

## Theoretical study of the isostructural transformation in ice VIII

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(Received 29 June 2004; published 14 January 2005)

We present a first-principles study of the structural and vibrational properties of  $D_2O$ -ice VIII. We do not confirm the existence of the structural discontinuity that was proposed on the basis of a neutron diffraction study and of a first principles calculation, although we reproduce well other physical properties, including the nonlinear behavior of phonon frequencies below 3 GPa. This study brings about the necessity of further experiments to investigate the structure of ice VIII at high pressure. The relationship between phonon frequencies and structural parameters is clarified in detail.

DOI: 10.1103/PhysRevB.71.012102

PACS number(s): 62.50.+p, 63.20.-e, 83.80.Nb

Ice has an intricate phase diagram and at least thirteen crystalline phases have been identified experimentally so far.<sup>1</sup> Among them, ice VIII, a stable phase in a wide pressure range at low temperatures, is perhaps the most convenient phase for experimental and theoretical investigations, since it can exist from  $\sim 80$  GPa to ambient pressure with a large variation in the hydrogen-bond length. It has a simple structure with four water molecules per unit cell and hydrogens (deuterions in the present study) are completely ordered. Phase boundaries between ice VIII, VII, and X have been identified by inspecting Raman and infrared modes' dependences on pressure and temperature.<sup>2</sup> Also nonlinearities in the vibrational spectrum were revealed below a few GPa.<sup>3</sup> They seemed to be related with a pressure-induced isostructural phase transformation near 1 GPa in which the  $z$  coordinate of oxygen [ $z(O)$ ] varied discontinuously but without any symmetry change<sup>3</sup> in the structure. A first-principles calculation later appeared to confirm the discontinuity in  $z(O)$ , although no discontinuity in related vibrational frequencies was found.<sup>5</sup> Our recent study of  $H_2O$ -ice VIII under decompression reproduced the nonlinear behavior of various phonon frequencies and bond lengths and indicated that these can be viewed as precursors of hydrogen-bond network reconstruction.<sup>4</sup> Here we reinvestigate by first principles the behavior of phonon frequencies and the structural parameters in  $D_2O$ -ice VIII under decompression. We clarify the relationship between these quantities and compare them with experimental data and previous calculations that lead to the proposal of the isostructural transformation.

Ice VIII consists of two interpenetrating hydrogen-bond networks, each one containing oxygens at the sites of a diamond lattice (Fig. 1). Ice VIII is antiferroelectric with dipole moments oriented in opposite directions in each network. The unit cell of ice VIII is body-centered tetragonal with space group of  $I4_1/amd$  and has four water molecules. This tetragonal symmetry allows a relative shift of the hydrogen-bond networks with respect to each other along the  $c$  axis. This displacement is reflected in the tetragonal distortion parameter  $\epsilon = 2c[0.125 - z(O)]$  and is accompanied by a deviation of  $z(O)$  from 0.125. These deviations are related to the tetragonal distortion and they vanish in the high temperature and high pressure cubic forms of ice VIII, ice VII, and ice X, respectively.

We adopt norm-conserving pseudopotentials<sup>6</sup> and the Perdew-Burke-Ernzerhof functional for the generalized-gradient approximation.<sup>7</sup> A plane-wave basis set with a cut-off energy of 100 Ry and 11  $k$  points in the irreducible wedge of the Brillouin zone are used. Lattice constants and atomic coordinates are fully optimized at arbitrary pressures by using a damped form of variable-cell-shape dynamics.<sup>8</sup> Phonon frequencies are computed in the framework of density-functional perturbation theory.<sup>9,10</sup> It was demonstrated that this method can describe structural and vibrational properties of ice VIII appropriately.<sup>4</sup>

Table I shows the structural parameters of ice VIII optimized at 2.4 GPa. This level of agreement in lattice parameters and bond lengths between our results and experimental data<sup>11</sup> is reassuring. Pressure dependent intramolecular stretching and translational mode frequencies are shown in Fig. 2. Our calculations reproduce well the experimental behavior. Below 3 GPa intramolecular stretching mode frequencies increase nonlinearly, with the  $\nu_3 E_g$  mode frequency surpassing that of the  $\nu_1 B_{1g}$  mode. At low pressure translational mode frequencies decrease nonlinearly. In Ref. 12,

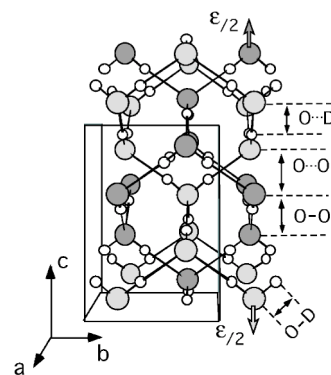


FIG. 1. Structure of ice VIII. Its conventional unit cell is shown by a rectangular parallelepiped. Light and dark gray spheres denote oxygens on two different interpenetrating hydrogen-bond networks. Small and white spheres represent deuterions. O-D and O...D are intramolecular and hydrogen-bond lengths, respectively. O-O and O...O are the distances between nearest oxygens connected or not by hydrogen-bonds, respectively. Arrows show displacements of the two networks allowed by the tetragonal symmetry.

