High Pressure Research
Vol. 29, No. 2, June 2009, 208–211

Nature and stability of ice X[†]

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(*Received 6 September 2008; final version received 23 September 2008*)

A study of pressure effects on the vibrational frequencies of ice X is performed to shed light on the existence and stability of this phase. The analysis reveals: (i) its stability range, (ii) the soft phonon nature of the transition at high pressures to the *Pbcm* structure proposed by Benoit et al. (M. Benoit, M. Bernasconi, P. Focher, and M. Parrinello, *New high-pressure phase of ice*, Phys. Rev. Lett. 76 (1996), pp. 2934–2936.) and (iii) the phonon collapse associated with the dynamical disordered structure at low pressures. Additionally, a topological analysis of the electron localization function and the electron density through the atoms-in-molecules formalism clarifies the chemical nature of ice X.

Keywords: ice X; density functional perturbation theory; chemical bonding; electron localization function.

1. Introduction

The study of the high-pressure phases of ice is essential in many areas of science such as molecular science and earth and planetary sciences. Both experimental and theoretical investigations face problems.

Experimentally, X-ray diffraction is unable to probe the proton positions, while neutron scattering can not be performed at very high pressures. Indirect information about the phase transformations can be obtained from Raman and IR experiments, but they are also linked to very low scattering cross sections of the phases at such high pressures. Theoretical challenges are the consideration of the quantum fluctuations of the protons, the inclusion of anharmonicity and the description of the hydrogen bond within density functional theory (DFT). Among the known phases of ice, the highest pressure form known to date, ice X, has two symmetric OH-bonds for each hydrogen atom, and hence it is no longer molecular. It belongs to the cubic space group $Pn\bar{3}m$ with oxygen and hydrogen atoms located at $2a$ (0,0,0) and $4c$ $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ sites, respectively [1]. It comprises a bcc packing of oxygen atoms, tetrahedrally coordinated to hydrogen atoms located exactly midway between two neighboring oxygen atoms. Observation of this theoretically proposed phase has been claimed by spectroscopical [2,3] and X-ray diffraction

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[†] This paper was presented at the XLVIth European High Pressure Research Group (EHPRG 46) Meeting, Valencia (Spain), 7–12 September, 2008.

ISSN 0895-7959 print/ISSN 1477-2299 online

DOI: 10.1080/08957950802564031
http://www.informaworld.com

experiments [4,5]. *Ab initio* molecular dynamics simulations also confirm its appearance under compression such that the distances between the two neighboring oxygen atoms are smaller than 2.27 Å [6]. However, the nature of this phase and its possible phase transitions to low-pressure and high-pressure polymorphs of ice are still subject to debate.

Here, we report a first-principles study of the phonon frequencies of ice X under pressure to gain insight into its stability under (de)compression. In addition, the nature of the chemical bonding is characterized through the topological analysis of the electron localization function (ELF) [7,8] and the electron density under the atoms-in-molecules [9] (AIM) formalism.

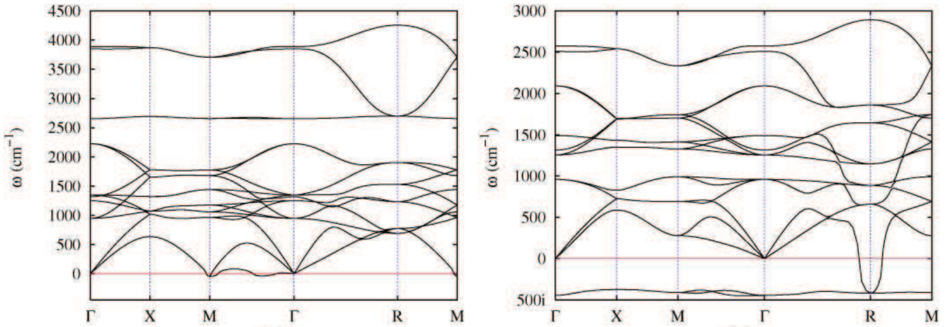
2. Computational details

Phonon frequencies were calculated within the density-functional perturbation theory as implemented in the Quantum-ESPRESSO package [10]. The total energies required in the calculation of the phonons were obtained using the Perdew–Burke–Ernzerhof parametrization of the exchange correlation potential [11]. The ion–electron interaction was described by both ultrasoft [12] and norm-conserving [13] pseudopotentials. For the ultrasoft pseudopotentials, the electronic wave functions and charge density were found to be converged, with a kinetic energy cutoff of 60 and 600 Ry, respectively, while a bigger kinetic energy cutoff of 120 Ry was required for norm-conserving pseudopotentials. Brillouin zone integrations were performed with $8 \times 8 \times 8$ k-point meshes [14]. To compute the full phonon dispersion curves, we computed the interatomic force constants by the Fourier transformation of the dynamical matrices computed on (8,8,8) regular q-point grids. Additionally, a topological analysis of the electron density and the ELF was performed with the CRITIC code [15]. To obtain both scalar fields, we use the all-electron WIEN2k [16] and CRYSTAL98 [17] codes, respectively.

3. Results and discussion

3.1. *Dynamical stability*

The calculated phonon dispersion curves for the ice X structure (Figure (1)) versus pressure allow us to distinguish three stages. From 110(97) GPa to 420(408) GPa, all the phonon frequencies calculated using norm-conserving (ultrasoft) pseudopotentials are positive, indicating that ice X is a stable phase.



