

New High-Pressure Phase of Ice

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Based on *ab initio* constant pressure molecular dynamics simulation, we predict a new phase transition in ice from ice X to a new phase (ice XI) at ~ 3 Mbar and room temperature. Ice XI preserves the symmetric hydrogen bond and is a wide gap insulator up to and beyond 7 Mbar. This new phase is stable up to 2000 K at 4 Mbar, where the system shows large protonic diffusion.

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The study of the high-pressure region of the ice phase diagram is very important for condensed matter and planetary physics [1–3]. Furthermore, it sheds light onto one of the most important interactions in nature, namely, the hydrogen bond. However, the behavior of ice at high pressure is still largely unknown. The highest pressure investigated so far has been 1.28 Mbar [4]. Experimental and theoretical evidence seem to indicate that in this pressure range the crystal structure (ice X) is that of the cuprite, compatible with a symmetrized hydrogen bond [5–8]. As to higher-pressure behavior there has been a number of intriguing proposals including metallization [5] and transition into antifluorite structure [5,9,10]. Here we study the high-pressure behavior of ice by using *ab initio* constant pressure molecular dynamics [11,12]. We demonstrate the dynamical stability of ice X, thus lending further theoretical support to the experimental conjectures, and we predict a phase transition from ice X to a new phase (ice XI) at ~ 3 Mbar and room temperature. Ice XI preserves the symmetric hydrogen bond and is a wide gap insulator up to and beyond 7 Mbar. In ice XI the oxygen atoms substructure becomes rather close packed in a distorted hcp structure. This new phase is stable up to 2000 K at 4 Mbar, where the system shows large protonic diffusion.

Use of *ab initio* method is essential to describe the hydrogen bonding at these pressures, and constant pressure *ab initio* molecular dynamics method has proven to provide reliable prediction of new crystalline phases [11–14] without any initial guess on the final structure. It is therefore ideally suited for the investigation of matter under these extreme conditions.

In the dynamical simulation we adopted gradient corrections to local-density approximation for the exchange energy part following Becke [15]. This choice has been shown to describe well the hydrogen bonding in water [16]. Ultrafast Vanderbilt pseudopotentials [17] were used for oxygen and hydrogen. The electronic wave functions were expanded in plane waves up to a kinetic energy cutoff of 40 Ry. This high cutoff turned out to be necessary to achieve convergence in the structural properties at 3 Mbar. An integration time step of 5 a.u. was used. For technical reasons we used the deuterium mass. This is unimportant

for the classical equation of state. Quantum corrections have been evaluated with the hydrogen mass. The sampling of the Brillouin zone was restricted to the Γ point of a 16 H₂O molecule supercell.

Starting from an ice VIII-like configuration [18], we equilibrated the sample at the pressure and temperature of 1.5 Mbar and 290 K. In this thermodynamic state the system assumed spontaneously an ice X structure. The oxygen atoms form a bcc structure and the hydrogen atoms sit midway between two neighboring oxygen atoms, leading to a symmetrized hydrogen bond. Further increase in the pressure at ~ 3 Mbar induced a change in the simulation box, reflecting a phase transition from ice X into a new structure. The new phase (ice XI) was identified to be orthorhombic with four H₂O molecules per primitive cell. The space group is *Pbcm* with only one H₂O molecule in the asymmetric unit. In terms of the two independent internal structural parameters u , v , the positions of the atoms are O at $(u, v, \frac{1}{4})$, H1 at $(0, v - \frac{1}{4}, \frac{1}{4})$, and H2 at $(\frac{1}{2}, \frac{1}{2}, 0)$. In the Wyckoff notation these are the positions $4d$, $4d$, and $4b$, respectively [19]. The structural parameters change continuously with pressure. The average values obtained from the dynamical run, well inside the new phase at 4 Mbar and 290 K, are $a = 2.22$ Å, $b/a = 1.61$, $c/a = 1.55$, $u = 0.252$, and $v = 0.434$.

In ice XI the oxygen substructure is a distorted hexagonal-close-packed (hcp) geometry, thus at the transition the O-O coordination number increases from 8 to 12. The 12 nearest neighbors distances are spread within 0.13 Å due to the distortion. The transformation path observed in the simulation is similar to that proposed for the bcc \rightarrow hcp transitions in many metals including Zr, Ti, and Li [20]. Namely, we found that the planes transform as $(110)_{\text{bcc}} \rightarrow (001)_{\text{hcp}}$ and the directions as $[1\bar{1}0]_{\text{bcc}} \rightarrow [1\bar{1}0]_{\text{hcp}}$, where the hcp notation is used also for the quasihcp structure of ice XI. These relationships are due to the fact that the $[001]_{\text{bcc}}$ axis contracts in order to produce a nearly triangular lattice in the $(110)_{\text{bcc}}$ plane. This is accompanied by the alternate sliding of $(110)_{\text{bcc}}$ planes which leads to the ABAB stacking of the hcp phase. In the X \rightarrow XI transformation both the contraction along $[001]_{\text{bcc}}$ and the sliding of $(110)_{\text{bcc}}$ planes are not

