

Pressure-Induced Phase Transformations in Ice

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Using molecular-dynamics calculations, we show that at 80 K, ice Ih undergoes a transition to a high-density amorphous (hda) form at about 13 kbar. At higher pressures, the calculated oxygen-atom radial distribution function shows strong resemblance to that of ice VIII. The most characteristic feature of hda ice, namely the peak observed around 3.5 Å in the oxygen radial distribution function, is ascribed to molecules occupying interstitial-like sites. On warming of a sample of hda ice recovered at zero pressure, the structure evolves to a lower-density form. These observations are in good accord with available experimental data.

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Ice has a very rich phase diagram. Under different specific temperature and pressure conditions, it can exist in polymorphic forms with unique crystallographic structures.¹ Amorphous ice, on the other hand, can be prepared by supercooling of liquid water² and/or deposition of the vapor onto a cold surface.³ Recently, Whalley and co-workers discovered⁴ a new method of making amorphous ice by pressing the solid beyond the extrapolated low-pressure melting line of ice Ih. It was found⁴ that when ice is compressed to ~ 10 kbar at 77 K, a new phase of density 1.31 g cm^{-3} is formed. This transformation is sudden and is accompanied by a large volume reduction. The x-ray powder-diffraction pattern of a sample recovered at atmospheric pressure showed that it has a noncrystalline structure. When the latter was heated to about 140 K a second transformation was detected.⁵ This new phase, which has a much lower density, was also found to be amorphous.

Very recently, oxygen pair-correlation functions have been obtained for both the high- and low-density amorphous phases by x-ray powder diffraction.⁶ It was shown that in both structures the nearest-neighbor coordination number is about 4 and the shortest O-O separation is 2.8 Å. The most significant structural difference is observed for next-nearest neighbors. In low-density ice, the mean distribution of the next-nearest neighbors is centered around 4.5 Å, which is very close to the value in normal ice, whereas in the high-density phase there is a peak around 3.5 Å. The structure of the high-density amorphous (hda) ice has been interpreted as due to "bending of hydrogen bonds [and] distortion of the O-O-O angles out of the ideal tetrahedral value."⁶ In this Letter, we report new results on this novel solid-solid phase transformation obtained by the constant-pressure molecular-dynamics (MD) technique.⁷ The mechanism of the phase transition is investigated through a careful analysis of the changes in the relevant radial distribution functions (rdf's) computed at different applied pressures.

The details on the method of constant-pressure MD simulation and its applications to the study of molecular

solids have been reviewed recently.⁷ Our calculations were performed with a system containing 128 water molecules that interacted via the TIP4P intermolecular potential function⁸; long-range electrostatic interactions were handled by an Ewald method. The initial positions of the 128 oxygen atoms were taken from the known x-ray structure of ice Ih and the water orientations were assigned in an *ad hoc* manner conforming to the Bernal-Fowler rules.⁹ The proton positions were randomized until a sample with zero dipole moment was obtained.¹⁰ This potential, and system size, have been shown to be adequate to represent the structure of both water⁸ and dense ices.¹¹ A conventional constant-volume MD calculation was first carried out to equilibrate the solid at 80 K. Then the constant-pressure calculation was initiated with temperature maintained at ~ 80 K and the pressure set at the desired value. In a typical run, 4000 time steps of interval 2 fs were used for equilibration and an additional 4000 time steps for the accumulation of structural and dynamical information.

The variation in the computed density of the ice sample as a function of external pressure is plotted in Fig. 1 (upper curve). At 91 K under atmospheric pressure the *calculated* density for ice Ih is 0.958 gm cm^{-3} . This is slightly larger than the observed value¹² of 0.932 gm cm^{-3} and is likely due to a minor inadequacy in the potential. From the initial slope of the pressure versus density curve, we estimated the bulk modulus for ice to be 80 kbar, which compares favorably with the experimental value of 89 kbar obtained recently by Brillouin spectroscopy.¹³ Below 7 kbar, ice Ih seems to compress elastically. However, between 10 and 17.5 kbar the calculated density changed in a fashion resembling the experimentally observed "pseudo first-order" transition.⁴ The calculated transition region is broader than the experimental one, presumably because of the size of system used in the simulation. In the transition region, the density changed from 1.10 to 1.34 gm cm^{-3} , corresponding to a 22% decrease in the molar volume. The maximum slope of the curve occurred at 13.6 kbar and is taken as

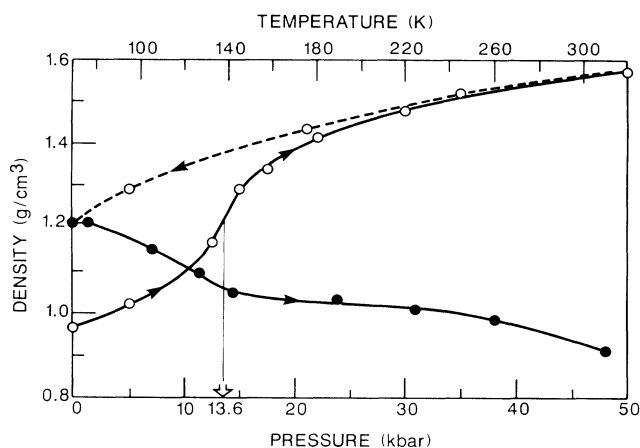


FIG. 1. Isothermal compression curve (open circles) for ice Ih showing the transition to an amorphous structure at 13.6 kbar. The dashed line is the decompression path to zero pressure. The filled circles show the effect of heating the zero-pressure amorphous sample.

the transition pressure for this transformation process. Beyond 22 kbar, the density increase is approximately linear with applied pressure.

