

Structural Instability in Ice VIII under Pressure

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Below 125 K, tetragonal ice VIII remains in a metastable form at ambient pressure. This form has long been considered to be identical to ice VIII, although unexplained discrepancies exist between their vibrational spectra. Neutron diffraction studies reveal an isostructural phase transformation below 2 GPa related to a weakening of the bonds between the two D₂O sublattices of ice VIII. In this new phase, ice VIII', the tetragonal distortion is 20% larger than in ice VIII, which accounts for the differences between the vibrational frequencies of the two phases. [S0031-9007(97)02963-3]

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The pressure-temperature phase diagram of water ices is extremely complex. The various solid forms of H₂O and D₂O have been and still are the subject of intense activity in experimental and theoretical physiochemistry. These studies are also of relevance to planetary science since water ices under a few GPa are major constituents of the larger ice moons such as Titan and Ganymede. Modeling of these bodies requires, among other things, a precise knowledge of their structural properties which govern their mechanical and thermodynamic behavior.

A remarkable feature of water ices is the large number of metastable modifications which can be retrieved at ambient pressure and low temperature. In addition to ice *I_h*, at least eight solid phases can be generated by pressurizing to 2–3 GPa and pressure quenching at low temperature. One of these is ice VIII, which is the ordered form of the higher-pressure ices. It is stable above 2 GPa at 265 K and can be retrieved at ambient pressures at temperatures below ~125 K. Hence, ice VIII has been studied outside of the high-pressure apparatus at ambient pressure, and the properties of such samples have been generally considered as representative of the stable high-pressure modification.

It has nevertheless long been noted [1] that between 2 GPa and ambient, strong nonlinearities occur in various properties. Raman-active vibron frequencies, for instance, measured at 3 GPa and above [1–3] do not extrapolate down to the ambient pressure values obtained from retrieved samples [4] (Fig. 1). The same is true for the phonon modes [1,2]: An extrapolation of the infrared active translational frequencies from high-pressure values down to ambient [3,5] shows a ~20% discrepancy with respect to the retrieved sample values [6] (Fig. 2). Finally, inelastic incoherent neutron scattering experiments on ice VIII show that lattice transla-

tional frequencies are 20% lower at ambient pressure [7,8] than at 2.2 GPa, implying an apparent pressure coefficient of 20 cm⁻¹ GPa⁻¹, in sharp contrast with its well-established value of 7 cm⁻¹ GPa⁻¹ for pressures above 3 GPa [1–3]. In principle, this problem might have been resolved by optical studies (Raman infrared) between 0 and 3 GPa at low temperature. However, this has not been possible below ~1 GPa because devices such as diamond anvil cells do not allow full decompression of a sample at low temperature: Even with zero thrust on the anvils, pressures of the order of 1 GPa remain locked in the experimental volume. By contrast, large volume setups permit full depressurization at low temperatures, but without any optical access. We have therefore performed low-temperature neutron scattering measurements in the Paris-Edinburgh pressure cell [9], which makes it possible to compress D₂O into the stability domain of ice VIII, and then decompress the sample completely while measuring the evolution of its structural parameters.

Time-of-flight neutron diffraction measurements were performed at the POLARIS station of the U.K. neutron spallation source ISIS. Samples of 99.5% deuterated D₂O (supplier, EURISO-TOP) were loaded into the spheroidal space (initial volume, 88 mm³) between tungsten carbide anvils [9] and pressurized with a V3 Paris-Edinburgh setup [10], with a modified hydraulic ram to accommodate helium gas as the hydraulic fluid. Cooling of the cell was achieved with a liquid nitrogen bath, and heaters and thermocouples were used for the adjustment and control of the cell temperature. The cell was cooled down to 240 K, then pressurized to a few GPa so as to cross the I-II-VI-VIII phase boundaries, breaking up the crystallites and generating as good a random powder sample as possible. The cell was then cooled down to 85 K, and diffraction patterns were collected as the

