

## New High-Pressure Phase of Solid $^4\text{He}$ Is bcc

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The effect of isobarically heating solid  $^4\text{He}$  at high density is investigated with use of constant-pressure molecular-dynamics calculations and a realistic interatomic pair potential. At  $P \sim 16$  GPa the observed sequence of stable phases with increasing temperature is fcc  $\rightarrow$  bcc  $\rightarrow$  liquid. The presence of a new, thermally stabilized, bcc phase for high-density solid  $^4\text{He}$  is thus confirmed.

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The behavior of solid helium at high densities continues to attract attention.<sup>1-6</sup> The recent observation of a cusp point on the melting curve of solid  $^4\text{He}$  around room temperature suggested a triple point and hence the presence of a new high-pressure solid phase.<sup>6</sup> While no direct evidence was obtained for a solid-solid phase transition, the characteristics of melting changed above the cusp point; the enhanced premelting and smaller volume change were interpreted as evidence for the presence of a bcc solid.<sup>6</sup>

The interatomic pair potential for He is well established.<sup>7</sup> Moreover, computer simulation techniques have now advanced to the point that it is possible to explore directly the relationship between an interatomic potential and its preferred crystal structure at finite temperature.<sup>8,9</sup> Hence, the question of a possible solid-solid phase transition occurring in solid  $^4\text{He}$  at high pressures and the nature of the phases involved are amenable to direct investigation. Accordingly, we have carried out a series of isobaric molecular-dynamics simulations.<sup>8</sup> Under an external pressure corresponding to about 16 GPa, we observed the following sequence of stable phases with increasing temperature: fcc  $\rightarrow$  bcc  $\rightarrow$  liquid. The presence of a stable bcc phase preceding the melting of high-density  $^4\text{He}$  thus confirms the speculations based upon the anomalous behavior of the melting curve.<sup>6</sup> If corresponding-states arguments are invoked, other insulating crystals will likely also exhibit a bcc phase when subjected to analogous conditions of temperature and pressure.

The constant-pressure molecular-dynamics (MD) technique that we employed is documented in the literature<sup>8</sup> and so we omit most of the details. Essentially, the equations of motion are in-

tegrated by standard techniques for a system of 432  $^4\text{He}$  atoms initially arranged on a body-centered tetragonal lattice with periodic boundary conditions. If the lengths of the basis vectors of the MD cell  $a$ ,  $b$ , and  $c$  are in the ratios  $1:1:\sqrt{2}$  the system is equivalent to an fcc lattice, whereas if the ratios of  $a:b:c$  are  $1:1:1$  and the angles  $(a,b)$ ,  $(b,c)$ ,  $(a,c)$  are still  $90^\circ$ , the system is bcc. The new MD method allows the system to change both its volume and shape in response to any instantaneous imbalance between an externally applied pressure and spontaneously generated thermal stresses. By this technique several solid-solid phase transitions have been successfully investigated.<sup>8,9</sup> In particular, a previous study of the relative stability of fcc and bcc lattices employing the Lennard-Jones 12-6 potential established that at low temperature and pressures the close-packed structure is preferred.<sup>8</sup> Although still widely used as an effective pair potential for the rare gases, the 12-6 potential is unfortunately a poor approximation to their true potentials.<sup>10</sup>

Accordingly, in our simulations that are designed specifically to model He, we have employed a realistic pair potential.<sup>7</sup> Before describing our results we mention two questions, not specifically addressed here, that perhaps will deserve further study: quantum effects and three-body forces. Our defense for their omission from our calculations is based largely on pragmatic and intuitive arguments. First, it is known that quantum effects have only a modest influence on the location of the He melting line around room temperature.<sup>4</sup> Second, if solid He can be approximated by an oscillator model obeying the Grüneisen equation of state, then the leading quan-

tum contribution to the pressure is given by  $\Delta P_Q = (3\gamma RT/20V)(\theta/T)^2$ . With use of extrapolations of lower-pressure data<sup>3</sup> to estimate the Grüneisen parameter  $\gamma$  and the Debye temperature  $\theta$ , we obtain  $\Delta P_Q V/RT \sim 1$  which is small compared with the pressure of interest to us here ( $PV/RT \sim 20$ ).

Finally, we note that of all the rare gases, three-body forces are the smallest in helium<sup>10</sup>; we estimate  $\Delta P_3 V/RT \sim 0.4$ . Moreover, we are interested in a possible fcc  $\rightarrow$  bcc phase transition and since it is known that at constant density three-body forces are essentially identical in these two structures<sup>11</sup> they are not likely to greatly influence such a transition. We now describe our results.

