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Evidence for symmetry-reduction in solid H₂O above 222 GPa

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Water (H₂O), one of the most consequential compounds in the Solar System, governs the structure and dynamics of icy planets, the terrestrial water cycle, and through the pressure-induced transition from hydrogen to ionic bonding, it exhibits marked changes over the pressure range of planetary interiors. While many materials are expected to favour simple, densely packed lattices with increasing compression, as observed in water ice-X, others exhibit unexpected structural complexity at extreme pressures. Here we report experimental evidence that water ice undergoes a transformation from ice-X to a less symmetric structure

21 above 222(12) GPa. Synchrotron X-ray diffraction reveals a distortion of the cubic lattice
22 consistent with either *Pbcm* or *P4₂/nnm* symmetry, the former being strongly favorable by *ab*
23 *initio* calculations. This transition marks the onset of a new regime of structural complexity
24 in high-pressure H₂O, redefining the upper stability limit of ice-X.

25 Water-ice, crystal structure, high pressure, XRD

1 Introduction

Compression of condensed matter under a wide range of pressures induces the formation of structures, compositions, and types of chemical bonding that are vastly different from those observed under ambient conditions¹. Examples such as the complex hP4 phase of transparent sodium at 240 GPa², polymeric nitrogen at 140 GPa³, and NaCl₃⁴ at 70 GPa indicate the range of dramatic changes in material properties that occur at extreme pressure. In particular, these changes often lead to the formation of low-symmetry structures, contrasting with the previously held assumption that pressure favors simple, densely packed atomic arrangements⁵. A prominent example of pressure-induced bonding transformation, with implications for planetary science, is H₂O. At low pressures, hydrogen bonding governs the behavior of H₂O and OH-bearing materials, including both organic and inorganic matter. However, as pressure increases, this H-bonding is gradually replaced by ionic bonding or a complex combination of ionic and hydrogen-bonded states.

The phase diagram of H₂O is surprisingly complex, with more than 20 phases that have been detected with laboratory measurements or predicted with computer simulations *ab initio*. This extensive polymorphism has led to the continuous exploration of new ice phases^{6–13}. The structural diversity arises primarily from density-driven effects within the relatively fragile hydrogen-bonded network characteristic of the ices, most of which exist at modest pressures and below room temperature. Upon compression, the steric rearrangements of this network culminate in the formation of ice-VII at approximately 2.2 GPa, a superposition of two cristobalite-type H-bonded network structures translated relative to each other by $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Ice-VII then undergoes a gradual continuous

transformation from this H-bonded network into cuprite-type ionic ice-X across a broad pressure range^{14–23}.

At multimegabar pressures, early computer simulations by Benoit *et al.*²⁴ predicted the cubic ice-X structure to transform into a lower-symmetry structure with $Pbcm$ symmetry, resulting from phonon instability²⁵. Following up on²⁶, several new crystal structures have been predicted with theoretical methods^{27–29} leading to the following series of phase transformations $Pbcm \rightarrow Pbca \rightarrow P3_121 \rightarrow Pcca \rightarrow P2_1/c$ at pressures of 770, 810, 1440, and 1960 GPa, respectively. H_2O is predicted to decompose at ~ 5000 GPa²⁹, possibly transforming into H_2O_2 and a hydrogen-rich system pertaining to H_4O ³⁰, or H_3O and determining planetary dynamism³¹. However, a recent study predicted a new $Pa\bar{3}$ ice phase stable above 2200 GPa³².

At high temperature, there is less uncertainty about the mobility of H in dense H_2O : Cavazoni *et al.*³³ predicted water to assume a superionic state at temperatures above ~ 2000 K above 150 GPa. It was assumed that the oxygen nuclei of superionic water ice form a b.c.c. sublattice until Wilson *et al.*³⁴ showed with *ab initio* free energy calculations, that above ~ 100 GPa, a close packed f.c.c. lattice is strongly favored, which was later confirmed with laboratory measurements³⁵, though recent calculations suggest a plastic flow for superionic ice at planetary conditions³⁶. The fundamental response at 0 K has been revisited recently by Reinhardt *et al.*³⁷ using *ab initio* simulations that include nuclear quantum effects and further confirmed that at ≥ 300 GPa, the $Pbcm$ phase is favorable over several other candidate structures all of which were more favorable than ice-X. An energetically competitive candidate with tetragonal space group $P4_2/nmm$ also

found (6 meV/molecule enthalpy difference from $Pbcm$ at 320 GPa) and was labeled as ortho-X³⁷.

2 Results

Here we report experimental evidence for the transition of ice-X into a less symmetric phase above 222(12) GPa, marking the onset of a new regime characterized by increasing structural complexity. Where at modest pressures, numerous structurally complex ices emerge from steric rearrangement of the H-bonded network, the densest of which, ice-VII, transitions upon further compression approaching 50 GPa into the cubic, cuprite-type ice-X phase³⁸. Our study marks the upper pressure boundary for the ice-X regime, using experimental synchrotron XRD and theoretical modeling. The transition from ice-X ($Pn\bar{3}m$) to a lower symmetry phase that can be described either by an orthorhombic ($Pbcm$) or the tetragonal ($P4_2/nnm$) structure of H₂O-ice.