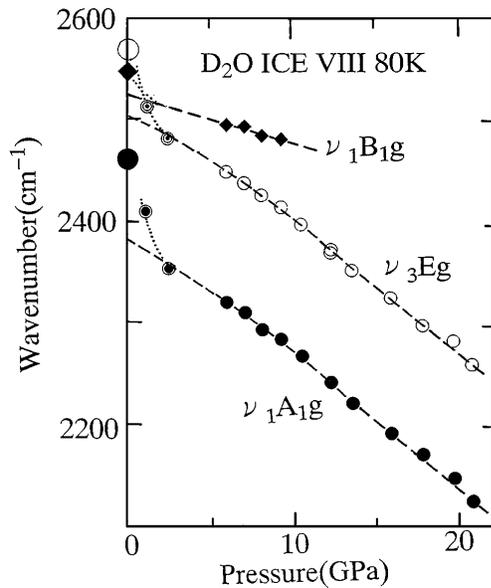


FIG. 1. Raman-active frequencies in D_2O versus pressure at 80 K. The results for the ν_1B_{1g} , ν_3E_g , and ν_1A_{1g} modes above 5 GPa (diamonds, empty circles, and filled circles, respectively) are from Ref. [3]. These results are the same within experimental error as those of Ref. [1,2] at 100 K. The points shown between 1.5 and 3 GPa for the ν_3E_g and ν_1A_{1g} modes (ringed dots) are from Ref. [1]. The ambient pressure values (enlarged symbols) are those obtained at 100 K from Ref. [4]. The dotted lines show the apparent departure from the extrapolated high pressure behavior (dashed lines) below 3 GPa.

sample was decompressed to ambient pressure by steps. At zero load on the ram, the residual sample pressure (up to 1 GPa) was completely released by slightly unscrewing the front breach of the cell. Diffraction patterns were collected over a scattering angle range of $2\theta = 90 \pm 7^\circ$. After focusing the individual detector spectra and correcting the summed diffraction pattern for the effects of attenuation by the anvil and gasket materials [11], the lattice and structural parameters were obtained by full-profile Rietveld refinement using the GSAS package [12].

The equation of state of D_2O VIII was determined at 85 K for pressures up to 4 GPa using a sample obtained by slurring powdered lead (5N submicron powder) in D_2O (1:4 by volume). The equation of state of lead has been measured at 300 K [13], and values for 85 K were calculated using universal equations of state [14] and the volume thermal expansivity of lead ($\alpha_V = 8.1 \times 10^{-5} \text{ K}^{-1}$) between 85 and 300 K. The molar volumes V of D_2O and of Pb, calculated from the refined lattice constants at five pressure points between 0 and 4 GPa, were compared with previously published results [15]. Using the procedure described in Ref. [15], we obtained: $V_0 = 12.04 \text{ cm}^3/\text{mol}$, $B_0 = 23.8(1.4) \text{ GPa}$ and $B' = 4.5(1.5)$ for D_2O VIII at 85 K. The experimental values of V/V_0 measured with the lead pressure calibrant are identical within 0.2% to

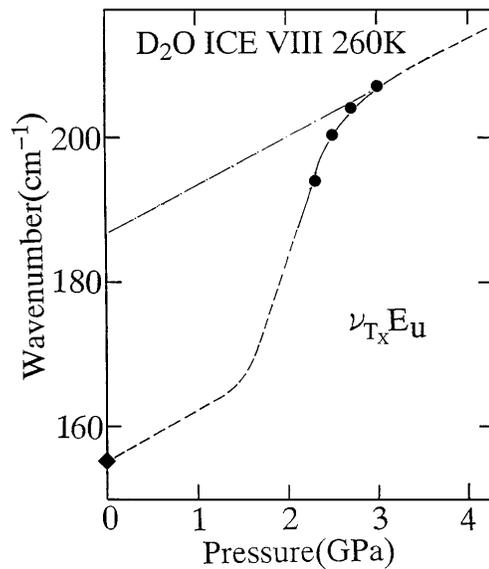


FIG. 2. Wave number of the infrared-active translational $\nu_{T_x, T_y} E_u$ mode at 260 K. Diamond, ambient pressure point from Ref. [6]; filled circles, experimental values from Ref. [3,5]. Note that the ambient pressure value was measured at 100 K and has been corrected for the difference in temperature by shifting the frequency down by 6 cm^{-1} , using a temperature coefficient of $-0.24 \times 10^{-3} \text{ K}^{-1}$ [2,3]. The dashed line is a guide to the eye.