(a) (b)

Figure 1. Phonon dispersion curves of the ice X structure at (a) 420 GPa and (b) 105 GPa, calculated using norm-conserving pseudopotentials.

At higher pressures (Figure 1(a)), the progressive appearance of a double-unstable mode at the M point (M4) is related to the transition to the orthorhombic *Pbcm* structure proposed by Benoit et al. [18]. Moreover, the appearance of instabilities around the Γ-point signals that the transformation also involves a distortion of the cell parameters from their ideal values. When decreasing the pressure below 110(97) GPa, the frequency of a mode at the R point becomes imaginary. Interestingly, the irreducible representation (R5+) associated with this mode leads to the tetragonal $I41/amd$ structure of ice VIII. This initial softening is followed by a sudden flattening and collapse of the vibrational mode in the entire Brillouin zone (Figure 1(b)). Hence, a dynamically disordered structure is generated in agreement with previous experimental and theoretical data. What is more, the eigenvector associated with this phonon corresponds to the antisymmetric stretching (T_2) of tetrahedra, which leads to the recovery of the molecular nature of the phase. In particular, at Γ, freezing in the atomic distortions involved in this mode leads to a $P4_2nm$ space group with O and H atoms at $2a$ and $4c$ positions, respectively. The calculation of the energy as a function of the phonon amplitude reveals the appearance of a double-well potential when decreasing the pressure, which explains the dynamically disordered structure.

3.2. *Chemical bonding*

Calculations of the band structure at several pressures show that ice X is an insulator. Moreover, the flatness of the bands implies high electron localization: a suggestion that is clear in the real space visualization of the electron density (ρ) and ELF. As shown in Figure 2(a), the strong symmetric H-bonds in ice X generate a three-dimensional network of strong charge accumulation ($\nabla^2\rho < 0$) surrounded by regions of charge depletion ($\nabla^2\rho > 0$). The numerical evidence relies on the homogeneity index defined as $\rho_c^{\min}/\rho_b^{\max}$, where $\rho_c^{\min}$ and $\rho_b^{\max}$ are the absolute minimum and maximum electron density among the AIM critical bond points of the unit cell. This has a low value of $\approx$0.10, increasing slowly with pressure. The ELF value along the bond path O−H−O of the ice X structure at several cell parameters is plotted in Figure 2(b). As pointed out previously [19], the ELF minimum between the oxygen-valence basin and the hydrogen basin is correlated with the AIM critical point. The very high value of the ELF at this minimum indicates a strong bond. Whereas the negative Laplacian at the AIM critical bond point signals its 'covalent' character. As the pressure increases, there is a displacement of both the AIM critical bond point and the ELF minimum toward hydrogen. It is related with an increase of the oxygen polarization

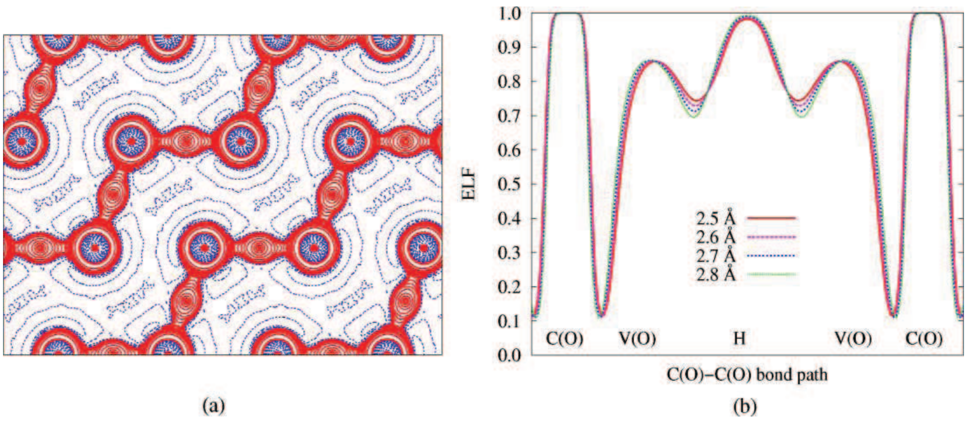


Figure 2. (a) Electron density Laplacian maps in the (1 1 0) plane of ice X at 141 GPa. Solid (red) and dashed (blue) isolines stand for charge accumulation and charge depletion, respectively (color online). (b) ELF value [8] along the O−H−O bond path at different lattice parameters. C(O) and V(O) denote oxygen core and valence basins, respectively.

in the direction of the bond. The Laplacian becomes more negative at the AIM critical bond point, increasing the charge flux toward the bond. In addition, the ELF value increase at the ELF minimum implies strengthening of the bond. Moreover, the existence of a monosynaptic hydrogen valence basin (valence basin that shares a boundary with one core basin) implies a ‘true chemical bond’. It is also to be noted that both the AIM and ELF analysis reveal O−O interactions. The existence of ELF maxima midway along the half of the H−H paths requires further study.

4. Conclusions

DFT calculations give a clear picture of a symmetric ice X phase with no molecular character. It is linked by soft phonon transitions to ice VIII (or disordered ice VII) at low pressure and to a putative *Pbcm* structure at high pressure, hence these transitions should happen easily and without significant hysteresis.

Acknowledgements

We thank J. Contreras-García for discussions and supplying the CRITIC code. This work was supported by EPSRC.

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