Anomalous Isostructural Transformation in Ice VIII

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The recently reported isostructural phase transformation in ice VIII has been examined using first-principles calculations. This novel transformation has been reproduced in detail, and the theory provides insight into the exact nature of this transformation. The calculation shows that (1) the hydrogen-bonded component of the oxygen network relaxes differently than the non-hydrogen-bonded oxygen part of the lattice, and (2) the internal geometry of water molecules is influenced by the structural transformation. This transformation does not conform to the conventional thermodynamic definition for structural phase changes but can be interpreted as a structural relaxation. [S0031-9007(98)07143-9]

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The application of pressure to ordinary ice has led to a very rich series of crystal structures with widely varying properties. These phases often serve as model compounds for the study of physical properties in a material where there is a large amount of information about the inter- and intramolecular interactions. A particularly simple structure is found in ice VIII (space group $I4_1/amd$, tetragonal with four molecules per unit cell) which can be described as two interpenetrating cubic lattices each constructed of nearly tetrahedrally coordinated water molecules [1,2]. The hydrogen bonds in the lattice are significantly longer (2.92 Å at 1 bar and 100 K) than that found in ice I*h*, the stable structure for solid H_2O at 1 bar. The water molecules in each sublattice are fully ordered with their dipole moments directed in opposite directions parallel to the c crystallographic direction. In addition, ice VIII transforms to an orientationally disordered phase, ice VII, with an average cubic symmetry for the oxygen atoms when the temperature exceeds 0.2 °C at 2 GPa. A particularly interesting feature of ice VIII is that it can be recovered at ambient pressures and low temperatures. The antiferroelectric phase has also revealed interesting behavior at very high pressures [3] where the hydrogen bonds approach a centrosymmetric configuration, and this is the subject of much current research [4–6].

Recently, based on neutron scattering determination of the structural parameters, a new isostructural phase denoted as ice VIII$'$ with no change in the crystal space group and was proposed for the D_2O ice VIII when the pressure was lowered below 4 GPa at 85 K [7]. The signature of the transition is a fairly rapid drop in the oxygen atom position parameters. In the neutron diffraction experiment, the z coordinate of the oxygen atom, z(O), was found to decrease abruptly from 0.110 to 0.106 when the pressure is lowered below 7 GPa. It was also suggested that there may be evidence of nonlinear behavior in this parameter at about 1 GPa. Interestingly, no discontinuity or other unusual behavior in the volume or in the c/a ratio of the tetragonal structure was reported. It is also significant that the crystal symmetry is preserved in the proposed phase transition. These observations suggested that the transition may be second or higher order. Although there is evidently an abrupt change in the oxygen atom positional parameter, this information alone is not sufficient to identify the phenomenon as a thermodynamic phase transition. In this Letter, we explore the mechanism of this novel observation through a detailed theoretical study of the pressure dependence of the structure of ice VIII using first-principles total-energy methods.

The pseudopotential plane-wave method based on density functional theory was employed [8] for total energy calculations. The Perdew-Wang generalized gradient corrected functional was used for the exchange correlation [9]. The interactions between the core ions and electrons were described by the Vanderbilt ultrasoft pseudopotentials [10]. High accuracy calculations are required in order to obtain reliable structural and energetic information. Therefore, special care has been taken to ensure convergence in both plane-wave energy cutoff and k-point sampling. An energy cutoff of 600 eV and a 48 special k-point mesh selected by the Monkhorst-Pack scheme [11] was found to be sufficiently accurate for the convergence of total energies and structural parameters. The calculated O-H bond length and H-O-H bond angle for an isolated water molecule were 0.971 Å and 104.0°, respectively. These values can be compared with the corresponding experimental values of 0.957 Å and 104.5° [12]. The theory predicted a slightly longer O-H bond length in the isolated molecule, which carries onto the crystal calculations, and is likely due to small imperfections in the pseudopotentials. For each volume, an energy minimization structural optimization was performed and the internal coordinates and c/a ratio were optimized. The frozen phonon method [13] was used to investigate the frequency of the internal A_{1g} symmetric stretching mode and the A_{1g} lattice mode for translational vibrations parallel to the c axis [14]. Although calculations were carried out on H_2O ice VIII, no significant difference is expected from that of D_2O ice except that the kinetics of the transformation and the transition pressure may be affected by isotope substitution. The vibrational frequencies would also be affected by isotope substitution, but only by a scaling factor.