those calculated with a Birch-Murnaghan equation of state with the above parameters, which is well within the experimental uncertainties of 0.5%. The equation of state is completely regular within this precision. If a volume effect was responsible for the nonlinearities in the vibrational mode frequencies, their high-pressure variation and the known equation of state of D_2O VIII would require a discontinuity of over 20%. Hence, the nonlinearities are not a volume effect at all. Similarly, we could not detect any discontinuity in the c/a ratio larger than 0.2%, which shows that the variation of the internal coordinate $z(O)$ (see below) affects very little, if at all, the c axis of the tetragonal lattice.

Structural refinements of the D_2O VIII diffraction patterns were performed at 26 pressure points between 0 and 7 GPa, in four separate loadings. From the width of the long d -spacing (112)/(200) diffraction doublet, two of the loadings yielded samples which were free from internal strain, whereas the other two exhibited some broadening to the extent $\Delta d/d \sim 8 \times 10^{-3}$ with refined thermal parameters $\sim 50\%$ higher than for the unstrained samples. Sample strain also caused a systematic and pressure-independent offset of the values obtained from least-squares refinement for some of the structural parameters. For example, the fractional oxygen coordinate $z(O)$, refined to values systematically $\sim 0.6\%$ higher for the strained samples [Fig. 3(a)]. Internal strains were found to occur regularly on recompression of the samples but, in a few instances (seven data points), reasonably

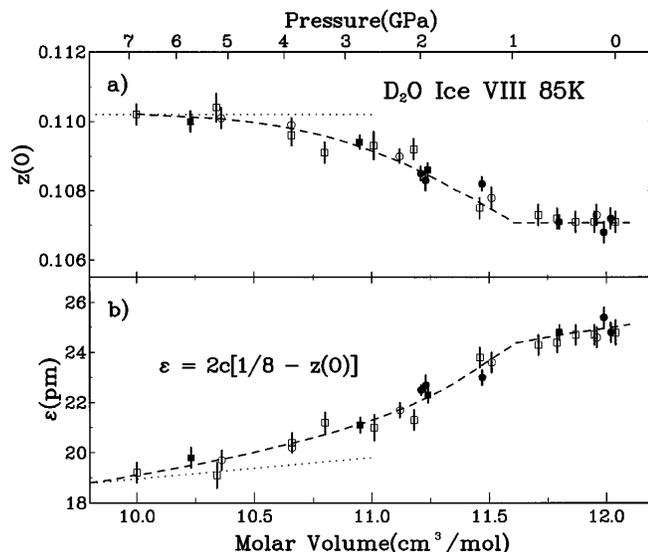


FIG. 3. (a) Fractional coordinate $z(O)$ and (b) tetragonal distortion parameter ϵ [16] of D_2O VIII at 85 K. The filled and empty symbols represent points obtained from the two unstrained and the two strained samples, respectively. In (a) the ordinate scale refers to the refined values of $z(O)$ for unstrained samples. For the two strained samples, a systematic offset of 0.0006 was found at all molar volumes, and the values of $z(O)$ for these samples have been shifted down by 0.6% at all pressures. All error bars shown are the estimated standard deviations from the profile refinements. The dashed curves shown are guides to the eye. The dotted lines represent the extrapolated high-pressure behavior of $z(O)$ and ϵ from this work and from Ref. [15,17].

strain-free samples could be obtained after recompression to various pressures up to 5 GPa, and these results are included in Fig. 3.

The oxygen coordinate $z(O)$ has been found to extrapolate to a constant value of 0.1102 at high density and 300 K [15], shown as a dotted line in Fig. 3(a). The nonlinear variation of $z(O)$ with the molar volume V and the change in slope of the $z(O)$ versus V curve around 1 GPa clearly points to an isostructural transformation process. Nevertheless, the dashed curves in Fig. 3 are only a guide to the eye since the transition point shown by the abrupt slope changes at ~ 1 GPa cannot be located to better than ± 0.2 GPa in view of the precision of the data points. The other fractional z coordinate, $z(D)$, follows the same behavior, and its ambient pressure value is also 2.5% lower than the extrapolation to ambient of the high-pressure variation [15].

