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3 **Atomic distribution and local structure in ice VII from in-situ** 4 **neutron diffraction**

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22 **Author Contributions:** K.Y. and K.K. designed and carried out the experiments and their
23 analyses. K.Y., K.K., S.K., O.F., and M.T.F. performed single-crystal neutron diffraction
24 measurements. K.Y., K.K., J.A., S.M., and T.H. performed powder neutron diffraction
25 measurements. T. I., T.S., K.S., and T.K. contribute to the development of the diamond anvil cell.
26 H.K. directed the research.

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1 **Abstract**

2 Ice polymorphs show extraordinary structural diversity depending on pressure and temperature.
3 The behavior of hydrogen-bond disorder is not only a key ingredient for their structural diversity
4 but also controls their physical properties. However, it has been a challenge to determine the
5 detail of the disordered structure in ice polymorphs under pressure because of the limited
6 observable reciprocal space and inaccuracies related to high-pressure techniques. Here we
7 present the first elucidation of the disordered structure of ice VII, the dominant high-pressure form
8 of water, at 2.2 GPa and 298 K from both single-crystal and powder neutron diffraction
9 techniques. We reveal the three-dimensional atomic distributions from the maximum entropy
10 method and unexpectedly find a ring-like distribution of hydrogen in contrast to the commonly-
11 accepted discrete sites. In addition, total scattering analysis at 274 K clarified the difference in the
12 intermolecular structure from ice VIII, the ordered counterpart of ice VII, despite an identical
13 molecular geometry. Our complementary structure analyses robustly demonstrate the unique
14 disordered structure of ice VII. Furthermore, these noble findings are related to the proton
15 dynamics which drastically vary with pressure, and will contribute to an understanding of the
16 structural origin of anomalous physical properties of ice VII under pressures.

17

18 **Significance Statement**

19 Ice VII is a textbook example of a hydrogen-disordered solid, but the exact distribution of
20 hydrogen atoms is still unknown. Here we report the detailed atomic distribution and local
21 structure of ice VII revealed from neutron diffraction data of both single-crystalline and powder
22 specimens under high pressure. Recent technical developments enabled a robust analysis of the
23 diffraction data: ice VII has a different intermolecular structure from its ordered counterpart, ice
24 VIII, even at short distances, despite their identical molecular geometry. Moreover, hydrogen has
25 an unusual ring-like distribution and an elongation toward hydrogen-bonded water molecules. Our
26 findings highlighted the uniqueness of the disordered structure of dense ice and open the door for
27 further understanding of network structure in extreme conditions.

28

29

30 **Main Text**

31

32 **Introduction**

33

34 Water freezes into various solid structures, including crystalline and non-crystalline phases, when
35 compressed or cooled down. Ice VII is one of its 20 crystalline phases and is stable at room
36 temperature between 2 and 60 GPa. In this pressure range, ice VII shows various anomalous
37 behaviors related to pressure-dependent proton dynamics such as a sharpening of the Raman
38 peak of its symmetric vibration mode at 11–13 GPa(1) which is caused by a cross-over of
39 dominant processes from molecular rotation to proton translation(2, 3). Ice VII also undergoes a
40 phase transition involving hydrogen-bond symmetrization toward ice X(4, 5). This anomalous
41 crystalline phase has attracted much scientific interest, and it hence appears crucial to
42 understand its detailed structure.

43 The structure of ice VII can be regarded as two interpenetrating diamond-like networks formed by
44 hydrogen-bonded water molecules (Figure 1a). In each network, water molecules are
45 orientationally disordered as those in other ice polymorphs (e.g. ordinary ice I_h(6)). Hydrogens of
46 each water molecule randomly occupy two of four sites toward the neighboring oxygens. In other
47 words, the overall structure of ice VII consists of a combination of various configurations. Ice VII
48 transforms into ice VIII by ordering the hydrogen positions (or molecular orientations) at low
49 temperatures (below 273 K at 3 GPa(7)). In ice VIII, the orientations of water molecules are well