Beginning at 78(1) GPa (Fig. S1,2)³⁹, we experimentally confirm the presence of ice-X phase using synchrotron XRD, and Raman spectroscopy, persisting up to 222(12) GPa. Figure 1a-d shows the integrated 1D pattern of the diffraction peaks of the H₂O sample and the rhenium gasket, with the 1D projection of the image plate data along its azimuthal angle. At 180(5) GPa the severe effects of non-hydrostaticity are apparent with a shift across the diffraction azimuthal (Fig. 1a). However, a single distinct Debye ring is observed, corresponding to the (110) reflection of ice-X. This pattern was obtained from the center of the ice-filled cell chamber in an experiment with 50 μ m culets where signal from the rhenium gasket remains invisible. In Figure 1b, the

deviatoric stress at 218(10) GPa is most notable for the H₂O sample in the azimuthal 1D projection, “snaking” between 3.4 and 3.6 Å⁻¹. Still, averaging across the full azimuthal of the XRD pattern integrates into a single diffraction peak, as indexed as cubic ice-X. Deviatoric stress in the XRD patterns is clearly evident in the H₂O sample above 126(2) GPa (Fig S1), and it is also observed in the diffraction data from the rhenium gasket. For an unstressed sample the unwrapped XRD pattern as an azimuthal projection would appear as a linear array, confined over a narrow angle.

At 222(12) GPa (Fig. 1c), the emergence of a second diffraction feature is labeled by a second tick mark. Upon further compression to 230(11) GPa (Fig. 1d), deviatoric stress relaxes and this secondary peak becomes fully resolved at a distinct Bragg angle. Figure 1e shows the full width at half maximum (FWHM) of the primary diffraction peak as a function of pressure. The FWHM initially broadens with increasing pressure, reflecting the continuing increase of deviatoric stress with non-hydrostatic compression, but above 218(10) GPa it narrows despite the emergence of a new feature. The combined FWHM of the split peaks is smaller than that of the single ice-X reflection, indicating stress release concurrent with a structural transition. The appearance of this new diffraction peak and the reduction in line broadening together signify a phase transformation. Figure 1f displays the Debye–Scherrer rings obtained at the highest pressure achieved in this study. The diffraction pattern shows signs of texturing; however, a quantitative assessment is not possible, as this would require measurements at diffraction angles beyond the accessible range. Acquiring statistically reliable diffraction data at such extreme pressures for a low-*Z* system remains particularly challenging.

Using *Ab initio* calculations, we study possible structural candidates for post-ice-X, identifying $P4_2/nnm$, $Pbcm$, and $P2_12_12$ as viable solutions (Fig. 2a). The relative enthalpies among these competing ice phases are consistent with previous reports^{24,26–29,37}, differing by less than 5 meV at 310 GPa (PBE; Fig. S3)³⁹. Such a narrow enthalpy window suggests that the metastable structures lying slightly above the $Pbcm$ ground state may be experimentally accessible, particularly under conditions where deviatoric stresses and other non-hydrostatic effects can promote non-equilibrium transformation pathways.

We found that the transition pressures from ice-X to $Pbcm$ or $P4_2/nnm$ have a spread between 220–350 GPa when considering a wide range of DFT exchange-correlation functionals different DFT functionals are employed (Fig. 2b). While not all these predictions may be always meaningful, they are able to provide with a match to the changes in lattice parameters as a function of pressure with those observed here in our XRD measurements. As the PBE and SCAN functionals are considered to describe water well, for example the multi phase P,T phase diagram at lower pressures⁴⁰, they are expected to provide a more reliable transition pressure of 300 GPa, but this is not necessarily the case at these high densities. Figure 2c presents a direct comparison between the experimental XRD pattern at 230(11) GPa and simulated patterns of the most energetically favorable predicted structures. Panel (i) shows a Rietveld refinement based on the $Pbcm$ model, applying a [001] preferred orientation to reproduce the relative peak intensities observed experimentally. The subsequent simulated patterns, all calculated at $V = 16.0 \text{ \AA}^3$ per 2 formula units, correspond to the idealized structures of (ii) ice-X ($Pn\bar{3}m$), (iii) $P4_2/nnm$, (iv) $Pbcm$, and (v) $P2_12_12$.

The XRD patterns above 220 GPa are possible to fit, across the selected range of the azimuthal, to either of the predicted $Pbcm$ and $P4_2/nnm$ phases. At 230(11) GPa the $Pbcm$ structure is fitted using Rietveld refinement providing cell parameters (Fig. 3a): $a = 2.402(1) \text{ \AA}$, $b = 3.700(2) \text{ \AA}$, $c = 3.580(1) \text{ \AA}$, and $V = 15.91(3) \text{ \AA}^3$, with atomic coordinates - H (1, 0.1980, 0.25), H (0.5, 0, 0), O (0.2519, 0.4479, 0.25) - were fixed to DFT determined values and not refined experimentally due to the limited data quality. To further account for the restricted data set and the presence of texturing, preferred orientation along the [001] direction was included in the refinement model ($wR = 0.334$). However, even after inclusion of preferred-orientation corrections, the $Pbcm$ model remains insufficient to fully reproduce the experimental diffraction pattern, most notably the emergence and observed intensity of the second diffraction feature. The $P4_2/nnm$ structure fitted using Rietveld refinement provides (Fig. 3b): $a = 2.486(1) \text{ \AA}$, $c = 2.588(2) \text{ \AA}$, and $V = 15.99(1) \text{ \AA}^3$, with atomic coordinates - H (0.75, 0.75, 0.75), O (0, 0, 0.5) - as also determined by DFT. This simpler, high symmetric solution describes the experimental data more accurately ($wR = 0.274$). Although the $P2_12_12$ structure is energetically competitive, it does not adequately reproduce the experimental data without introducing additional distortions to the ideal unit cell (Fig. S4)³⁹. At 230 GPa, the two diffraction peaks near $3.5 \text{ \AA}^{-1}$ were also modeled using two distinct volumes of the cubic ice-X structure to evaluate whether the splitting could arise from strong pressure gradients along the X-ray beam path. However, this approach yields an implausibly large pressure difference, equivalent to 190 and 262 GPa, indicating that the feature cannot be explained solely by non-hydrostatic stress.

