

Quartzlike polymorph of ice

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Among the crystalline forms of water, the familiar hexagonal and the metastable cubic modifications of ice I occur naturally on the Earth and in its atmosphere, while other ices exist only under high pressures. Using molecular-dynamics simulations we have examined the effects of static electric fields upon the freezing of water. A quartzlike ice polymorph has been produced under pressures of 3–5 kbar and at temperatures of 225–240 K. These results demonstrate a possibility of generating new forms of ice through the electrofreezing of water. [S0163-1829(96)00118-2]

I. INTRODUCTION

Water can exist in many crystalline forms; no less than twelve crystalline ice structures are currently known.^{1–7} Systematic studies of ice structures began in the first half of this century with the work of Bridgman and Tammann who discovered several high-pressure ice polymorphs.^{1,4} After further detailed investigations it became clear that some ice modifications can exhibit low-temperature proton ordering transitions,^{1,4,7} while some were found to have no field of actual stability on the equilibrium phase diagram for water, existing only as metastable phases.¹ More recently, theoretical studies have also revealed how water may look under ultrahigh pressures (of hundreds of GPa) when approaching metallization;⁸ such extreme conditions, as could exist in the interiors of large planets, are becoming feasible in the laboratory.

Using molecular-dynamics (MD) simulations⁹ we have examined the effects of applied electric fields in the crystallization of water. As various phenomenological observations have indicated,^{12–14} some dating from the previous century,¹⁵ an electric field can promote the nucleation of ice I from supercooled liquid water. This electrofreezing effect plays an important role in many natural processes, ranging from tropospheric dynamics to frost damage in living cells.^{12–16} In our previous study¹⁷ we have observed the field-induced nucleation of ice I_c at normal atmospheric and small positive pressures (from 0 to approximately 0.5 kbar) and at temperatures at or below 260 K for the TIP4P potential.¹⁸ We emphasize that the crystallization of molecular liquids has been rarely observed upon simple quenching¹⁹ within the time scale of a typical MD simulation due to the appearance of metastable glassy states which prevent a spontaneous nucleation of a molecular heterophase. In computer simulations of water, a highly polar substance, the application of an electric field facilitates the nucleation of polar ice from the metastable liquid (as it appears to in nature) providing a unique opportunity to study directly the process of crystallization of water at the molecular level.

II. RESULTS

We have found that application of an electric field to liquid TIP4P water under pressures of 3–5 kbar and at tempera-

tures of 225–240 K produces an ice polymorph with an open quartzlike structure (hereafter, ice XII), on a time-scale of typically 1 ns.²⁰ Our results indicate that under constant pressure conditions water expands upon freezing into this structure, as it does during the nucleation of ice I which also features an open crystalline packing. It is important to point out that the boundary conditions imposed during these liquid-to-solid transformations are not biased towards this structure, and the emerging ice crystals usually contain lattice defects and appear misaligned within the simulation cell. As in our earlier work¹⁷ on the crystallization of ice I we have also performed a series of liquid-to-solid simulations under constant density conditions. These conditions were found to be more favorable (in particular, at $\rho=1.16\text{--}1.20$ g/cm³ for TIP4P water) than constant pressure conditions for producing “good,” i.e., containing less defects, ice XII crystals.

To provide benchmark structural information, we have constructed and then optimized a defect-free crystal lattice of TIP4P ice XII.²¹ The lattice energy is a minimum at about 2 kbars over the temperature range 50 to 300 K, the latter being the estimated mechanical melting point. The temperature and the pressure dependences for the configurational energy and the density are shown in Fig. 1. The crystal structure of ice XII in its minimum energy configuration at 150 K ($U=-51.6$ kJ/mol, $\rho=1.137$ g/cm³) is shown in Figs. 2 and 3.