1 defined: hydrogens occupy two particular sites, and molecular orientations between the
2 interpenetrating networks are aligned antiparallel along the *c*-axis, which induces displacement of
3 the network relative to the other along the *c*-axis. This results in a tetragonal distortion of ice VIII.
4 The disordered structure of ice VII is generally represented by a cubic unit cell with space group
5 $Pn\bar{3}m$ (#224) in which oxygens locate at 2a site, and hydrogens at 8e site with occupancy of 0.5
6 (hereafter, this model is called a “single-site” model). The symmetric constraints simplify the
7 structure model as it needs only one parameter for the hydrogen position (*x*, *x*, *x*) and two
8 variables for atomic displacement parameters (ADPs) (three for anisotropic ADPs). The single-
9 site model reproduces well the diffraction patterns and therefore has been adopted in almost all
10 previous studies(8, 9). Nevertheless, structure refinements based on the single-site model are
11 known to cause a highly anomalous geometry of the water molecule, e.g. an unrealistically short
12 O-D covalent bond length (0.89 Å(10)) compared to those in ice VIII (0.97 Å)(10, 11) whereas a
13 computational study showed similar distances for both phases(12). This implies that water
14 molecules in ice VII are not in the positions assumed in the single-site model. The agreement of
15 the single-site model with the diffraction patterns appears to be a result of time and spatial
16 averaging in diffraction measurements.

17 On the other hand, more reasonable “multi-site” models have been proposed up to date to
18 describe the real structure of ice VII. In these models, the hydrogen atoms are located away from
19 a straight line between adjacent oxygens, especially toward the three non-bonded oxygens
20 belonging to the other hydrogen-bonding network(13). Oxygen positions were modelled mainly in
21 two ways: displacements toward $\langle 111 \rangle$ (14) or $\langle 100 \rangle$ (10) as illustrated in Figure 1b.
22 Displacements along $\langle 100 \rangle$ imply that ice VII favours local structures similar to those in the
23 ordered structure of ice VIII while displacements along $\langle 111 \rangle$ imply the opposite. The $\langle 111 \rangle$
24 model entails differences in hydrogen-bond length: a shorter one in which one oxygen gets close
25 to the neighbor and a longer one in which oxygen is away from the neighbor (14). The existence
26 of the bimodal probability of hydrogen-bond length is still controversial (17, 18). However, no
27 unambiguous structure refinements have been achieved so far because the atomic
28 displacements from the single-site position are very small (0.1 Å) and this parameter strongly
29 correlates with ADPs in the structure refinement. A computational study from density functional
30 theory (DFT) suggested a probability distribution similar to the $\langle 100 \rangle$ displacement of oxygen
31 rather than $\langle 111 \rangle$ although it also insisted that both displacement models are too simplistic(15).
32 In conclusion, the actual structure in ice VII has not been experimentally proven up to the present.
33

34 Here we report *in-situ* single-crystal neutron diffraction using a newly developed apparatus.
35 Previous powder diffraction studies had limitations in resolution related to peak duplicates in one-
36 dimensional diffractograms, whereas single-crystal diffraction can directly provide discrete
37 reflection intensities without peak overlap and can lead to a definitive conclusion by double-
38 checking with the well-established powder diffraction technique(16). In addition to the technical
39 improvements in measurements, non-conventional analytical approaches are also necessary to
40 reveal the detailed disordered structure of the dense ice without constraints from structure models
41 like the single-site model because conventional analyses have considerable difficulties in
42 modeling the real distribution. We applied a maximum entropy method (MEM) analysis to reveal
43 three-dimensional atomic distributions in the unit cell. Moreover, information on local structures
44 like the water geometry was extracted as interatomic correlation by total scattering analysis. For
45 these approaches, neutron diffraction is suitable for this study owing to its sensitivity to hydrogen
46 (deuterium). The scattering length does not decay according to $\sin\theta/\lambda \propto 1/d$ in contrast to x-ray
47 diffraction. Therefore, numerous reflections are observable even for low *d*-spacing, which allows
48 a structure analysis with high resolution in real space. Deuterated samples (D₂O) were used in all
49 the experiments instead of light water (H₂O) to avoid incoherent scattering. This isotope
50 replacement shifts the phase boundary between ices VI and VII toward slightly lower pressure but
51 does not affect significantly the disordered structures investigated in this study.
52
53