The $Pbcm$ and $P4_2/nnm$ structures can be viewed as distortions of the ice-X structure in

147 their lattice parameters (Figs 4a and 4b). Indeed, all theoretically predicted low-energy structures
 148 can be regarded as distortions of the ice-X structure, each exhibiting distinct symmetry-breaking
 149 features. We performed structural relaxation calculations with the CASTEP code ⁴¹ to compare
 150 the enthalpy of various structures with the newly observed phase. When these structures are re-
 151 laxated within DFT at lower pressures, most reverted back to the ice-X structure (specifically, below
 152 300 GPa for the PBE functional ⁴²). The transition from ice-X to $P4_2/nnm$ involves a tetrago-
 153 nal distortion of the lattice, characterized by an elongation of the c-axis and additional structural
 154 splitting. The ice-X to $Pbcm$ transition is more complex, involving a pressure-induced buckling of
 155 the oxygen sublattice. Both of these symmetry lowering transitions increase the density of H₂O,
 156 which is ultimately favored at high pressure. Figures 4a and 4b compare the experimental unit cell
 157 parameters with those calculated reported by Reinhardt *et al.*, ³⁷ and our own calculations using
 158 the PBE+D2 functional, for the $Pbcm$ and $P4_2/nnm$ solutions, respectively. The observed distor-
 159 tion away from cubic ice-X is better described by $Pbcm$ symmetry, rather than by the tetragonally
 160 distorted $P4_2/nnm$ solution.

161 The pressure-volume relations are shown in Figure 5a. At these pressures and for a low-Z
 162 material, combined with the limitations of powder averaging over the full azimuthal range (Fig.
 163 S6-7) ³⁹, the Rietveld refinement does not achieve statistical significance to determine which struc-
 164 ture is truly valid. Unlike most DAC XRD studies, data collection reported here was performed
 165 without rocking on the rotation axis or raster scanning over the sample to improve powder statis-
 166 tics. Each XRD measurement captures a stationary image, to avoid signal from the rhenium gasket
 167 overwhelming that of the sample, both small and a weak scatterer. Additionally, the use of such a

micro-focused beam of $1 \times 1 \mu\text{m}$ is suboptimal for achieving adequate powder averaging statistics.

A fundamental challenge to accurately capture the compressibility of materials is that standard equations of states (EoS) fail in accurately capturing the response of materials over very broad pressure ranges. This is relevant especially for systems that deviate from simple, hydrostatic compression behavior, particularly in solids where changes in bonding interactions modify the crystal structure, as in the transition from ice-VII to -X. The theoretical PV points from our molecular dynamics (MD) simulations do not conform well to any single EoS formulation, and fitted to third order EoS give non-physical values. When artificially fixing $V_0 = 37 \text{ \AA}^3$, values for $K_0 = 42.4 \text{ GPa}$, $K'_0 = 8.18$ are fitted, with the pressure derivative seemingly too large for comparable systems. The MD simulations capture a more complex, atomistic response of H_2O under compression, one that cannot be described adequately using a single EoS across the full pressure range. Nonetheless, we attempted to fit the PV data from our study, both independently and in combination with the ice-X data from Grande et al.⁴³, using a variety of standard EoS fits (Fig 5b).

A Vinet EoS is fitted to our experimental data set from 78 - 230 GPa, giving a compressibility of $K_0 = 52.52 \text{ GPa}$, $K'_0 = 6.61$, $V_0 = 30.22 \text{ \AA}^3$ (per 2 f.u., used as convention). Here, the issue that arises is for such a value of compressibility the Vinet EoS underestimates the starting volume of the system. When the pressure-volume range is extended to include the Grande et al., data to fit over 2.2 - 230 GPa, we calculate compressibility values of $K_0 = 13.34 \text{ GPa}$, $K'_0 = 7.13$, $V_0 = 40.01 \text{ \AA}^3$ (per 2 f.u.). This approach provides a bulk modulus value that is rather too small and non-physical in describing ice-X at such high pressures. Therefore, a second-order Birch-Murnaghan EoS along

the full pressure range of 2.2 to 230 GPa, giving a compressibility of $K_0 = 52.2$ GPa, $K'_0 = 4$, $V_0 = 35.23 \text{ \AA}^3$ (per 2 f.u.). For the loading at the highest pressures achieved (218-230 GPa), a small fragment of rhenium was present at the center of the sample (as shown in the 2D X-ray transmission map of the sample chamber in Figure S8³⁹). This provided excellent agreement between the equation of state (EoS) of rhenium and the strained diamond edge, which was measured at the highest pressure 232(9) GPa) using Raman spectroscopy^{44,45}. Throughout the study, we observed consistent pressure measurements between the EoS of rhenium and the strained diamond Raman edge, as illustrated in Figures S9-10³⁹. Consequently, we chose to present pressure values determined by the EoS of rhenium.

