New High-Pressure Phases of Ice

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An ionic model has been used in conjunction with classical constant-pressure molecular-dynamics calculations to explore the properties of possible high-pressure phases of ice. Around 100 GPa, the model is found to convert from the symmetric hydrogen-bonded cuprite structure (ice X) to a fully ordered antifluorite structure. On heating, the new phase, ice XI, becomes a fast-ion proton conductor.

The effect of pressure on the properties of ice crystals continues to attract the attention of experimentalists and theoreticians alike. The discovery that application of a relatively modest pressure to hexagonal ice, held at 77 K, yields a dense, amorphous phase has attracted considerable interest.[1-4] The polymorphism of ice is indeed remarkable. Below about 268 K, and at pressures in excess of about 2 GPa, water molecules in ice adopt a tetragonally distorted bcc structure. This proton-ordered structure (ice VIII) converts to a cubic, orientationally (proton) disordered phase (ice VII) on heating.[5] Raman spectroscopy has been used to monitor the effect of pressure on the O-H vibrations in ice VIII and the loss of asymmetry in the $O-H\cdots O$ hydrogen bonds.[6] Analysis of these measurements suggested the formation of a symmetric hydrogen-bonded ($O-H-O$) structure at 42 GPa. This phase, which has been labeled ice X, is believed to have the cuprite structure.

There have been a number of speculations[7,8] as to the nature of the phase diagram of ice at high pressure (see Fig. 1). These have been based on the plausible assumption that the bcc oxygen lattice will eventually transform to a more compact, fcc structure. When the pressure is increased, there is evidence for increased ionization, and theoretical studies have associated the formation of ice X with an ionization catastrophe.[7] Metallization has been postulated at extreme pressures.[7,8]

The theoretical studies mentioned above predicted the formation of the symmetric H-bond form of ice at around 45 GPa.[7] Subsequent Brillouin-scattering studies from solid ice held in a diamond anvil cell at room temperature revealed clear evidence for a phase transition in exactly the predicted pressure range.[9] Taken together, the weight of experimental evidence,[6,9] indeed, suggests the presence of ice X in the pressure range shown in Fig. 1.

A natural question to ask, therefore, is whether or not ice X will transform to a close-packed ice XI structure at even higher pressures than have been studied so far. An obvious candidate for the structure of ice XI is the antifluorite structure.[8]

In order to examine in detail the speculations that exist in the literature,[7,8] we have carried out constant-pressure molecular-dynamics (MD) calculations on an ionic model for ice X. The model consists of fully ionized water molecules, i.e., O^{2-} and H^+, which interact via purely electrostatic interactions augmented by short-range exchange repulsions between H^+-O^{2-} and O^{2-}-O^{2-}. However, in the latter case the bare Coulomb
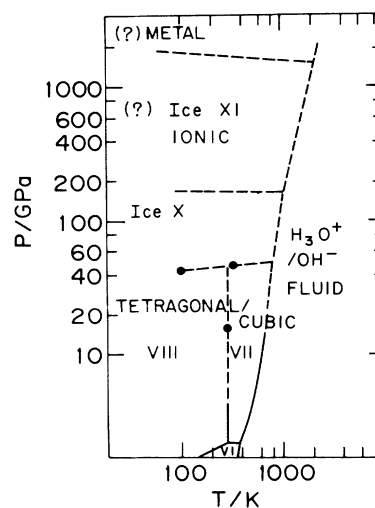

FIG. 1. A schematic phase diagram for ice at high pressures. The bold lines and filled circles are based on experimental data, whereas the dashed lines are speculative (see Refs. 7 and 8).

repulsion dominates.

Classical MD calculation based on this simple potential model suggests that ice X is, indeed, at least metastable at around 30 GPa at room temperature. Moreover, for our model, an increase of the nominal pressure to 90 GPa was sufficient to drive ice X into the anitfluorite ice XI structure. Proton-ordered ice XI appears to be particularly stable. However, on heating to $T \simeq 2000$ K, a fast-ion proton-conducting solid phase is formed. We have also studied the lattice vibrations in these new high-pressure phases. Profound changes are predicted to occur in the proton dynamics when ice XI is formed. These changes should be observable by spectroscopic techniques.

We now describe our calculations in more detail. The short-range potentials for the interactions between O^{2-} and H^+ and between O^{2-} and O^{2-} were obtained by our fitting an exponential repulsion to the energy values obtained with the modified Gordon-Kim electron-gas model and an O^{2-} wave function that was stabilized with a Watson sphere of radius 1.65 bohr.[10] The resulting potential yields an equilibrium structure for H_2O that is linear with an $O-H$ bond length, 0.95 Å, in agreement with the experimental value for an isolated water molecule. The linear geometry is a consequence of our using a pairwise additive ionic model. This discrepancy with the experimental bond angle (104°) is likely of little consequence in the ultrahigh-pressure regime where the water molecules are thought to be ionized.[7] Here, it is far more important to have a reasonable description of the short-range O^{2-}-H^+ interaction.

