an exponential-six type, which was fitted to shock-wave data and is considered an effective potential that includes possible many-body terms sampled in dynamic compression.¹⁴ The present calculations were performed for the hcp structure, with the thermal pressure determined by quasiharmonic lattice dynamics.^{23,24} At lower pressures, anharmonic corrections are required to represent accurately the vibrational dynamics of solid helium.^{1,10} However, at high pressures the quasiharmonic approximation becomes accurate and is sufficient for the present estimation of the thermal correction to the static equation of state.²⁵

The pressure-volume points obtained from the x-ray data are plotted in Fig. 2 along with the calculated equations of state at 300 K. The equations of state calculated with the Aziz-McCourt-Wong and Ceperley-Partridge potentials give pressures (or volumes) that are significantly higher than the experimental data. The results with the Ross-Young potential, on the other hand, are in better agreement with the measurements, particularly in the lower pressure range. This agreement is considered excellent, if we consider the fact that the potential was obtained from a fit to shock-wave data in the 10000-K range at significantly expanded volumes.¹⁴ The comparison suggests that many-body forces, not included explicitly in the calculation with the Aziz-McCourt-Wong and Ceperley-Partridge potentials but included implicitly in the Ross-Young function, may introduce a softening of the equation of state at high densities. This observation is consistent with the analysis of the equation of state of neon measured by (powder) x-ray diffraction to 110 GPa.²³ We note that the Ross-Young potential is also likely to become too stiff at higher pressures, as evidenced by the disagreement at 23.3 GPa.

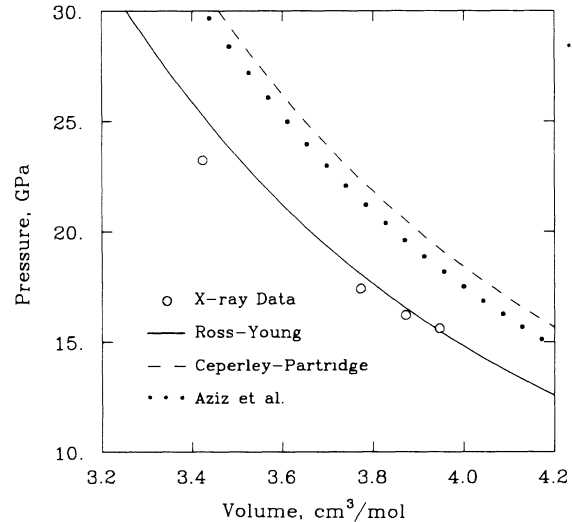


FIG. 2. Pressure-volume equation of state for solid hcp helium at 300 K. The curves correspond to theoretical equations of state calculated in the present study from previously reported pair potentials for helium (see text): Ross-Young (Ref. 14); Ceperley-Partridge (Ref. 21); and Aziz, McCourt, and Wong (Ref. 22).

The most significant result of the present study is its implications for the phase diagram of helium at high pressure. The relative stability of the fcc and hcp phases of solid helium at low pressures and temperatures (<1 GPa and <20 K) has been the subject of numerous experimental and theoretical studies.^{1,3,4} The only high-pressure x-ray diffraction study of the phase boundary is the pioneering work of Mills and Schuch to 0.45 GPa.³ Franck and Daniels determined the phase boundary to 0.9 GPa by optical methods and found significant hysteresis on increasing and decreasing pressure.⁴ Loubeyre *et al.*⁶ measured the melting curve by optical techniques to 15 GPa and 350 K and reported evidence for a triple point at 299 K and 11.8 GPa. In addition, it has been proposed that a second hcp phase is stabilized at ultrahigh pressures (>1 TPa).¹⁰ More recent work has suggested that this phase may occur at lower pressures,¹³ consistent with the observations of Jephcoat *et al.*²⁶ of the fcc-hcp transition sequence in solid xenon beginning as low as ≈ 15 GPa. These results have given rise to the construction of a rather complex phase diagram for solid helium at high pressures, with two separate stability fields for the hcp structure.¹³

The present results for helium are shown in the phase diagram in Fig. 3, along with selected previous determinations. Clearly established by experiment are the hcp and fcc structures and phase boundary at low pressures and temperatures, the melting curve, and the hcp structure at 15.6 to 23.3 GPa at 300 K from the present study. We note that if the fcc-hcp boundary has slight upward curvature, in contrast to the downward curvature predicted by early calculations,⁹ the phase line will meet the cusp in the melting curve reported by Loubeyre *et*

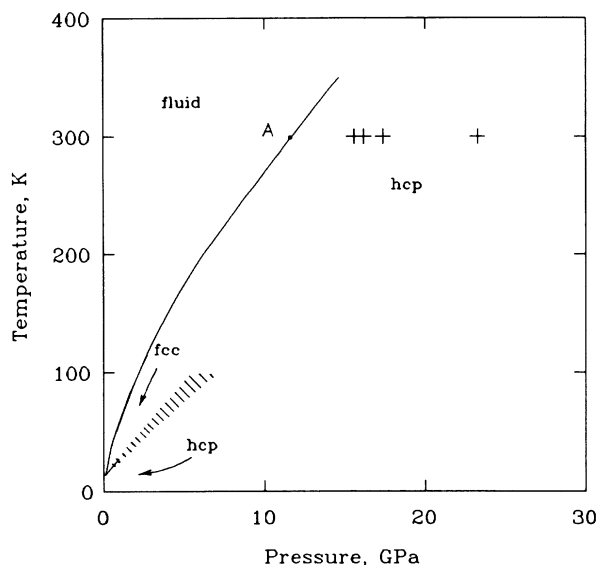


FIG. 3. Phase diagram for helium. The crosses correspond to the pressure-temperature points of the present study. The shaded area is extrapolated from the optical study to 0.9 GPa by Franck and Daniels (Ref. 4). Point A is the inflection point along the melting curve reported by Loubeyre *et al.* (Ref. 6).

*al.*⁶ It may therefore be useful to consider that the cusp on the melting curve is due to the fcc-hcp-fluid triple point, instead of that of fcc-bcc-fluid suggested previously.^{6,11-13} We note that currently there is no experimental evidence for the bcc phase of solid helium at high pressures; moreover, its thermodynamic stability in the present P - T range is not supported by recent free-energy calculations.¹⁵ Unfortunately, limitations on synchrotron beam time prevented the extension of the present measurements to examine the behavior of helium over a wider P - T range, and the existence of a stability field for the bcc structure (or any other phases) nearer the melting curve at high pressure cannot be ruled out. The present study emphasizes the need for careful structural studies as a function of pressure (and temperature) in order properly to identify possible structures in even simple and comparatively well-understood systems such as solid helium.

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