Performing spectroscopic measurements at such extreme pressures also presents several intrinsic challenges. Diamond anvils are often susceptible to fracture when exposed to tightly focused laser illumination. In addition, both the sample and the diamond culets often exhibit a high density of defects that generate intense broadband fluorescence, which significantly reduces phonon lifetimes and leads to pronounced signal broadening. This broadening is further exacerbated by sampling within a highly strained region of the sample chamber, where non-hydrostatic stresses distort vibrational features and complicate spectral interpretation. Alternatively, here we calculate the corresponding vibrational spectra for the different candidate phases investigated in this study. Vibrational mode calculations were carried out with both Raman and IR activities computed to generate intensity projections. The theoretical Raman or IR spectra were calculated with DFPT, using the LDA XC-functional, at 260 GPa. A characteristic of the symmetrization of the spectroscopic O-H-O stretch and suppression of the OH molecular mode is evident in ice-X and

the post phases. The LDA XC-functional gives a very similar spectral output to the PBE choice, although for PBE we examined only 350 GPa, for reasons stated earlier. The simulated spectra were convolved with a pseudo-Voigt function using a full width at half maximum (FWHM) of 20 cm^{-1} to account for predominately strain broadening. For the IR data, additional normalized overlays, in pastel tones, were included to illustrate the expected appearance of each spectrum with a FWHM of 100 cm^{-1} , reflecting the typically lower spectral resolution of IR spectroscopy, where broad features often arise from overtones and anharmonic coupling of fundamental vibrations.

The Raman signal, even when accounting for strain broadening, should still allow the two alternative phases, $Pbcm$ and $P4_2/nmm$, to be distinguished from one another, and from ice-X. In ice-X the triply degenerate T_{2g} is distinctive and splits when symmetry lowering to the $P4_2/nmm$ phase. The $Pbcm$ phase exhibits two distinct lower-frequency modes, A_{1g} and B_g , respectively, which would be the most definitive features confirming the emergence of this distinct phase (Fig. 6a(top)). This is important as DFT calculations often underestimate vibrational frequencies; therefore, it can be expected that the more dominant features of the various phases are hidden beneath the highly strained diamond first-order phonon peak by around 200 GPa. The $Pn\bar{3}m$ structure of ice-X possesses O_h point group symmetry, with its dominant infrared-active mode assigned as T_{1u} . Upon symmetry lowering, this triply degenerate vibration splits into A_{2u} and E_u components in the $P4_2/nmm$ phase (D_{4h}), and further into B_{2u} , B_{3u} , and B_{1u} modes in the $Pbcm$ phase (D_{2h}). The infrared scattering cross-section of water is significantly larger than its Raman counterpart, making IR spectroscopy the preferred probe under such conditions. However, due to substantial experimental broadening at these extreme pressures, distinguishing among the

candidate phases remains challenging, as illustrated in Figure 6a(bottom).

For lower pressures of ice-X up to 125 GPa we were able to carry out experimental Raman spectroscopy to investigate the response of the primary Raman mode, T_{2g} , (Fig. 6b). The T_{2g} mode signifies the onset of H-bond symmetrization in ice-X. Its near linear pressure response aligns well with the pioneering work of Goncharov *et. al.*⁴⁶ (Fig. 6c), and can be correlated with its emergence at lower pressures, as reported by Grande *et. al.*⁴³. The diamond Raman edge was also measured to determine pressure (Fig. S10³⁹). By 125 GPa, the signal-to-noise ratio significantly deteriorated due to the inherently low Raman scattering cross-section of water-ice and our use of low laser powers. We did not continue with these measurements until again at 230 GPa, where no Raman signature from the sample could be discerned. We did not attempt to measure Raman spectra for the two lower pressures, as we were interested in attempting to measure the emergence of new Raman modes because of symmetry lowering away from a BCC structure evolving from ice-X.

The two energetically competing structural models of $Pbcm$ and $P4_2/nnm$ for the observed distorted post ice-X phase (Fig. 2) both show an anisotropic ionic O-H bond. This anisotropy is not a mere by-product of a general lattice distortion as both the oxygen and hydrogen atoms would distort simultaneously, but rather the primary driver of the lattice deformation itself. With increasing pressure, both the anisotropy of the cell parameters and the O-H bond vector lengths grow (Fig. 4), indicating that the ionic bond evolves in a fundamentally directional manner. The emergence of this anisotropic phase has implications that extend beyond condensed-matter physics. Space-telescope observations from Kepler, CoRoT and TESS⁴⁷ have revealed that planets between

Earth and Neptune in size, those most common in our galaxy ⁴⁸, likely host vast H₂O reservoirs. Voyager 2's flybys of Uranus and Neptune showed gravitational data consistent with models incorporating thick mantles of water ice extending from 15 to 830 GPa ⁴⁹, though alternative interior models suggest stratified layers of water within their mantles ⁵⁰. The structure of water ice at multi-megabar pressures critically influences its density, conductivity and heat transport, which underpin models of interior dynamics and magnetic activity in ice-rich worlds such as Uranus, Neptune and sub-Neptunes ⁵¹. Such pressure-induced evolution is likely intrinsic to the behavior of H₂O under extreme compression and, therefore, expected to influence its state under the thermodynamic conditions of planetary interiors, even if the low-symmetry phase identified here is not thermodynamically stable at such planetary interior temperatures. Whether this modification of the O-H bond facilitates chemical reactivity with surrounding materials ^{52,53}, or stabilizes alternative stoichiometries such as H₃O ³¹ remains an open question.