All of the calculations were carried out under a nominal pressure of 15.2 GPa but when due allowance is made for the contribution from  $\Delta P_Q$  and  $\Delta P_3$  the effective external pressure is approximately 16 GPa. Figure 1(a) shows how at 310 K an initial ideal bcc structure, whose MD cell started with  $a = b = c = 14.44 \text{ \AA}$  and  $(a, b) = (b, c) = (a, c) = 90^\circ$ , evolved spontaneously to a fcc-like structure whose MD cell had  $\vec{a} = (12.52 \text{ \AA}, -1.28 \text{ \AA}, 0)$ ,  $\vec{b} = (1.40 \text{ \AA}, 13.39 \text{ \AA}, 1.00 \text{ \AA})$ ,  $\vec{c} = (0.03 \text{ \AA}, -0.18 \text{ \AA}, 17.53 \text{ \AA})$ , and  $(a, b) = 90^\circ$ ,  $(b, c) = 89.2^\circ$ ,  $(a, c) = 89.6^\circ$ . The transformation was completed over a period of 1500 time steps of 1.23 fs and the resulting fcc structure was stable when followed for a further 6500 steps. We conclude therefore that under the conditions  $T = 310 \text{ K}$ ,  $P = 16 \text{ PGa}$ , solid  $^4\text{He}$  is fcc. However, at higher temperatures, for example at 360 K [see Fig. 1(b)], the reverse behavior was exhibited, namely starting from an fcc MD cell with  $a = b = 12.85 \text{ \AA}$ ,  $c = 18.17 \text{ \AA}$ ,  $(a, b) = (b, c) = (a, c) = 90^\circ$ , the system evolved spontaneously to become predominantly bcc with an MD cell  $\vec{a} = (12.04 \text{ \AA}, -3.50 \text{ \AA}, 0.56 \text{ \AA})$ ,  $\vec{b} = (-0.66 \text{ \AA}, 12.52 \text{ \AA}, -0.10 \text{ \AA})$ ,  $\vec{c} = (0.36 \text{ \AA}, -0.97 \text{ \AA}, 20.35 \text{ \AA})$ ,  $(a, b) = 109^\circ$ ,  $(b, c) = 95^\circ$ , and  $(a, c) = 87^\circ$ . Between these two temperatures the system is observed to oscillate from fcc to bcc as a function of time but with a definite preference for bcc as the temperature increases. We have attempted to classify the character of these "mixed" crystals by monitoring the distribution of neighbors around a given atom and also the distribution of angles specified by the interatomic bond vectors. In this way individual atoms are classified as either bcc-like or fcc-like and we have an efficient means to follow the time evolution of the crystal structure. Typical plots are shown inset in Fig. 2(a), which also shows the variation of the enthalpy  $H$  as a function of