Oxygen-atom rdf's calculated at different external pressures are shown in Fig. 2. At zero pressure, the calculations yield a stable ice Ih structure; the tetrahedral hydrogen-bonding network of the water molecules in crystalline ice gives rise to the peaks at 2.8, 4.5, and 5.2 Å in the oxygen atom rdf and no intensity around 3.5 Å. Below 12.5 kbar, there is a gradual broadening in the oxygen distribution at the second and third coordination shells. Apart from a slight shortening in the O-O distances due to compression of the unit cell, the coordination number of the first nearest neighbors remains unchanged from the ideal value of 4. This observation indicates that the local geometry around the water molecules is not affected significantly; only the long-range order has been partially disrupted. In contrast, it is apparent from the rdf's in Fig. 2 that there are large structural rearrangements when the external pressure is increased from 10 to 15 kbar. These structural changes parallel the abrupt increase in the density of the ice sample (Fig. 1), thus supporting the notion of a pseudo first-order solid-solid phase transition.⁴

The most dramatic signature of the structural transformation is the appearance of a new peak in the oxygen-atom rdf around 3.2 Å. As the pressure increases further, the intensity of this peak becomes stronger and its position moves gradually closer to the first peak. The rdf immediately beyond the first peak then no longer falls to zero. In the new structure, the peak originally centered at ~ 4.5 Å has completely vanished and is now replaced by a featureless distribution with no evidence of coordination shells.

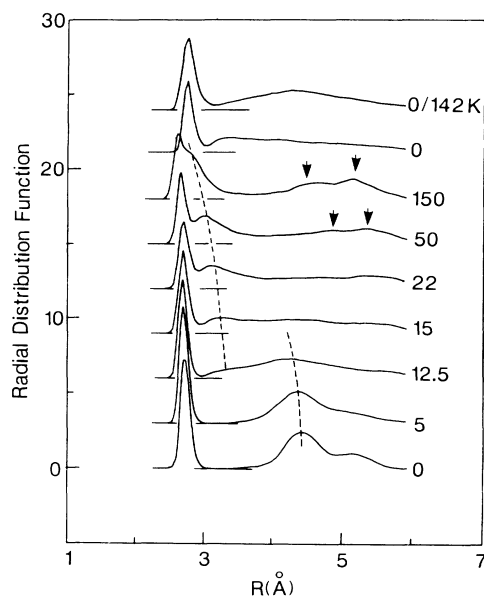


FIG. 2. Oxygen-atom radial distribution function for various pressures (kilobars) at approximately 80 K, except as indicated. The dashed lines follow the major structural changes before and after the phase transition. Arrows mark the re-emergence of structure at high pressure.

We have recovered hda ice at atmospheric pressure by slowly releasing the pressure (dashed curve in Fig. 1). The density of the recovered sample is 1.22 gm cm^{-3} . As shown in Fig. 2 (second curve from the top), the next-nearest-neighbor peak at ~ 3.4 Å in the rdf, although still visible, has become broad and there is no evidence for long-range structural order.

The mechanism of the phase transition to the hda structure deduced from an examination of configurations generated in the MD calculations is as follows. Below the phase transition, broadening of the 4.5- and 5.2-Å peaks is primarily due to small random static displacements of the water molecules from their equilibrium positions in the ice Ih structure. These displacements are directed towards the open spaces of the hexagonal structure. At higher pressure, the displacements are sufficiently large that the ice Ih structure collapses. The resulting structure maintains short-range tetrahedral order but the formerly empty interstitial sites are now partially occupied, giving rise to the 3.2-Å peak in the oxygen-atom rdf.³

When the ice sample is subjected to even higher pressure (50 to 150 kbar), the peaks at 4.5 and 5.2 Å start to reappear (see arrows in Fig. 2). This observation strongly suggests that the higher-density ice has regained some long-range structural order. The calculated density at this pressure is 1.88 gm cm^{-3} , which is, incidentally, very close to that of ice VIII.¹⁴ Comparison of the oxygen-atom rdf of ice VIII obtained from our previous

MD calculations¹¹ to that of this hda ice (Fig. 2) reveals a strong similarity between the two calculations. The close resemblance of the O-H radial distribution functions is even more striking. The integrated coordination number for the oxygen-atom rdf from 2.4 to 3.5 Å is ~ 8 for both ices. This suggests that the filling of interstitial sites in hda ice is now largely complete. Ice VIII is composed of two interpenetrating antiferroelectric ice Ic lattices.^{14,15} It is probable that our sample does not achieve this complete orientational ordering and is, therefore, more appropriately regarded as a quenched ice VII sample. In view of these remarks, it is not an unreasonable conjecture that real hda ice might eventually convert into ice VIII at much higher pressure. Examination of the phase diagram of ice¹ does not rule out such a possibility.