3 Conclusions

In conclusion, we report the first measurements of statically compressed H₂O-ice above pressures of 222(12) GPa, marking a transition from the ice-X phase to a denser, lower symmetry phase. Both *Pbcm*, the energetically predicted ground state, and *P4₂/nmm* are possible to model against the experimental XRD patterns. The measured equation of state for ice-X and the evolution of the cell parameters of the newly observed phase align well with theoretical models. These experiments highlight the complexities of compressing H₂O under high pressures, including the effects of deviatoric stress and the limitations of powder diffraction techniques for such low-Z systems. This

work underscores the need for further high-pressure studies to explore the behavior of water and related systems, e.g. H_xO or $OH+X$, under extreme conditions.

4 Methods

High pressure experiments Diamond anvil cells with 30 or 50 μm culets are used and liquid H_2O samples were loaded into 20 or 30 μm , sample chambers respectively, that are micromachined into Re gaskets⁵⁴. A total of 5 DAC loadings were prepared. To protect the diamonds during pre-indentation the Re foil is electroplated with a layer of Au that measures only a hundred nanometers in thickness. This process prevents any cold welding of the gasket material to the diamond culet when making very thin gaskets, approximately 6 μm . The issue of non-hydrostaticity is a major challenge in studying low-Z materials at extreme pressures. For water-ice in a DAC, conventional pressure-transmitting media cannot be used, as they may induce clathrate formation. The efficiency of direct laser absorption using mid-IR energies diminishes approaching 100 GPa. Although it is not possible to mitigate the issues of non-hydrostaticity, in this study we could improve powder averaging for powder statistics. All Samples are compressed to between 20 and 50 GPa before being heated using a CO_2 laser to recrystallize a finely powdered ice sample⁴³. Samples are heated approximately 500 K above the melt for any given pressure and for durations of 60 s. The melt-quench process is repeated until the powder statistics are redeemed sufficient. This dramatically improves powder statistics for XRD and allows more reliable indexing due to better resolution throughout the rest of the compression run.

Synchrotron X-ray diffraction Angle-dispersive synchrotron X-ray diffraction experiments were conducted at HPCAT, 16 ID-B Beamline of the Advanced Photon Source ($\lambda = 0.4066 \text{ \AA}$ and $\lambda = 0.42459 \text{ \AA}$), and Beamline 12.2.2 at the Advanced Light Source ($\lambda = 0.4132 \text{ \AA}$). Raman spectroscopy measurements were conducted. To achieve ultra-high pressures, we minimized laser exposure ($\leq 10 \text{ mW}$, 532 nm) to avoid potential damage to the diamonds. Raman spectroscopy was carried out again only at the final highest pressure using a 632.8 nm excitation laser ($\leq 1 \text{ mW}$). The pressures present here with the equation of state (EoS) of rhenium by Anzellini et al.,⁴⁴, and backed up by measurements using the pressure shift of the diamond Raman edge⁴⁵, see Figures S9-10, and Table S1-2³⁹.

Ab initio calculations *Ab initio* molecular dynamics (MD) simulations were performed with VASP code^{55,56} and the PBE functional⁴² unless otherwise reported, with a plane-wave cutoff of 1100 eV . Fixed volume (NVT) MD was performed for H_2O ice-VII and ice-X EoS using a 0.5 fs timestep, $16 (2 \times 2 \times 2 \text{ k-points})$ and 128 water molecules (Gamma-point sampling), as well as the $P4_2/nmm$ structure with 52 molecules ($2 \times 2 \times 2 \text{ k-points}$), which was found to be stable. K-point sampling converged the pressure to within 1 GPa to that of denser sampling, and finite-size effects on the EoS were found to be small. Glassy ice was simulated by flash-freezing high-temperature liquid ice into a high-density amorphous structure, which diffused extremely slowly at 300 K , to give an upper-bound to the density (see Figures S10-11)³⁹. Our theoretical volume-pressure values computed from AIMD at 300 K are in good agreement with our experiments values presented here, as well as previous observations^{10,43,57,58} (Fig. 5a). Theoretical vibrational spectra (wavenumber

and intensities) were calculated using density functional perturbation theory (DFPT), using the CASTEP code⁴¹ with norm-conserving pseudopotentials and an increased plane-wave energy cutoff of 1500 eV. We chose to use functionals that could stabilize post ice-X forms of high pressure ice under 300 GPa in order to give examples of the expected spectra.

Supplementary information This work is accompanied by supporting information that is provided

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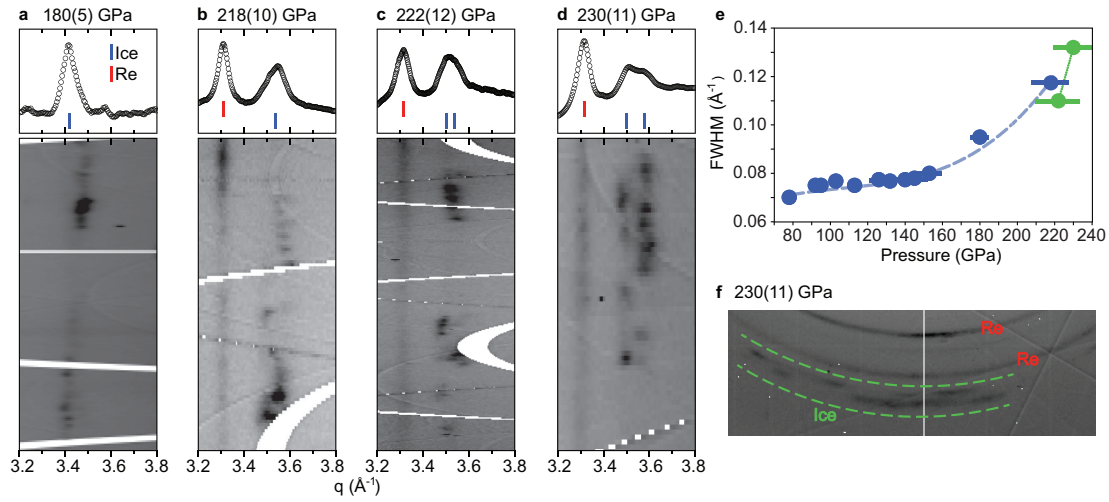