complete. The final result is a distorted hcp substructure of oxygen atoms. The hydrogen atoms follow rigidly the displacements of the oxygen atoms still sitting midway between the two neighboring oxygen atoms. A projection of ice XI on the almost hexagonal plane is reported in Fig. 1(a). The angle ϕ in Fig. 1(a) measures the sliding of the original $(110)_{\text{bcc}}$ planes, and is $\phi = 23^\circ$. Chains of oxygen atoms bonded by hydrogen atoms are apparent along the $[010]$ and $[001]$ directions (Fig. 1). The original tetrahedral coordination of oxygen in ice X is now distorted. Nevertheless, the hydrogen bonding is preserved and the new phase appears as a compromise between the tendency towards close packing which would favor the ideal hcp phase (with $b/a = 1.733$, $c/a = 1.634$, and $\phi = 30^\circ$) and the conservation of hydrogen bonds which would favor the tetrahedral coordination of ice X (with $b/a = c/a = 1.414$ and $\phi = 0$).

The precise determination of the transition pressure from the dynamical run is difficult, due to well-known hysteresis effects and also to insufficient sampling of the Brillouin zone (BZ). For these reasons we performed static calculations of the ice X and ice XI equations of state at zero temperature and at full convergence in the BZ integration. In these calculations, in order to further check the sensibility of the results on the pseudopotential choice, we used a conventional norm-conserving pseudopotential

[21] and a plane wave expansion up to 100 Ry. We also added the effect of zero point motion.

The equations of state of ice X and XI are reported in Fig. 2. The antifluorite structure proposed in previous works [5,9,10] is much higher in energy than either ice X or ice XI and foremost it is unstable with respect to some phonons at the Γ point. Its equation of state is reported in Fig. 2 for the sake of comparison with ice X and ice XI. Indeed the antifluorite has a much higher Madelung energy than the Cu_2O structure of either ice X or ice XI which is closely related to ice X. Furthermore, it is incompatible with the formation of a tetrahedral network of hydrogen bonds. The result of Ref. [10] is probably due to an overestimation of the O-O repulsion which would favor the close-packed antifluorite structure and to the difficulty of modeling the hydrogen bond in this extreme regime.

The structural parameters of ice XI as a function of pressure at 0 K are reported in Table I. Ice XI continuously evolves from ice X towards ideal hcp upon increased pressure, starting to be stable around ~ 3.5 Mbar, close to the transition pressure seen dynamically. We checked the dependence of the structural parameters on exchange and correlation functionals by computing the equation of state of ice X and ice XI with the Becke exchange [15] and Lee-Yang-Parr correlation functionals [22]. The effect of the latter functional is a reduction of the pressure (~ 0.4 Mbar)

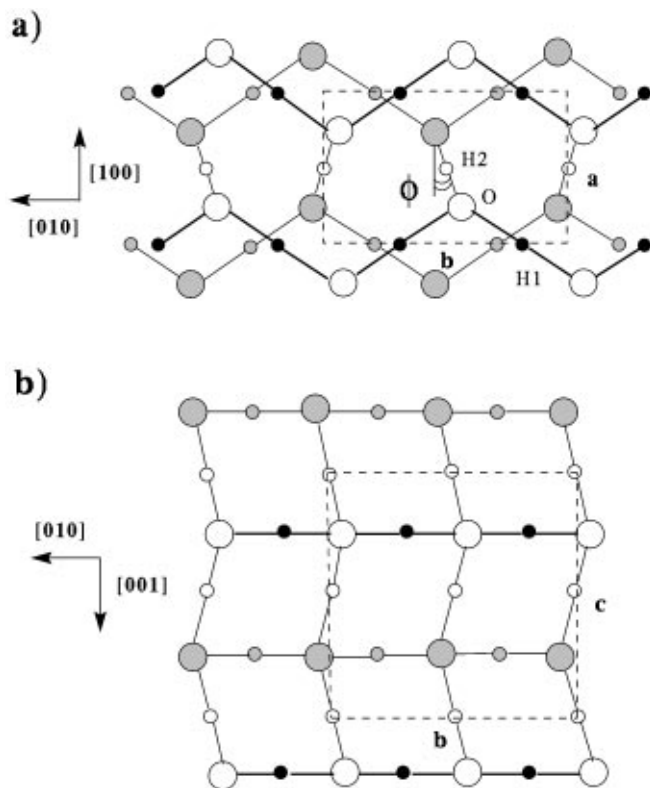


FIG. 1. (a) Projection of ice XI structure on the orthorhombic (001) plane. Black and grey atoms belong to different (001) planes. White hydrogen atoms lie in between those planes. The unit cell is marked by dashed lines. (b) Projection of ice XI on the orthorhombic (100) plane.