54

Results

1
2 The MEM analysis is based on the principle of maximum entropy, a part of Bayesian statistics,
3 which expects the most probable density distribution to be one with the largest information
4 entropy under constraints on the observed structure factors F_o and their uncertainties σF_o .
5 Results of MEM analyses on both single crystal and powder diffraction data show ring-like
6 distributions of deuterium around the $\langle 111 \rangle$ axes, direction toward the oxygen of hydrogen-
7 bonded water, away from the position assumed in the single-site model (Figures 2a and 2b), and
8 the ring is slightly distorted to a triangular shape. Their maxima are displaced from the axes by
9 0.1–0.2 Å. These are similar to the reported values (13, 14), but such a ring-like distribution can
10 only be approximately described by the displacement ellipsoid conventionally used in least-
11 squares structure refinements. The corners of the triangular-like distribution are in staggered
12 directions to other deuterium sites covalently bonded to the oxygen as previously suspected(13).
13 From Figures 2c and 2d, the distance between the maxima of density assigned to deuterium and
14 the average oxygen site is shorter than a plausible covalent O-D bond length of 0.97 Å as found
15 in ice VIII(10, 11). This explains that the conventional structure analysis using the single-site
16 model results in a shorter (average) O-D covalent bond, whereas the deuterium in ice VIII does
17 not show such spreading distribution (Figure S4).
18 On the other hand, oxygens show more elongated distributions toward the O-D covalent bond
19 (Figures 2c and 2d), which corresponds to $\langle 111 \rangle$ direction in the ice VII structure rather than
20 $\langle 100 \rangle$ or $\langle 110 \rangle$ directions. However, the density distributions are not tetrapodal but pyramidal,
21 meaning that other components such as along $\langle 100 \rangle$ are not fully excluded. The real disordered
22 structure would be the combination of dominant displacements toward $\langle 111 \rangle$ and some other
23 components with variations. The more diffuse features in the single-crystal data compared to the
24 powder data would be mainly due to the achieved resolution for the observed diffractions.
25 Nonetheless, our examinations from two distinct experimental setups, at different neutron
26 sources, different high-pressure devices, and different detectors, suggest the feature of $\langle 111 \rangle$
27 displacement of oxygen is real and intrinsic for ice VII. This is hence consistent with the model
28 proposed by Nelmes *et al.*(14).
29 These displacements of oxygen and deuterium were partly proposed in the previous studies(13,
30 14), but our study shows for the first time unambiguously the three-dimensional distribution in ice
31 VII by the model-independent MEM approach. Our result shows that the structure of ice VII is
32 clearly distinct from the single-site model. The ring-like distribution of deuterium can be ascribed
33 to the time and spatial average of water molecules in different orientations rather than a distortion
34 of water molecules themselves like DOD bending. Such displacement induces bending of the
35 hydrogen-bonding networks from an ideal diamond-like network with cubic symmetry.
36 It should be noted that the density distribution of deuterium also elongates toward oxygens of the
37 neighboring water molecules. This suggests two possibilities. One explanation is that hydrogen-
38 bonded water molecules get closer, which means the network structure is modified. The other
39 explanation is that the interpenetrating hydrogen-bonding network locally displaces along $\langle 111 \rangle$.
40 This would mean that the local structure of ice VII differs from that of ice VIII, the hydrogen-
41 ordered phase, with displacement along $\langle 100 \rangle$.
42 Relating to the displacement of oxygen along the $\langle 111 \rangle$ direction, a modulated structure was
43 previously proposed from single-crystal x-ray diffraction(19, 20). In our single-crystal neutron
44 diffraction, however, no superlattice reflection was observed similar to any other studies using
45 powder x-ray and neutron diffraction. There is no technical reason why such reflections cannot be
46 observed in our experiment because the intensity of the superlattice reflection should be
47 comparable to that of 111 reflections (see Figure 2 in ref(19)) which were observed in our study.
48 The origin of the previously reported superlattice reflection remains hence unclear.
49 In order to reveal the short-range structures of ice VII such as interatomic distances and local
50 ordering, the correlation functions were derived from the total scattering of powder diffraction
51 instead of extracted intensities of the Bragg peaks as in the conventional structure refinements
52 and the MEM analysis. The exact O-H(D) distance in ice I_h was derived from the total scattering
53 analysis(21).