Figure 1: Evidence of symmetry change in water ice from X-ray diffraction. Shown are 1D azimuthal projections of image plate data at 180(5), 218(10), 222(12), and 230(11) GPa, with corresponding integrated 1D patterns above. Blue tick marks denote water-ice peaks and the red tick mark indicates rhenium. (a) At 180(5) GPa, ice-X is observed under non-hydrostatic conditions. (b) At 218(10) GPa, anisotropic strain broadens the integrated peak. (c) At 222(12) GPa, a new diffraction ring emerges from the ice sample. (d) At 230(11) GPa, two distinct diffraction rings appear, indicating a departure from the bcc ice lattice. Unlike the strain broadening seen at lower pressures, the integrated pattern here shows distinct peak splitting consistent with a crystallographic symmetry change. (e) FWHM of the primary ice feature as a function of pressure, showing a discontinuity and sharp drop above 218(10) GPa, marking the phase transition. Fits are provided as a visual guide. (f) 2D image plate data at 230(11) GPa, with Debye-Scherrer rings in the highlighted green region corresponding to the new ice phase.

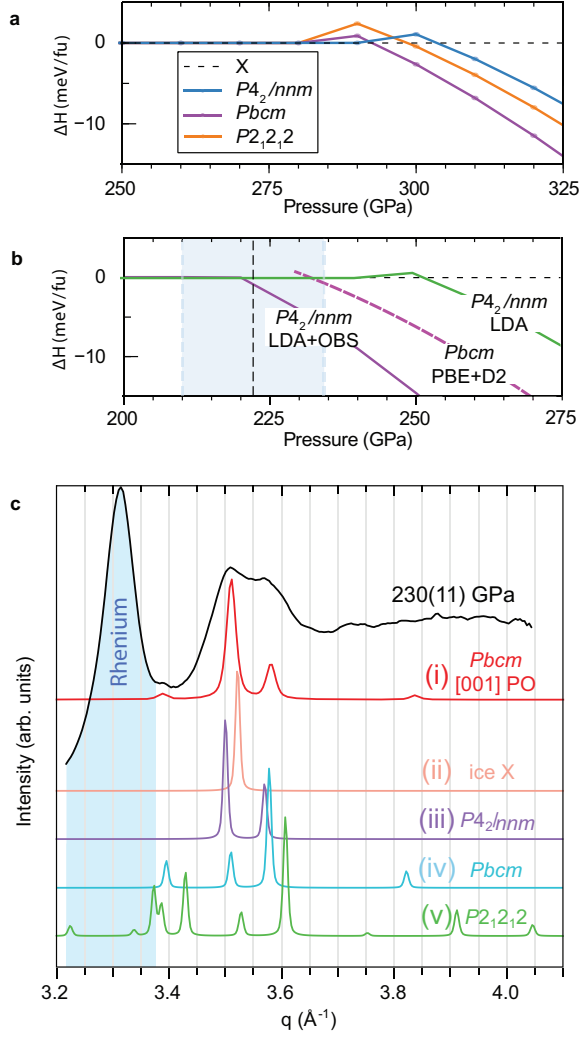


Figure 2: Theoretical and experimental analysis of post-ice-X phase stability. (a) Relative enthalpy of ice-X compared to the three lowest-energy higher-pressure phases ($P4_2/nnm$, $Pbcm$, and $P2_12_12$) as a function of pressure. (b) Relative enthalpy of $P4_2/nnm$ and $Pbcm$ with respect to ice-X, calculated using various DFT exchange-correlation functionals and dispersion corrections. The vertical dashed line indicates the experimental transition pressure identified in this work. (c) Integrated experimental XRD pattern at 230(11) GPa compared with simulated patterns of ice-X and the three candidate structures: (i) Rietveld refined $Pbcm$ phase with [001] preferred orientation (PO); (ii) ice-X ($Pn\bar{3}m$); (iii) $P4_2/nnm$; (iv) $Pbcm$; and (v) $P2_12_12$, all calculated at $V = 16.0 \text{ \AA}^3$ per 2 formula unit.