Constant-pressure MD calculations have proved to be remarkably successful in probing high-pressure phase transformations in atomic and molecular solids.[11,12] Some notable successes include the prediction of a new high-pressure phase for solid N_2,[12] and the recent work on high-pressure amorphous ice.[3] The present MD calculations on ice X were carried out with a periodically replicated cubic or tetragonal MD cell. The latter is known to be a particularly convenient way to study the bcc to fcc transition in atomic systems[13] and hence is likely also useful here for the cuprite to antifluorite transition.

In the case of the tetragonal cell, we used 108 O^{2-} ions and 216 H^+ ions. Constant-volume MD calculations were first carried out to determine the pressure at $T = 300$ K when the ice X lattice constant was set at $a = 2.61$ Å, which corresponds to a symmetric $O-H-O$ hydrogen-bond distance of 2.26 Å. Because of the high density of the system, the frequencies of vibration of the ions are also high. Accordingly, we used the deuteron mass for the H^+ and a rather small time step, $\Delta t = 5 \times 10^{-17}$, to integrate the equations of motion. From a MD run of $64\,000 \Delta t$, we find the calculated pressure for D_2O to be 32 GPa. The MD calculations yield atom-atom radial distribution functions for O-O, O-D,

and D-D that were clearly indicative of a well-ordered solid (see Fig. 2). A constant-pressure MD calculation was then carried out on ice X with the pressure set at 32 GPa. The MD cell remained tetragonal and showed no tendency to deform, even after $32\,000 \Delta t$. From this observation, we concluded that ice X was at least metastable for our ionic model.

At the end of the constant-pressure MD run on the cuprite structure, we brutally increased the pressure to 90 GPa. As a result of this sudden massive increase in pressure, the temperature rose to $\simeq 1000$ K and ice X evolved gradually into a new structure (see Fig. 2), which was readily identified as an ordered antifluorite structure with an fcc packing of O^{2-} ions and a lattice constant $a = 3.05$ Å. The stability of this new phase was tested by continuing the MD calculation for a further $60\,000 \Delta t$. We also carried out additional independent MD runs using a cubic MD cell and an initial ideal antifluorite arrangement of ions. The antifluorite phase, ice XI, proved to be stable to a further 50% increase in the pressure and to the effect of heating (however, see below).

Several attempts were made to study the reverse transitions ice XI $\rightarrow$ ice X by suddenly reducing the nominal pressure from 90 GPa to either 30 GPa or 0. In no case did we observe the complete reverse transformation; under the most favorable circumstances about one-third of
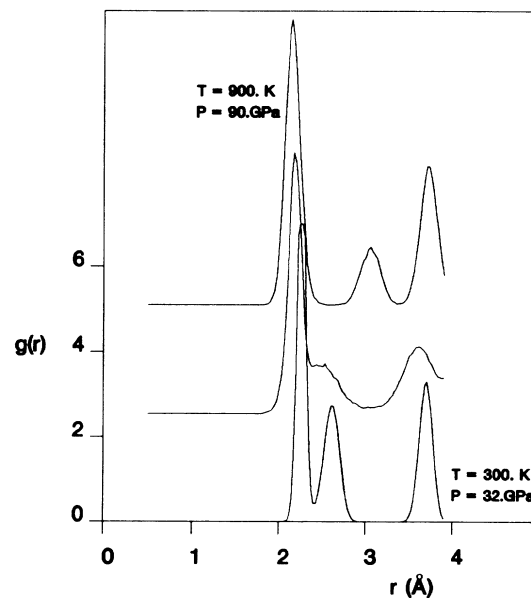

FIG. 2. Pair distribution functions for oxygen atoms in high-pressure ice. The lower curve is calculated for ice X at a nominal pressure 32 GPa and $T = 300$ K and is characteristic of a bcc lattice. The middle curve shows the system $2000 \Delta t$ after a sudden increase in the pressure to 90 GPa. The upper curve is the distribution function after $10\,000 \Delta t$ and is indicative of a fcc packing (ice XI).

the sample transformed back to ice X. This observation suggests that the free energies of the two phases are at least quite competitive.

Fluorite and antifluorite lattices are known to become fast-ion conductors at high temperatures.[14] Accordingly, we carried out an extensive series of MD heating runs on ice XI held at $a = 3.0$ Å. Indeed, as might have been expected, this system did eventually becomes a fast-ion proton (deuteron) conductor at around 2000 K. This fact was verified by examination of the phase-space trajectories of the deuterons which unequivocally establish that the D^+ ions are diffusing through the stable fcc lattice of O^{2-} ions. The ionic displacements (see Fig. 3) are clearly characteristic of a fast-ion conductor.[14] The calculated diffusion constant for D^+ in ice XI at 2000 K was 2×10^{-5} cm^2/s.

The phase transformations outlined above all involve significant changes in the proton (deuteron) sublattice. In an attempt to highlight this, the dynamics of these structures was probed with $Z(t)$, the velocity autocorrelation functions of the ion, plus the autocorrelation functions of the crystal dipole moment and polarizability.[15] The significance of the latter two is that their Fourier transforms yield the infrared and Raman spectra, respectively, whereas the former essentially yields the phonon density of states. As an example, in Fig. 4 we show $Z(\omega)$ for the acoustic (O^{2-} power spectrum) and optic (D^+ power spectrum) regions in ice XI. These spectra resemble qualitatively experimental $Z(\omega)$ data for PbF$_2$ and BaF$_2$.[16] The sharpness of the peaks in Fig. 4 is due to the high density and relatively low temperature ($k_B T \simeq 200$ cm^{-1}), plus the fact that the sample only supports those modes consistent with the periodic boundary conditions.