Each water molecule in the structure of ice XII has four nearest hydrogen (H) bonded neighbors at distances of 2.70–2.75 Å. The nearest-neighbor coordination polyhedron deviates from the ideal tetrahedral shape by tilting and contraction along the *c* direction. The two nearest H-bond acceptors in the ice XII structure are found essentially in tetrahedral sites (as viewed in the local frame of a central molecule), while the two nearest H-bond donors are shifted away from their ideal tetrahedral positions.²² An important structural feature of ice XII distinguishing it from the known high-density crystalline forms of water is the absence of interstitially coordinated molecules. It is now well-documented that this interstitial coordination of non-H-bonded water molecules, found in the liquid²³ and the high-density amorphous or crystalline forms^{1,24} at separations of 3.2–3.8 Å, disap-

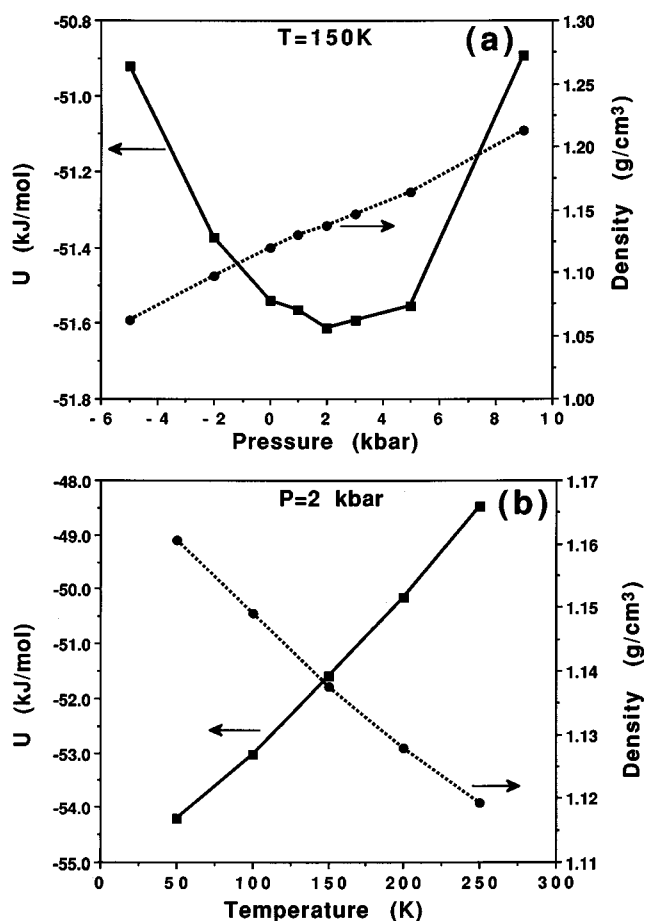


FIG. 1. The pressure (a) and the temperature (b) dependences for the configurational energy (the solid line) and the density (the dashed line) for TIP4P ice XII.

pears upon the formation of the low-density crystalline, I_h and I_c , and amorphous phases.^{17,24,25} Thus, ice XII can be identified as another four-coordinated, “low-density” crystalline ice structure.

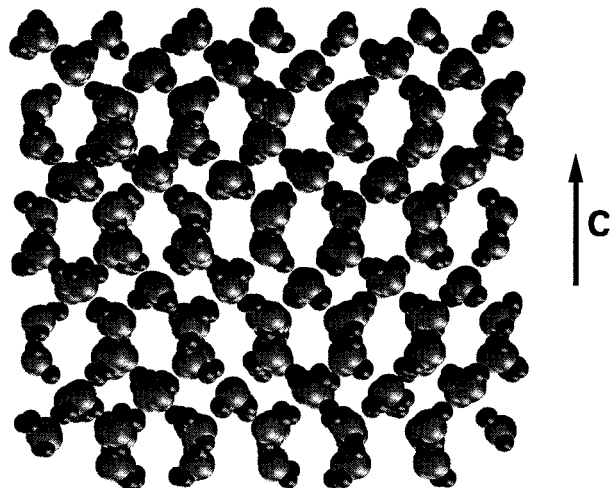


FIG. 2. The structure of ice XII (antiferroelectric) at a temperature of 150 K and a pressure of 2 kbars. The gray and the black spheres represent, respectively, the oxygen and the hydrogen atoms of the water molecules.