TABLE I. Structural parameters of ice VIII at 2.4 GPa. The unit is angstrom. See Fig. 1 describing the meaning of O-D, etc.

	$a$	$c$	O-D	O···D	O-O	O···O
Calc.	4.658	6.709	0.9874	1.883	2.870	2.760
Expt. (Ref. 11)	4.656	6.775	0.9684	1.911	2.879	2.743

$\nu_{Tz}B_{1g}$  and  $\nu_{Tx,Ty}E_g$  modes were assigned to a single Raman peak of  $207.5 \text{ cm}^{-1}$  for  $D_2O$ . However, our results show that the  $\nu_{Tz}B_{1g}$  mode frequency is definitely higher than  $\nu_{Tx,Ty}E_g$  mode. This is caused by the tetragonal distortion. Therefore, in Ref. 12 the peak at  $207.5 \text{ cm}^{-1}$  and the higher one at  $249.1 \text{ cm}^{-1}$  that was not assigned to any mode should have been assigned to  $\nu_{Tx,Ty}E_g$  and  $\nu_{Tz}B_{1g}$  modes, respectively. Similarly, experimental data that were referred to as the  $\nu_T = \nu_{Tz}B_{1g} + \nu_{Tx,Ty}E_g$  phonon mode in Ref. 13 should correspond to the  $\nu_{Tx,Ty}E_g$  mode only. Here no discontinuity is identified in any of these modes, although it could be expected from experimental data at  $\sim 3 \text{ GPa}$ .<sup>3</sup>

One neutron diffraction measurement<sup>3</sup> and one first-principles calculation<sup>5</sup> indicated that  $z(O)$  changes abruptly from one constant value to another [denoted by dashed and solid lines in Fig. 3(a)], suggesting an isostructural phase transformation. However, our results shown in Fig. 3(a) indicate that  $z(O)$  varies smoothly without any discontinuity;

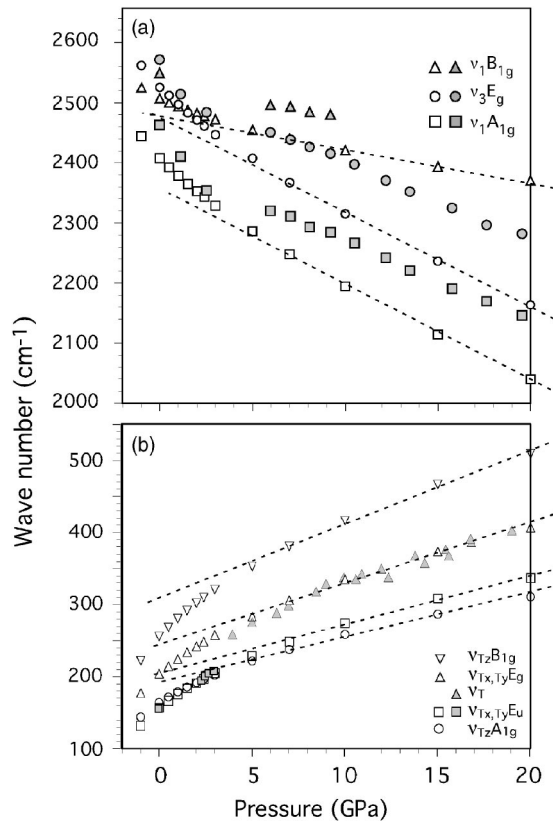


FIG. 2. Pressure dependence of several frequencies of (a) intramolecular stretching modes and (b) translational modes in  $D_2O$ . White and gray points refer respectively to our calculations and experiments (Refs. 3 and 13). Dashed lines are guides to the eye.