From an analysis of the power spectra of the infrared- and Raman-active modes (not shown), we predict a Raman-active mode at $\simeq 900$ cm^{-1}, and an infrared mode at $\simeq 700$ cm^{-1} in ice X. After the transformation to ice XI, these peaks shift to $\simeq 1800$ and 1100 cm^{-1}, respectively. The large shift in the Raman mode is likely a consequence of the charge in symmetry and the higher coordination number.[16]

In summary, we have used a simple ionic model and classical constant-pressure MD calculations to explore the phase diagram of ice in the high-pressure region. We find evidence for the existence of a new phase, ice XI, around 1 Mbar, which appears to become a fast-ion (proton) conductor at high temperatures. We further suggest that the transition between ice X and ice XI should be observable in a Raman experiment, since the requisite pressure can now be achieved.[17] Can our calculations be trusted? The most serious assumption we have made, apart from the notion that the system is ionic, concerns our use of classical mechanics to describe the proton (deuteron) motion.[7] We have therefore estimated the quantum (zero-point energy) correction to the calculated pressure in ice X by invoking the approximation $\Delta P_z = \gamma E_z / V$, where V is the volume, P_z and E_z are the zero-point pressure and energy, respectively, $\gamma = -d \ln \bar{\omega}/d \ln V$, and $\bar{\omega}$ is a mean vibrational frequency. The relevant quantities were estimated by the study of the density dependence of the deuteron power spectrum, $Z(\omega)$, such as shown in Fig. 4. As a result of these additional MD calculations, we concluded that our
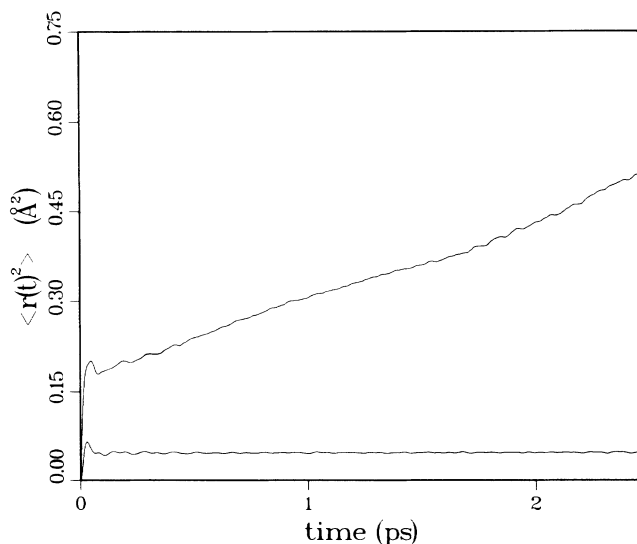

FIG. 3. Mean square displacements as a function of time for O^{2-} (lower curve) and D^+ (upper curve) in the antifluorite phase at 2000 K (see text).
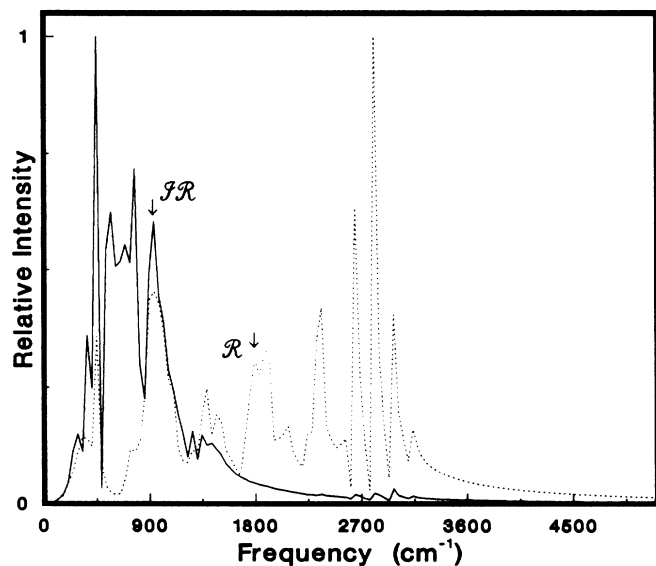

FIG. 4. Power spectra $Z(\omega)$ associated with deuteron motion (dashed curve) in ice XI and oxygen atom motion (bold curve). Also indicated are the infrared (IR) and Raman (R) frequencies (see text).

nominal classical pressures are likely in error by about a factor of 2. If this crude estimate proves to be reliable, the transition pressure for deuterated ice X → ice XI is estimated to occur between 100 and 200 GPa. Recent developments in the field of quantum simulation techniques that exploit the isomorphism between a quantum particle and a classical ring polymer should make it possible to carry out more reliable estimates of the properties of our simple model.[18,19]

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