The tetragonal distortion parameter ϵ [16], which represents the distance between the two interpenetrating D_2O sublattices of the ice VIII structure, shows a 20% increase with decreasing pressure, from 20 pm at 4 GPa to 25 pm at ambient pressure [Fig. 3(b)]. Thus, the two sublattices slide past each other, indicating a weakening of the internetwork bonds along the c axis, until they reach a new stable energy minimum at a density of

$\sim 11.7 \text{ cm}^3/\text{mol}$. We refer to this more weakly bonded variety of tetragonal ice as ice VIII' in the following. The bonds between the two sublattices are largely ionic, so the decrease in internetwork bond-strength implies a decrease of the effective charge. The charge density which leaves the ions could then participate in the covalent bonds and increase the O-D intramolecular bond strength, leading to a decrease of the O-D bond length, as possibly observed: an average of eight low-pressure points suggests a decrease of 0.5 pm between 2 and 0 GPa, a much larger reduction than that expected from the 0.04(4) pm/GPa variation found at pressures above 2 GPa [17]. However, the overall precision and reproducibility of the O-D bond-length values are such that this result, although suggestive, requires further investigation.

Understandably, this weakening of the internetwork bonding on decreasing pressure is most strongly felt by the phonon modes which involve these bonds to first order, e.g., the $\nu_{T_x, T_y} E_u$ mode which also decreases by $\sim 20\%$ in frequency in the low-pressure region (Fig. 2). The effect of the increase in the O-D bond strength is to increase the frequencies of the vibron modes in ice VIII' since the restoring forces are mostly O-D springs with only a small admixture of O...O bonds (Fig. 1).

Analogous behavior has been observed for $z(O)$ between 2 and 3 GPa at higher temperature [15,17], but in that case the occurrence of ice VI below 2.0 GPa interrupts the transformation process from ice VIII to VIII'. Such is not the case at 85 K, but it is to be noted that the change in slope of the $z(O)$ and ϵ curves at ~ 1 GPa lies just below the extrapolated VIII-VI transition line at that temperature (1.4 GPa) [18]. The nonlinear behavior appears to be fully reversible—as in a second-order phase transition—as shown by the seven upstroke points which lie on the common line of the data obtained on decompression. Nevertheless, the number of data points around 1 GPa is insufficient to establish firmly the presence of an abrupt discontinuity in the slope of the $z(O)$ and ϵ curves versus molar volume, so that this behavior can only be assigned to a transformation of second order or higher.

Isostructural second-order phase transformations, which are not infrequent, may, on occasion, be associated with a first-order phase transition. The second-order process may occur before the first-order transition sets in, as in the case of nitrogen [19], or after, in which case the second-order discontinuity in the thermodynamic derivatives is hidden by the occurrence of the first-order process, which is the case for InN [20] and for premelting processes [21]. In the present case, the process, which is interrupted when pressure is decreased by the VIII \rightarrow VI transition at high temperatures, is revealed at lower temperatures by the metastability of ice VIII which inhibits the transition to ice VI. This transition has been well documented down to 200 K and 1.7 GPa only, and ice VIII is known to be metastable at ambient pressure up to ~ 125 K only.

Between these two temperatures, the behavior of ice VIII on decompression has not been reported.

The transition point between ices VIII and VIII' is at 1.0(0.2) GPa at 85 K. Within error, this point lies on the extrapolated melting line of ice I_h . This may well be only a coincidence but, in view of the role played by this virtual melting line in the transition between ice I_h and the high density amorphous variety, it would be worth exploring the VIII-VIII' transition line at temperatures above 85 K to assess its pressure-temperature dependence.

Hence, more than ever, it would be worthwhile to perform optical experiments in this region of the ice phase diagram which, coupled with *ab initio* calculations for the tetragonal ices, would improve our understanding of its complex behavior.

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