1 The total correlation functions $T(r)$ of ice VII and VIII from powder diffraction at 274 K and 2.2
2 GPa has a similar profile in the short- r region (Figures 3a and 3b). Assuming that each correlation
3 has Gaussian type distribution, $T(r)$ can be divided into several peaks. The representative
4 geometries are listed in Table 1 with corresponding geometry obtained by the Rietveld analysis
5 using the single-site model. The Rietveld analysis resulted in the O-D length of 0.9163 (5) Å in ice
6 VII, significantly shorter than that of 0.9681 (8) Å in ice VIII which agree well with previously
7 reported values(10, 11). Our fitting of $T(r)$ gave an O-D distance of 0.9662 (5) Å for ice VII,
8 proving the suggested similarity of its intramolecular structure with ice VIII(22). The coordination
9 numbers of the covalent O-D were estimated to be 1.8 for both ices VII and VIII. The slightly small
10 value from the ideal number 2.0 would be ascribed to the systematic error related to the overall
11 scaling of the scattering patterns, such as multiple scattering and attenuation. The molecular
12 geometry of water in ice VII is hence identical to that in ice VIII, *i.e.* the apparently short O-D
13 length in ice VII results from time- and spatial-average in Rietveld analyses.

14 To compare interatomic correlations at longer distances we discuss the pair distribution function
15 $G(r)$ instead of $T(r)$. Figure 3c shows that both ices VII and VIII have a peak at 0.97 Å, which
16 corresponds to the O-D covalent bond as discussed for $T(r)$. On the other hand, the profiles differ
17 from each other in the region longer than the lattice parameter a_0 of ice VII. This mean that ice VII
18 does not have the same interatomic correlation as ice VIII over the distance of the second
19 nearest neighbors. Especially, ice VIII has a tiny bump at 1.9 Å which corresponds to hydrogen-
20 bonded O...D whereas that region in ice VII is smooth. Such difference in the correlation function
21 is attributed to the molecular ordering in each phase. Based on a reported DFT-based
22 calculation(23), local configurations like ice VIII are not dominant at pT conditions where ice VII is
23 stable but other configurations have comparative populations. These are consistent with the
24 atomic distribution obtained from the MEM analysis in which $\langle 100 \rangle$ displacements are not
25 observed.

26 27 **Discussion**

28
29 The atomic distribution observed in the MEM analyses would reflect the dynamic natures of ice
30 VII. The total scattering analyses revealed that the water molecule has chemically plausible
31 geometry in ice VII, as expected in the case of ice I_h (21). The disorder comprises the molecular
32 orientation and their displacements from the average positions, resulting in the unusual atomic
33 arrangements of ice VII described by the discrete atomic sites in the single-site and multi-site
34 models in conventional structure analyses. Spectroscopic studies(24–26) and the quick
35 transformation from ice VIII to ice VII(2) imply that the disordering of ice VII takes place
36 dynamically at around 300 K. The atomic distribution is related to such dynamic conversion
37 among the configurations. The dynamic motions in ice are expressed mainly by two components,
38 rotation and translation. Their contributions depend on pressure in a contrasting way. At lower
39 pressures, water molecules have enough space to flip and rotation motion is dominant. Under
40 higher pressure, the water molecules get closer and become difficult to flip. On the other hand,
41 reducing the intermolecular distances enhances the probability of translation of deuterium
42 between neighboring water molecules. The cross-over of two dynamics takes place at around 10
43 GPa, first suggested from Raman spectroscopy(1) and recently proven from dielectric
44 measurements(27), and illustrates the origin of previously-reported anomalies: *e.g.* peak widths of
45 stretching mode(1), phase transition kinetics(2), electrical conductivity(25), and proton
46 diffusion(26). In conventional structure refinements, ADPs decrease with increasing pressure ($2 <$
47 $p < 10$ GPa) and become almost constant above 10 GPa(8, 14, 28). This suggests that atomic
48 distribution in ice VII will be more localized up to 10 GPa. The localized distribution should be
49 linked with the suppression of rotational motion.