The experimental observed structural changes [7] are completely reproduced by the calculations (Fig. 1). The sudden drop in z(O) from 0.115 to 0.110 is predicted at a volume of 63 Å^3/primitive cell or approximately 10 GPa. The calculated values are in favorable agreement with the observed onset of the structural change at 7 GPa where the z(O) decrease by 0.004 (inset Fig. 1). More significantly, the calculations reveal that the change in the atomic position is reversible when the pressure is increased. The volume dependence of the total energy, the unit cell dimensions a and c, and the frequencies and the internal structure of water molecules are shown in Fig. 2. No discernible discontinuity can be detected in both the total energy and the unit cell dimensions in the entire volume range [Figs. 2(a) and 2(b)]. These observations show that the observed structural changes are not associated with a first-order transformation. Figure 3 shows the calculated volume dependence of internal structural parameters which accompany the sharp change in the fractional coordinate z(O).

A careful examination of the local structure of the water molecule reveals details of the structural changes. As shown in Fig. 3(a), the calculated trend and absolute change in the O-H bond length with pressure is in excellent agreement with that reported from a detailed neutron diffraction study of ice VIII [15,16]. The calculated rate of change of O-H bond length with volume of 7×10^{-4} Å^{-2} agrees with the recent experimental value [15,16] reported by Besson *et al.* which is almost an order of magnitude smaller than those previously suggested. Moreover, the theory predicts a region near the structural anomaly where the H-O-H angle diminishes more slowly with increasing volume. This is shown in Fig. 3(b) where it is apparent that there is a pressure region where the change in the H-O-H angle with change in volume decreases. An interesting feature of the local structure in the lattice is the volume dependence of the hydrogen-bonded O—O distance and the nonbonded O—O distances as shown in Fig. 3(c). It was reported [2] from a detailed neutron diffraction study at 2.4 GPa that the nearest *nonbonded* O—O distances were significantly shorter than the *hydrogen-bonded* distances. The present calculation confirmed this observation. The calculated nonbonded and hydrogen-bonded distances at 2.4 GPa are 2.756 Å and 2.875 Å, respectively, and are in excellent agreement with the experimental values of 2.743(9) and 2.879(1) Å. The remarkable behavior of the calculated two nearest-neighbor O···O distances is shown in Fig. 3(c). The hydrogen-bonded distances show a monotonic change in length with pressure whereas the nonbonded distances show a distinct change in pressure dependence at the structural transformation. The structural transformation therefore can be described by a sudden movement of the interpenetrating hydrogen bonded networks in opposite directions while maintaining the continuous pressure dependence of the hydrogen bond distances when the pressure is lowered. The only distinct structural features that may act as order parameters for the proposed phase transformation are the sudden changes in (1) the intermolecular O—O distances or to a much lesser extent (2) a change in the intramolecular O-H bond length or H-O-H angle. In this case, the O-H bond length decreases smoothly with increasing volume, but there is a clear region where the H-O-H bond angle changes more slowly with change in volume. The H-O-H angle decreases from nearly tetrahedral to the experimental value of 106° at low pressure.