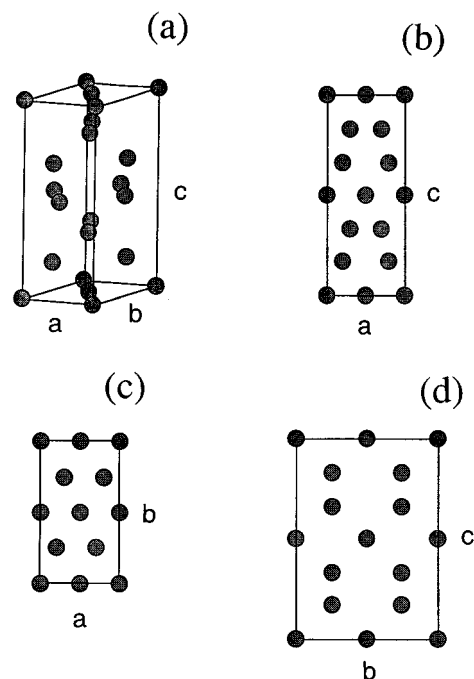


FIG. 3. General view (a) and the crystallographic projections (b) 010, (c) 001, and (d) 100 of the unit cell for ice XII displayed in Fig. 2; only the oxygen positions are shown. The unit cell is primitive orthorhombic, with the dimensions $a=4.135$, $b=7.418$, and $c=10.356$ Å. The space group is $Pnc2$ and the number of water molecules per unit cell is 12. The oxygen coordinates are: $2(a)$ $Z_1=0$; $2(b)$ $Z_2=1/2$; $4(c)$ $X_3=1/4+u$, $Y_3=1/4$, $Z_3=1/3$, and $X_4=3/4+u$, $Y_4=1/4$, $Z_4=1/6$ with $u=0.05$.

III. CONCLUDING REMARKS

Given our observations, experimental efforts are certainly needed to examine whether ice XII can exist as a stable form capable of coexistence with other ices (II or III which are believed to be the equilibrium stable phases at the temperatures and pressures under consideration^{1,4}) or whether it can emerge only as a metastable phase. Very recently, Baez and Clancy have suggested that another quartzlike ice structure (with an orthorhombic $P2_12_12$ symmetry and six molecules per unit cell) is the thermodynamically preferred solid structure for SPC/E water at 1 bar.²⁶ We may remark that existing computer simulation techniques, while being a powerful tool in studying solid-solid transformations of the displacive type (such as of the high-to-low quartz), are not yet well equipped to mimic directly transformations of the reconstructive type involving drastic changes in the local coordination, for instance between various ice structures.²⁷ Experiments that may detect ice XII include freezing, under pressure, liquid water confined between charged metallic electrodes²⁸ or between (piezoelectric) quartz slabs, seeding^{2,29} supercooled high-density water with quartz crystals, and other isostructural materials. Due to distortion from ideal tetrahedral coordination, the nearest neighbors (H-bond acceptors and donors) in ice XII structure are geometrically nonequivalent (in the local frame). Hence, one might try to grow ice XII from H_2O - D_2O mixtures and electrolyte solutions;^{29,30} incorpora-

tion of asymmetric HDO molecules into the crystal lattice or ionic doping could provide its stabilization. No doubt, further experimental and theoretical work on ice XII will deepen our current understanding of water as a substance (and its relation to another important material, such as silica) and may well aid in explaining properties of metastable states³¹ of water.

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- ⁹Our observations are based on molecular dynamics simulations of the TIP4P (Ref. 10) model for water; several complementary simulations were also performed with the SPC/E (Ref. 11) water model. These widely accepted models are reasonably successful in describing the properties of the real liquid and various amorphous and crystalline ices. In our liquid-to-solid simulations 256 and 216 particle samples were used, respectively, in truncated octahedral and cubic simulation cells with periodic boundary conditions. A fourth-order Gear algorithm with a time step of 1.25 fs was used to integrate our Gaussian isokinetic equations of motion. Both constant pressure (Nose barostat) and constant density conditions were explored. The homogeneous electric field applied was typically 0.5 V/Å.
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- ²¹The ice XII emerging from liquid water under our applied field conditions is virtually 100% polarized (fully proton ordered). In our subsequent optimization of its crystal structure (performed with 360 water molecules) we adopted nonpolarized antiferroelectric proton ordering. The question whether real ice XII is proton ordered or disordered can, of course, be resolved only by experimental studies. In our lattice calculations we have allowed the simulation cell to change shape as suggested by M. Parrinello and A. Rahman [*J. Appl. Phys.* **52**, 7182 (1981)].
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