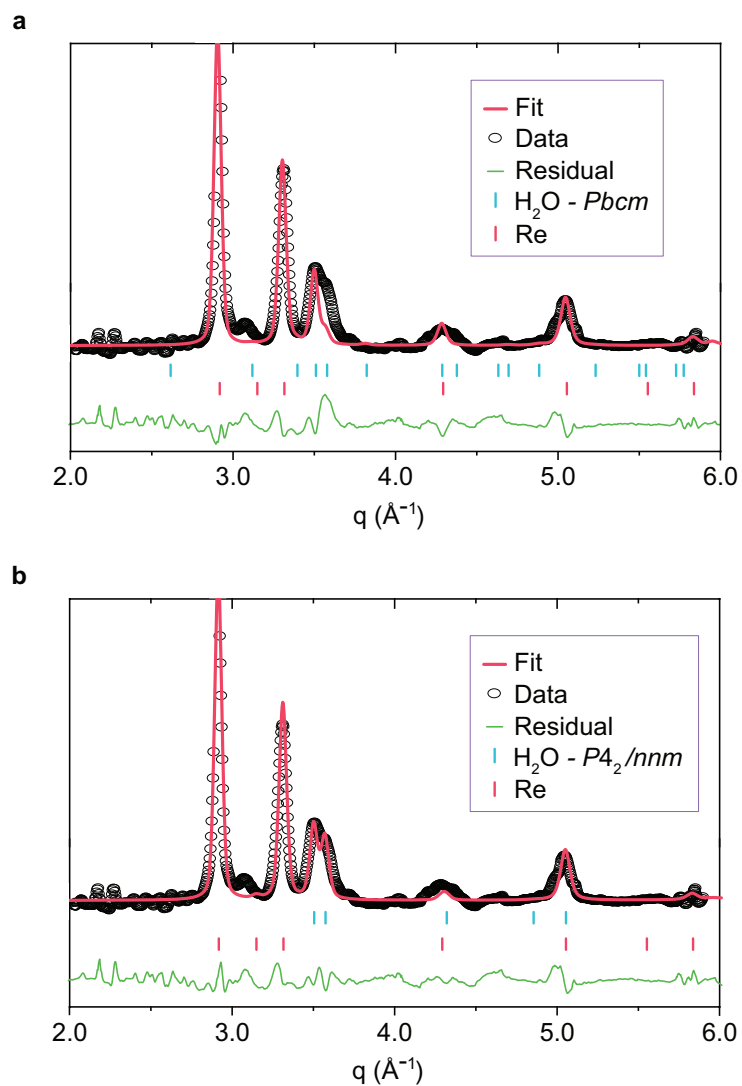


Figure 3: Rietveld refinement of the predicted water phases (the rhenium phase is fitted using Le Bail refinement), using (a) the $Pbcm$ model. ($wR = 0.334$), and (b) the $P4_2/nnm$ model ($wR = 0.274$).

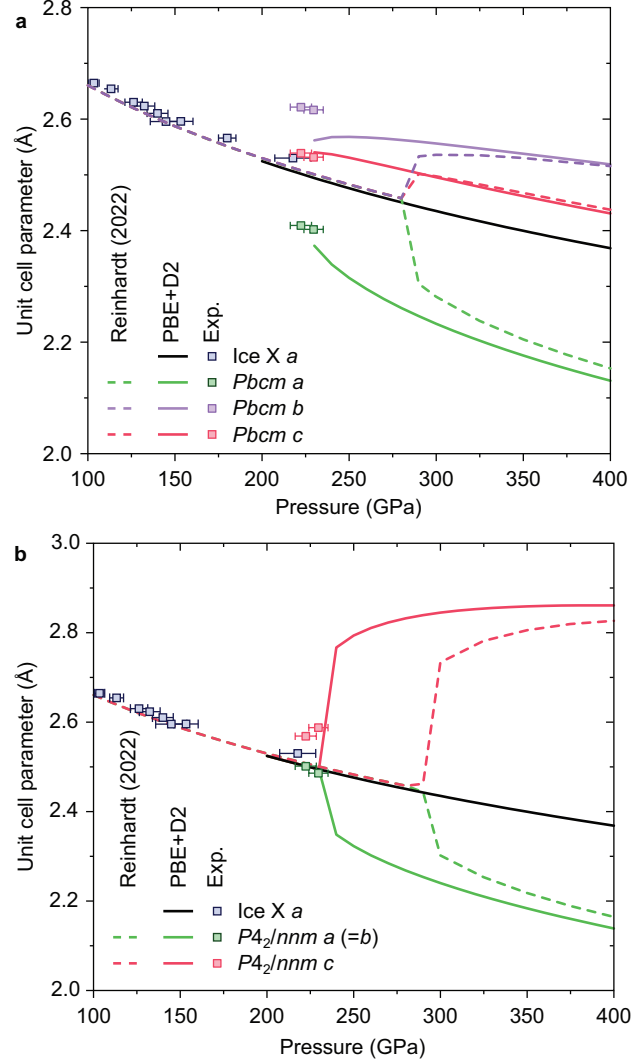


Figure 4: Lattice parameters of H₂O ice with pressure across the post-ice-X transition. Squares show experimental lattice parameters determined from X-ray diffraction. Solid lines show lattice parameters of ice-X and *P*₄₂/*nnm*-type ice from our own calculations. Dashed lines are from Ref. ³⁷ (a) Post-ice-X phase described as *Pbcm* model. Shown cell parameters for *b* and *c* are divided by $\sqrt{2}$. (b) Post-ice-X phase described as *P*₄₂/*nnm* model, as per the "ortho-X" structure described in Ref. ³⁷.