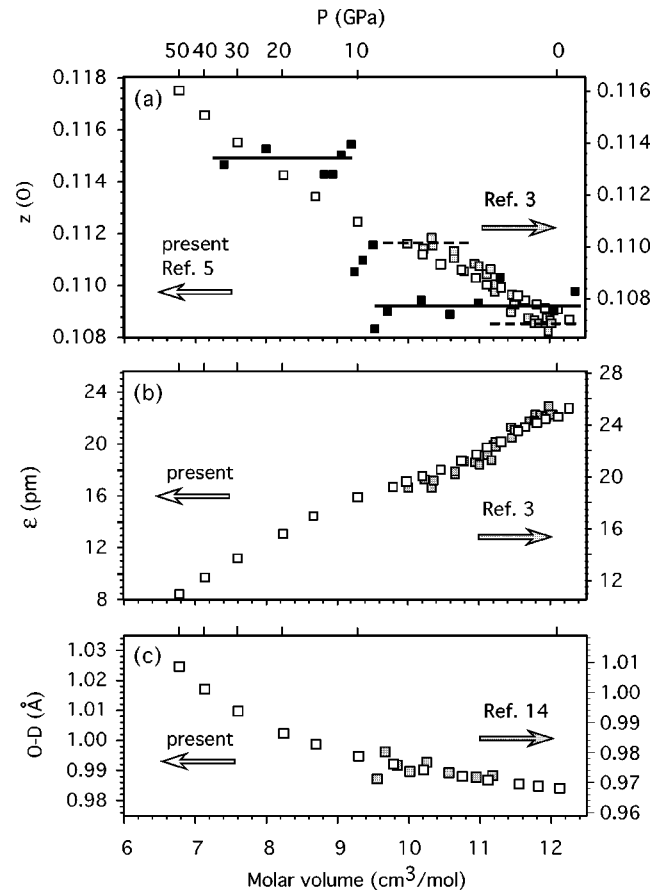


FIG. 3. Volume dependence of (a)  $z(O)$ , (b) the tetragonal distortion parameter  $\epsilon = 2c[0.125 - z(O)]$ , and (c) intramolecular distance O-D. White, black, and gray squares denote results of the present calculation, the previous calculation in Ref. 5, and the experiments in Refs. 3 and 14. In (a), dashed and solid lines represent two constant values of  $z(O)$  in Refs. 3 and 5, respectively. Values of pressure shown here are for the present calculation, not for results of Refs. 3, 5, and 14.

*we do not detect any signs of a phase transformation within our computational accuracy.* This is consistent with the continuous variation of the translational  $\nu_{Tz}A_{1g}$  mode frequency [Fig. 2(b)]. The atomic displacements in this mode are proportional to the distortions associated with the cubic-to-tetragonal symmetry. Instead, variations in  $z(O)$ , in the tetragonal distortion parameter  $\epsilon$ , and in the O-D bond length are very similar to the experimental ones,<sup>3,14</sup> except that  $z(O)$  does not plateau on a constant value as proposed in Refs. 3 and 14. Our results show that  $z(O)$  continues increasing continuously. This seems reasonable since at even higher pressures the tetragonal distortion vanishes with ice VIII transforming into cubic ice X, where  $z(O)$  is equal to 0.125 and  $\epsilon$  equal to zero. The calculation in Ref. 5 indicated that there was a discontinuity in  $z(O)$  and the upper constant value suggested by Refs. 3 and 14 was a real effect. More experiments are necessary to resolve this confusing situation, especially at high pressure near the phase boundary between ice VIII and cubic ice X.

The behavior of phonon frequencies and tetragonal distortion parameters are inter-related and also related with that of

the bond lengths O-D, O $\cdots$ D, O-O, and O $\cdots$ O (see Fig. 1 for definition): O-D decreases and O $\cdots$ D, O-O, and O $\cdots$ O increase nonlinearly with decreasing pressure.<sup>4</sup> The decrease of O-D, the intramolecular bond length, is reflected in the increase of intramolecular stretching mode frequencies [Fig. 2(a)], i.e., in the increase of this bond strength. Hence, the overestimation of O-D [Table I and Fig. 3(c)], which was observed also in other first-principles calculations,<sup>5,15</sup> is consistent with weaker intramolecular bonds and the underestimation of stretching mode frequencies with respect to experiments [Fig. 2(a)]. Similarly, the decrease of translational phonon frequencies corresponds to the increase of the intermolecular bonds lengths, O $\cdots$ D and O $\cdots$ O, i.e., weakening of bonds. With the decrease of O-D and the increase of O $\cdots$ D, the bonds between two oxygens bridged by the hydrogen-bond weakens and its length (O-O) increases. The increase of O-O leads to the increase of the lattice constant  $c$  and consequently to the increase of  $\epsilon$ .

In summary, we have investigated the structural and vibrational properties of ice VIII under decompression by first principles. The pressure dependence of experimental phonon frequencies and structural parameters has been reproduced very well. However, we have not detected any discontinuity in the structural parameters that previously suggested an isostructural phase transformation. Here we have also clarified the relationship between the pressure-induced behavior of phonon frequencies and structural parameters and shown their consistent behavior. It appears that further experiments are necessary to resolve these apparently conflicting results, particularly at high pressure closer to the ice X phase boundary.

We used the PWscf package.<sup>16</sup> Computations were performed at the Minnesota Supercomputing Institute. This research was supported by NSF Grants No. EAR-0135533 (COMPRES), No. EAR-0230319, and ITR-0428774 (Vlab).

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