When the MD ice sample recovered at atmospheric pressure is warmed slowly, a seemingly "sluggish" transition (lower curve in Fig. 1) occurred which was completed at ~ 140 K. The density of this high-temperature phase at 142 K is 1.06 gm cm^{-3} , which is about 13% less dense than the original sample. The oxygen-atom rdf of the high-temperature phase is displayed in Fig. 2 (top curve). It is apparent that the structure, although different from the hda ice, is still amorphous. The 3.5-Å peak present in the high-density phase has now disappeared. Beyond 3 Å, the long-range distribution of the water molecules is fairly broad with a weak maximum located at ~ 4.5 Å. It is remarkable that this feature in the oxygen-atom rdf of high-temperature amorphous ice is very similar to that of ice just prior to the pressure-induced phase transition (see rdf in Fig. 1 for 12.5 kbar). The similarity between these structures suggests that the addition of thermal energy to hda ice helps water molecules anneal out of the interstitial sites and relax back into a more ice Ih-type structure.

In summary, our calculations predict that when ice Ih is compressed at 80 K, an apparent first-order transition to an amorphous structure occurs around 13 kbar with an accompanying volume reduction of 38%. The density of this hda sample recovered at zero pressure is 1.22 gm cm^{-3} . Experimentally, this transition was observed at 10 ± 1 kbar with a volume change of 40%; the density of the zero-pressure hda sample is 1.19 gm cm^{-3} .⁴

The x-ray rdf of a sample recovered at atmospheric pressure has been measured by Bosio, Johari, and Teixeira.⁶ The most striking feature of the measurements is the presence of a peak around 3.5–3.6 Å. The oxygen rdf obtained from the simulation is consistent with this finding although the calculated peaks are somewhat broader than observed and shifted to smaller distances [Fig. 3(a)]. The discrepancy in the amplitude of the first peak in the rdfs is due mainly to the limited resolution of the experimental data.⁶ As mentioned above, analysis of the MD rdfs reveals that the peak at 3.5 Å can be attributed to the partial filling of the empty interstitial

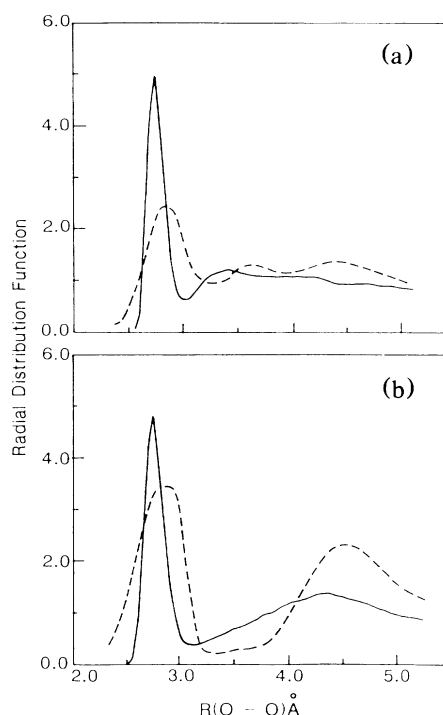


FIG. 3. Theoretical (solid line) and experimental (dashed line) oxygen-atom radial distribution functions for (a) high-density amorphous ice recovered at zero pressure at approximately 80 K, and (b) low-density amorphous ice obtained by warming of the hda sample.

sites within the ice Ih lattice as a result of the static displacements of water molecules.

Experimentally, a first-order transformation to a lower-density phase (0.94 gm cm^{-3}) was detected⁵ at ~ 140 K by the warming of hda ice at zero pressure. X-ray powder-diffraction studies^{5,6} showed that it also has a noncrystalline structure and, moreover, the rdf differs significantly from the hda form. The major difference between these two structures is that the next-nearest-neighbor peak in the low-density ice is clearly separated from the first peak and its position shifts from 3.5 to 4.5 Å. In comparison, the theoretical calculations produced a low-density ice with an oxygen-atom rdf very similar to experiment but again with the peaks shifted to slightly smaller distances [see Fig. 3(b)].

The picture of ice under pressure that emerges from the present MD studies accords very well with available experimental data. The calculations not only reproduce all the salient features, but also provide valuable information on the mechanisms of the two novel phase transitions. It will be of interest to see whether or not our prediction of a pressure-induced "recrystallization" of hda ice is actually observed experimentally.

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