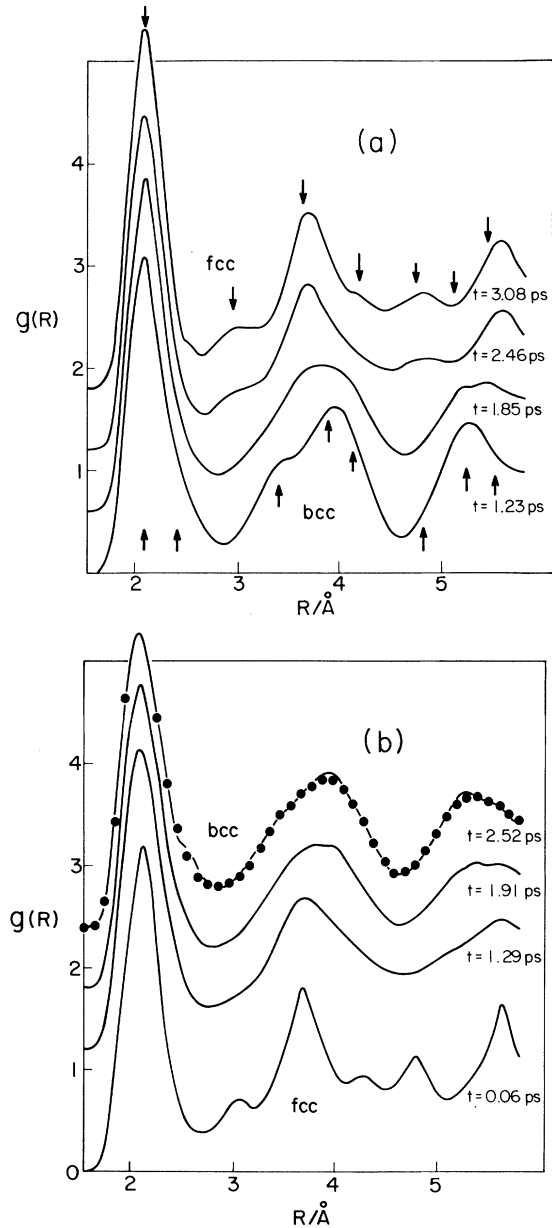


FIG. 1. (a) Time evolution of the pair distribution function,  $g(r)$ , for solid  $^4\text{He}$  at  $P = 16 \text{ GPa}$  and  $T = 310 \text{ K}$  starting from a bcc lattice at  $t = 1.23 \text{ ps}$  and finishing at  $t = 3.08 \text{ ps}$  with an fcc lattice. The arrows indicate peak positions in the ideal bcc and fcc lattices. (b) Time evolution of  $g(r)$  at  $P = 16 \text{ GPa}$  and  $T = 360 \text{ K}$  starting from an fcc lattice at  $t = 0.06 \text{ ps}$  and finishing with a bcc lattice at  $t = 2.52 \text{ ps}$ ; the dots are results for  $t = 6.47 \text{ ps}$ .

temperature for the three phases. Figure 2(b) gives an analogous plot for the density variations.

The arrow in Fig. 2(a) indicates the melting temperature predicted for the Aziz  $^4\text{He}$  potential<sup>7</sup>

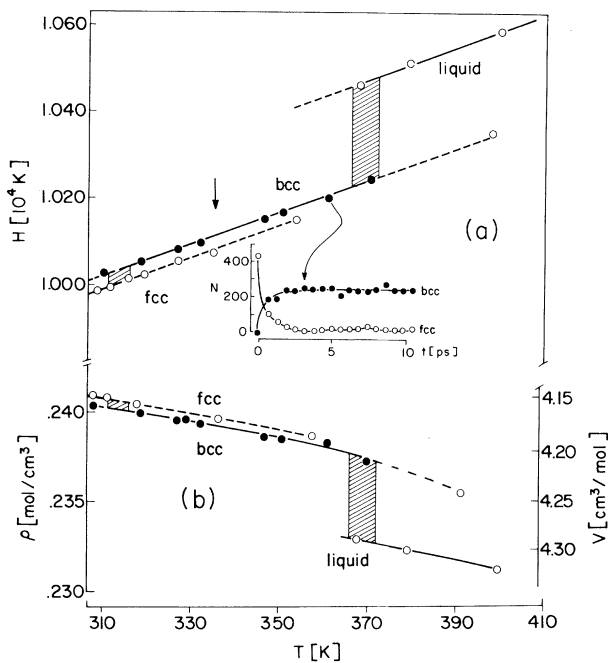


FIG. 2. (a) Temperature dependence of the enthalpy  $H$  for three phases of  $^4\text{He}$ . The inset indicates the evolution of local structure (circles, fcc; dots, bcc). The arrow indicates the melting temperature of the fcc phase calculated in Ref. 6 (see text) while the shaded regions indicate our estimated transitions. (b) Temperature dependence of the density  $\rho$  for solid  $^4\text{He}$  at  $P = 16$  GPa.

based upon a perturbation theory that used as a reference system Monte Carlo results for an inverse twelfth-power potential.<sup>4</sup> In our constant-pressure molecular-dynamics calculations, the system is still solid under these conditions, and hence our results point to shortcomings in the perturbation theory, under these extreme conditions. We note from Fig. 2(b) that the volume change on melting is about 2.1% at  $T \sim 370$  K. The experimental estimate<sup>6</sup> is certainly greater than 1%.

If we use corresponding-states scaling, an fcc-bcc-liquid triple point would occur in Xe at about  $P = 1.2$  Mbar and  $T = 10^4$  K. Unfortunately, under these conditions Xe may well no longer be an insulator<sup>12-16</sup> and in any case it may already be bcc for other reasons.<sup>17</sup> The rare gases Ne and Ar would appear to be more serious candidates to exhibit this phenomenon since their metallization occurs under more extreme conditions. However, the most promising candidate for study may well be solid hydrogen, which at room temperature and high pressure appears to be hcp.<sup>18-20</sup>

We estimate a possible hcp-bcc-liquid triple point at  $P = 26.5$  GPa and  $T = 950$  K. In studies of solid  $\text{H}_2$  the requisite pressure (density) has already been far exceeded, but studies have yet to be reported above room temperature.

In summary we have observed that at  $P \sim 16$  GPa, solid fcc  $^4\text{He}$  transforms to bcc before melting. Further work is needed to establish the range of existence of this new phase and to explore more deeply the reasons for its stability. These questions will be taken up elsewhere.

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