Based on an examination of the rapidly decreasing frequencies of the internal (molecular) Raman B_{1g}, A_{1g}, and E_g vibrations and the external (lattice) infrared (E_u)

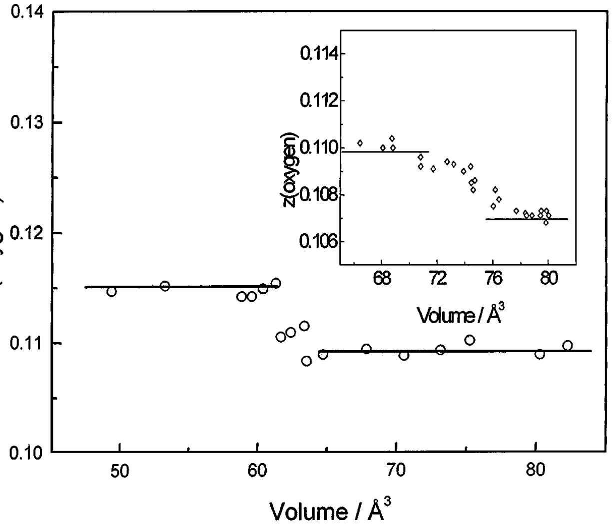

FIG. 1. The calculated pressure dependence of the fractional coordinate z(O) for ice VIII and the experimental data of Ref. [4] (inset). The solid lines are guides for the eye.

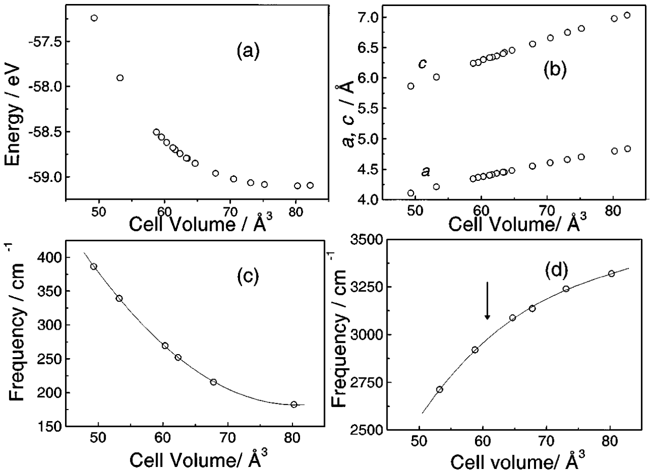

FIG. 2. The calculated volume dependence of the (a) total energy, (b) lattice constants c and a, (c) the frequency of the A_{1g} vibrational lattice mode, and (d) the calculated frequency of the A_{1g} internal mode. The arrow in (d) indicates the location of the isostructural transformation. The solid curves in (c) and (d) are polynomial fits to act as a guide for the eye.

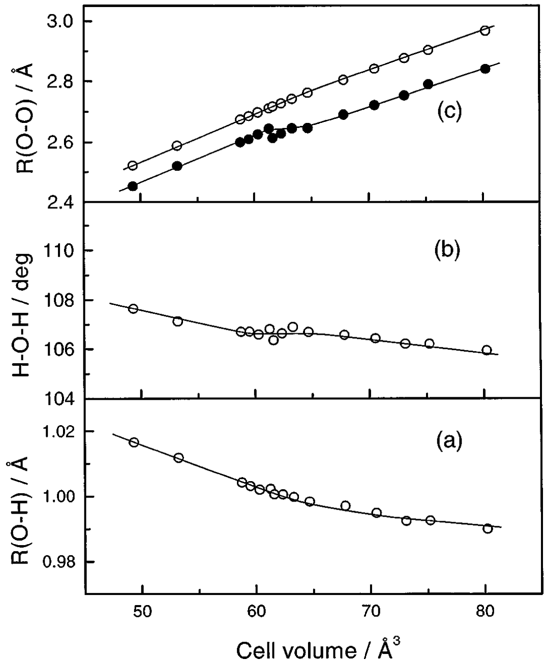

FIG. 3. The calculated volume dependence of the internal structural parameters of ice VIII: (a) the O-H bond length, (b) the H-O-H angle, and (c) the hydrogen-bonded (open circles) and nonbonded nearest neighbor distances (filled circles).