50 The representation with two types of dynamic movement in ice VII introduces an aspect to
51 attribute the observed unexpected distribution in ice VII to two features. First, the probability
52 density is distributed in a ring-like shape around the $\langle 111 \rangle$ axes. Second, the deuterium also has
53 elongated distribution toward the oxygen of hydrogen-bonded water. These distributions
54 correspond to instantaneous deviation from the average position. The ring-like distribution should

1 be related to a precession, assignable to rotational or librational motions of molecules, whereas
2 the elongation along the hydrogen bond would correspond to the translational motion of
3 deuterium approaching the hydrogen-bonded neighboring molecule.
4 In addition to the dynamic nature of ice VII, static configurations also play important roles in the
5 disordered structure of ice VII. The phase transition boundary between ices VII and VIII are
6 almost temperature independent below 10 GPa, consistent with an estimation from the Clapeyron
7 equation ($dp/dT = \Delta S/\Delta V$) with their little volume difference, $\sim 5 \text{ mm}^3/\text{mol}$ compared to the
8 Pauling entropy, $3.37 \text{ J}/(\text{K}\cdot\text{mol})$. On the other hand, the boundary slope becomes steeper at
9 higher pressures, suggesting that the volume change between ices VII and VIII is significant in
10 this pressure regime. *Ab initio* calculation estimated the energy gaps among molecular
11 configurations to be the smallest at this pressure regime, reproducing the tendency of the order-
12 disorder phase boundary between ices VII and VIII(23). Our total scattering analysis revealed the
13 clear difference in intermolecular structures of the disordered phase from the ordered counterpart.
14 Further investigation at higher pressures can provide direct evidence for the pressure-dependent
15 variation of the local structure as a result of the probability of dominant configuration. Moreover,
16 the turning pressure overlaps with where the cross-over of dynamics occurs (27). Fundamental
17 and detailed diffraction techniques can provide direct and pivotal information on the anomalous
18 physical properties of ice VII under pressure.
19 Our findings would also provide an approach to elucidate the behaviors of water molecules during
20 the phase transition to hydrogen-bond symmetrized ice X. Although spectroscopic studies
21 showed in the 1990s that ice VII transforms into ice X over 60 GPa in H_2O and 70 GPa in
22 D_2O (29–31), the symmetric structure of ice X has not been confirmed experimentally yet by
23 neutron diffraction. A powder neutron diffraction study of D_2O up to 60 GPa reported the
24 elongation of covalently-bonded O-D separation (28). The separation of the deuterium site
25 between the hydrogen-bonded water molecules also decreases, and its linear extrapolation
26 proposed an upper limit of the symmetrization to be at 113 GPa. Below 60 GPa, water is
27 considered to retain its molecular nature from spectroscopic studies(29–31) but the physical
28 properties of the BCC ice differ from ice VII(32–34), called ice VII'. In this pressure regime, the
29 bimodal potential curve of deuterium becomes unimodal and quantum tunnelling takes place
30 dominant. The atomic distribution and the correlation function can provide direct images to
31 observe the transient states toward the hydrogen bond symmetrization.

32 33 34 **Materials and Methods**

35 36 **Single-crystal neutron diffraction**

37
38 The single-crystal diffraction experiment was conducted at the D9 hot neutron single-crystal
39 diffractometer at the Institut Laue-Langevin (ILL, Grenoble, France). The data of ice VII was
40 collected at 298 K and 2.2 GPa using a diamond anvil cell specially designed for this study(35).
41 Single-crystalline specimens of deuterated ice VII were grown directly from a water-alcohol
42 mixture ($\text{D}_2\text{O}:\text{MeOD}:\text{EtOD} = 5:4:1$ in volume ratio) by cyclic heating and cooling over 2 GPa. The
43 pressure was estimated by the ruby fluorescence method(36).

44 45 **Powder neutron diffraction**

46 The powder diffraction experiments were conducted at the BL11 (PLANET) beamline(16) of the
47 Material and Life Science Experimental Facility (MLF) at J-PARC (Ibaraki, Japan) using the MITO
48 pressure-temperature variable system(37). Powder samples of deuterated ice VII were obtained
49 by compression of ice at 200 K, below the melting curve of ice phases. The repetitive solid-solid
50 phase transition contributes to preparing fine powder samples suitable for structure analyses. The
51 diffraction patterns of ice VII were collected at 2.2 GPa and temperatures of 298 K and 274 K. A
52 powder diffraction pattern of ice VIII was also collected at 274 K and 2.2 GPa for comparison. The
53 sample pressures were estimated from the equation of state of ice VII and VIII themselves(8).
54 The phase transition between ices VII and VIII is a 1st-order transition that shows hysteresis so that

1 both phases can metastably exist at approximately 274 K during cooling for ice VII or heating for
 2 ice VIII before the phase transition occurs.