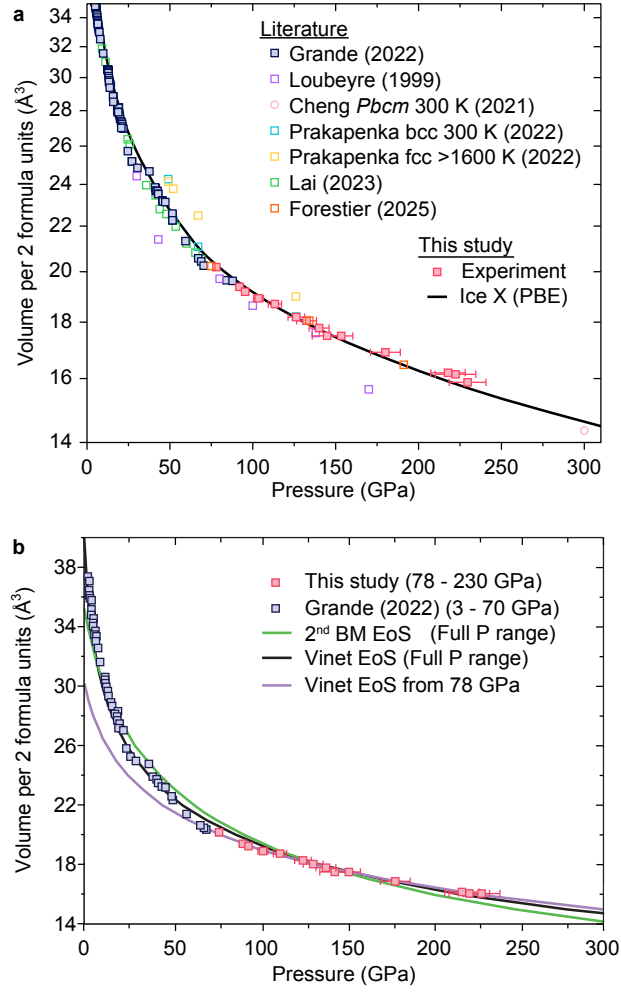


Figure 5: Ice volume relations **(a)** The volume-pressure relations of the experimentally determined values are plotted as red squares, and the theoretical $V(P)$ shown in black line, both shown as volume per 2 f.u. Relevant studies are compared, with experimental ^{10,12,43,58,59} and theoretical ⁵⁷ data presented as square or circle symbols, respectively. **(b)** The experimental volume pressure relations from this study and by Grande et al., ⁴³. The Birch-Murnaghan and Vinet equation of state fits to the respective data are shown.

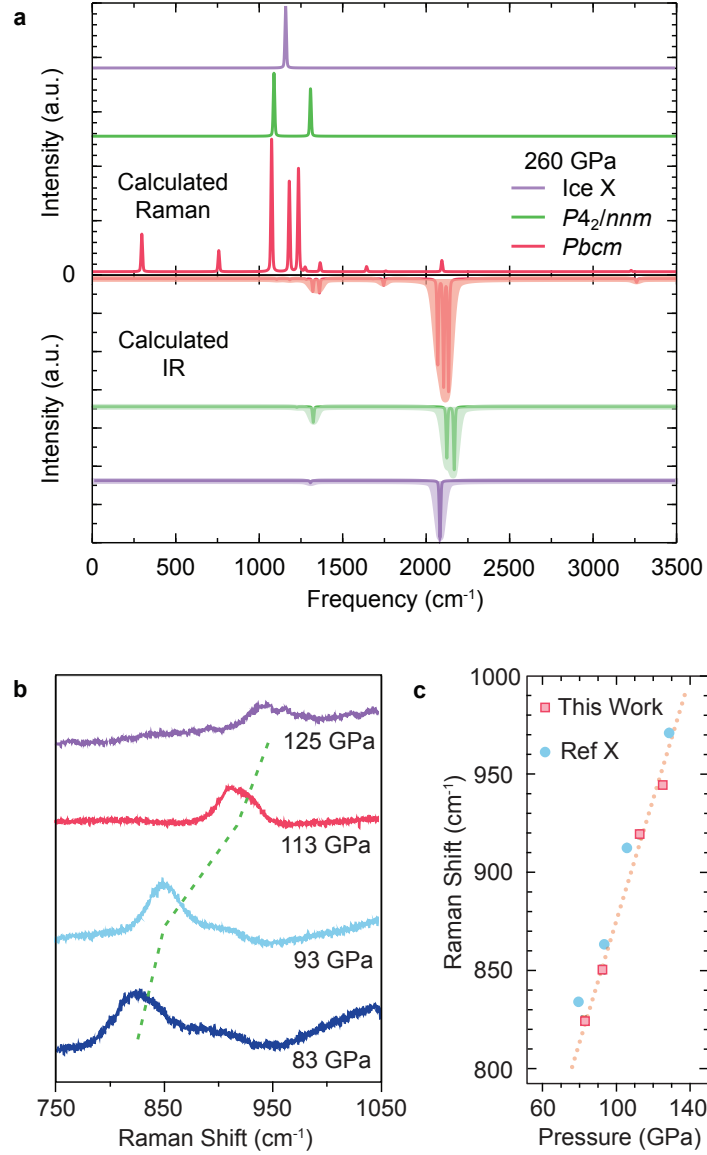


Figure 6: Spectroscopy results for the various expected phase(s) of water-ice at high pressures. **(a)** Theoretical Raman and IR spectra at 260 GPa calculated with DFPT, using the LDA XC-functional. **(b)** Experimental Raman spectroscopy data are presented as a stacked plot showing the Raman shift ice-X at increasing pressures of 83, 93, 113, and 125 GPa, respectively. The dotted line serves as a visual guide to the central frequency of the observed mode. **(c)** The Raman shift of the T_{2g} mode of our experimental data on ice-X compared to the work of Goncharov *et. al.*⁴⁶ at similar pressures.

Supplementary Files

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