mode for pressure below 4 GPa, it was suggested [7] that the transformation may be a second-order thermodynamic one. This could be due to a softening of a phonon mode at the Brillouin zone center. Since the crystal space group is preserved at the transformation, the only possible symmetry allowed lattice mode that preserves symmetry is the A_{1g} mode. To investigate this possibility, the volume dependence of the frequency of the lowest energy A_{1g} lattice mode is determined from the frozen phonon method. This A_{1g} optic mode involves motions of water molecules in each of the interpenetrating lattices along opposite directions in the z direction [14]. The calculation shows [Fig. 2(c)] a continuous decrease in the vibrational frequency but no anomaly that will suggest a softening within the pressure region where the discontinuity in $z(\mathrm{O})$ occurs is predicted. The calculated frequency shift from 10 GPa to ambient pressure of 70 cm^{-1} is in reasonably good agreement with the experimental value of $\sim$95 cm^{-1} consisting of a linear frequency shift of 6.6 $\mathrm{cm}^{-1}/\mathrm{GPa}$ over the pressure range 1–10 GPa plus a more rapid drop near ambient pressure [14,17]. Analysis of the limited experimental data available on the internal vibrations, such as the B_{1g}, A_{1g}, and E_g modes, shows a rapid increase in the frequencies when the pressure is below 3 GPa. Unfortunately, there is not sufficient experimental information to indicate whether a *discontinuity* has occurred in this pressure range. Similarly, the calculations do not show an abrupt change in the A_{1g} internal symmetric O-H stretch mode near the region of the structural relaxation. The calculated volume dependence of the intramolecular vibration after scaling by the measured isotope ratio [14] is in good agreement with experiment. The lack of a clear discontinuity in the calculated volume dependence of the A_{1g} symmetric stretching vibration [Fig. 2(d)] can be used to provide an estimate of the maximum contribution to the free energy change that may occur over the transformation region. The maximum discontinuous frequency shift consistent with the calculated dependence is at most a few tens of wave numbers that implies a very small contribution to the free energy change over the transformation region.

A classical thermodynamic transformation occurs when there is a discontinuity in a derivative of the free energy. Since the calculated total energy, calculated and experimental volume, and vibrational spectrum of ice VIII are smooth functions of the pressure, therefore, the enthalpy, volume, and entropy of the system are continuous over the pressure region where the O atom position parameter anomaly occurs. Thus, based on the theoretical result, and within the accuracy obtained with the present methods used, the observed phenomenon cannot be classified as bona fide phase transition. The observed structural change is probably the consequence of a delicate balance between dipole-dipole forces in the antiferroelectric lattice, hydrogen bond interactions, and the nonbonded repulsive forces. At the point where the transformation occurs, there is a large change in the parameter describing the separation of the two interpenetrating sublattices. That is, the separation of the sublattices as determined by the parameter $\varepsilon = 2c[0.125 - z(\mathrm{O})]$ increases by about 20% as the pressure is decreased. The dipole-dipole interaction energies are dominated by repulsive terms which means that the transformation, which depends on the balance of the hydrogen bond energies against the dipole-dipole interaction energies, occurs when the dipole-dipole contributions dominate suddenly. Consequently, the total energy of the system remains a continuous function of the volume/pressure. Since there is no discontinuous change in the total energy, volume, and vibrational spectrum at the current level of accuracy of the theory, therefore, the experimental observation indicates a minor relaxation of the internal structure of the ice lattice and does not constitute a structural phase transformation in the standard thermodynamic description. It should be emphasized, however, that this conclusion is limited by current accuracy of theory, and the possibility of a first- or second-order transformation cannot be totally eliminated.

There are a number of isostructural transformations now reported in the literature in materials including pure metals [18–20] to simple compounds [21] and minerals [22]. In the pure metals, Zn and Cd [18–20], the transformations have now been proven to be due to a change in the Fermi surface topological features. In the compound InN

[21], an anomalous behavior in the c/a ratio is attributed to an interaction between second neighbor in atoms in the wurtzite structure, resulting in a pretransition behavior near a first-order transformation to a NaCl structure. In several mineral systems, isostructural transformations have been reported [22], but theoretical studies remain to be completed. The transformation studied here may be related to these, and this study provides the first detailed theoretical characterization for a molecular solid and should provide the general principles that may be used to yield a unified picture of this phenomenon.

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