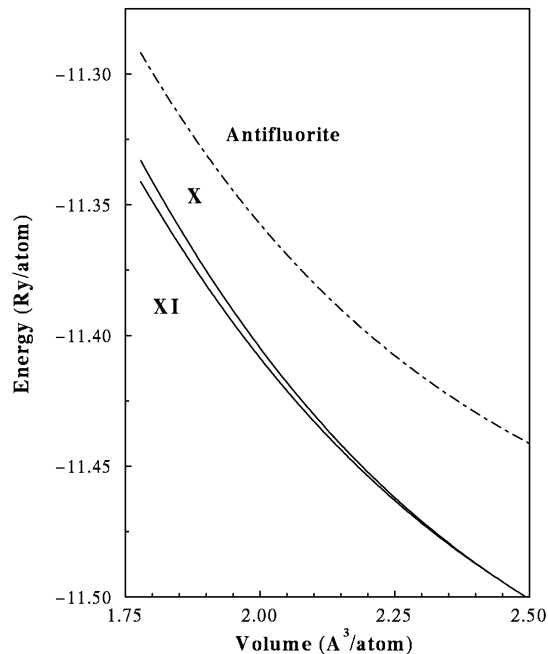


FIG. 2. Calculated equation of state at 0 K and full convergence in Brillouin zone integration of ice X, ice XI, and antifluorite. The antifluorite structure is unstable with respect to some phonons at the Γ point, and its energy is reported here only for the sake of comparison. The zero point energy as computed from the Γ point phonons in 16 H_2O molecule supercells of ice X and XI is added to the equations of state. The zero point energy further favors ice XI with respect to ice X by 0.6 mRy/atom at 4 Mbar. The zero point energy of antifluorite is not defined and it is taken equal to ice X.

TABLE I. Pressure dependence of the volume and structural parameters a , b/a , c/a , u , and v of ice XI along the equation of state in Fig. 2. The angle ϕ [see Fig. 1(a)] is also reported for comparison with the ideal hcp structure. These parameters are slightly different from those obtained from the dynamical simulation due to finite temperature and limited k point sampling in the dynamical run. The orthorhombic unit cell contains four H₂O molecules.

P (Mbar)	V (Å ³ /atom)	a (Å)	b/a	c/a	u	v	ϕ
6.6	1.89	2.01	1.71	1.63	0.255	0.415	29°5'
5.8	1.98	2.06	1.69	1.62	0.255	0.419	28°0'
4.7	2.13	2.14	1.64	1.59	0.254	0.429	24°7'
4.3	2.18	2.18	1.61	1.58	0.253	0.437	21°7'
3.8	2.27	2.22	1.59	1.57	0.252	0.443	19°8'

at low densities in Table I. However, at a given volume the structural parameters in Table I do not change.

The effect of the limited BZ integration is to favor ice XI, the difference in energy between ice X and XI at 4 Mbar being $\Delta E = 2.1$ mRy/atom (332 K/atom) with Γ point only and $\Delta E = 0.23$ mRy/atom at full convergence in BZ integration. Despite such a tiny energy difference ice XI at 4 Mbar is stable up to 2000 K, as deduced from the dynamical simulation. Around 2000 K the hydrogen atoms start to diffuse among the available sites midway between neighboring oxygen atoms (only 4 sites out of 12 are occupied in ice XI), still leaving the hcp substructure of oxygen stable [23]. The introduction of quantum tunneling effects could reduce the temperature and pressure at which the protonic diffusion sets in.

Ice XI is insulating up to and beyond 7 Mbar where the electronic band gap is as large as 10.8 eV. The band gap continuously increases in ice VIII and ice X up to ~ 12 eV at 3 Mbar. The gap widening is mainly due to Madelung effects, the first excitation being a charge transfer from oxygen to hydrogen. The highest occupied molecular orbital state is, in fact, a lone-pair p state of oxygen, and the lowest unoccupied molecular orbital is an antibonding orbital between s states of oxygen and hydrogen. Above 3 Mbar the electronic gap decreases in ice XI due to increase in band dispersion. The proposed metallization of H₂O [5] is therefore to be expected at much higher pressure.

In conclusion, we predict a new phase transition in ice from ice X to a new ice XI phase. The transformation is expected to occur between 3 and 4 Mbar, taking into account the computational uncertainty. Ice XI is stable up to 2000 K at 4 Mbar, and insulating up to and beyond 7 Mbar. The predicted transition pressure is within the range of pressure presently achievable in diamond anvil cells [24]. Furthermore, a softening of the [110] zone border phonon in ice X is likely to be a precursor of the ice X \rightarrow ice XI phase transition. Such a phonon softening could be detected at much lower pressure than the actual transition pressure. Ice at similar and higher pressures is present in Jovian planets and the present finding is of great relevance in planetary physics [2].

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