4 MEM analysis

5 The MEM analysis tends to give the most uniform distribution under conditions that satisfy the
 6 constraints. The information entropy S and the constraints C are defined as follows.

$$S = - \sum_{\mathbf{r}}^{\text{unit cell}} \rho(\mathbf{r}) \ln \left(\frac{\rho(\mathbf{r})}{\tau(\mathbf{r}) \sum_{\mathbf{r}}^{\text{unit cell}} \rho(\mathbf{r})} \right), \quad (1)$$

$$C = \frac{1}{N_k} \sum_{\mathbf{k}} \left| \frac{F_o(\mathbf{k}) - F_c(\mathbf{k})}{\sigma F_o(\mathbf{k})} \right|^2 - 1, \quad (2)$$

7 where $\rho(\mathbf{r})$ is the normalized density of scattering length at \mathbf{r} in a unit cell and $\tau(\mathbf{r})$ is the
 8 normalized density derived from prior information for \mathbf{r} , N_k is the number of structure factors, \mathbf{k} is
 9 the reciprocal lattice vector to identify each Bragg reflection, F_c is the structure factors calculated
 10 from $\rho(\mathbf{r})$. The most probable density distribution which maximizes S can be derived by a method
 11 of undetermined Lagrange multipliers (λ and μ).

$$Q = S - \lambda C - \mu \left(\sum_{\mathbf{r}}^{\text{unit cell}} \rho(\mathbf{r}) - 1 \right), \quad (3)$$

12 The third term in Eq. 3 is a constraint for the total normalized scattering length to be one. The
 13 MEM analyses for both single-crystal and powder diffraction were done using the *Dysnomia*
 14 program(38) and the practical and detailed schemes are in its manual. The crystal structures and
 15 density distribution map was drawn with the *VESTA* program(39).

16 Total scattering analysis

17 Structure factors, $S(Q)$, were derived after intensity corrections for background, absorption, etc.
 18 $S(Q)$ is related to the atomic pair distribution function $g(r)$ by Eq. 4. Derived correlation functions
 19 were analyzed in the forms of the total correlation function (TCF) $T(r)$ and the pair distribution
 20 function (PDF) $G(r)$ defined by Eqs. 5 and 6.

$$Q[S(Q)-1] = \int_0^{\infty} 4\pi\rho_0 r [g(r)-1] \sin(Qr) dr \quad (4)$$

$$T(r) = 4\pi r \rho_0 g(r) \quad (5)$$

$$G(r) = 4\pi r \rho_0 (g(r) - 1) \quad (6)$$

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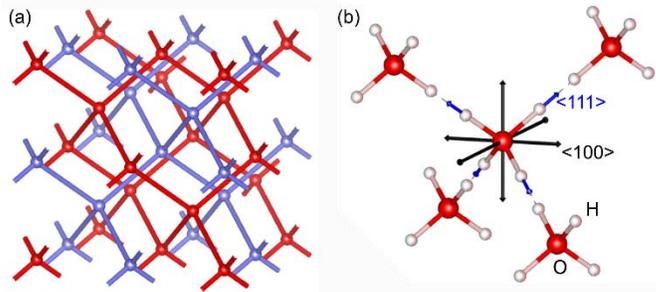
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1 **Figures and Tables**

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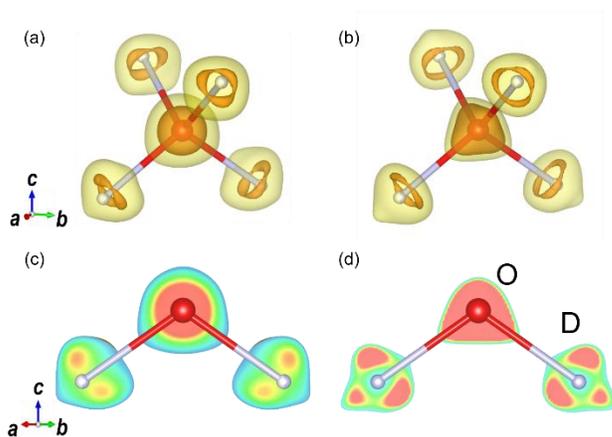
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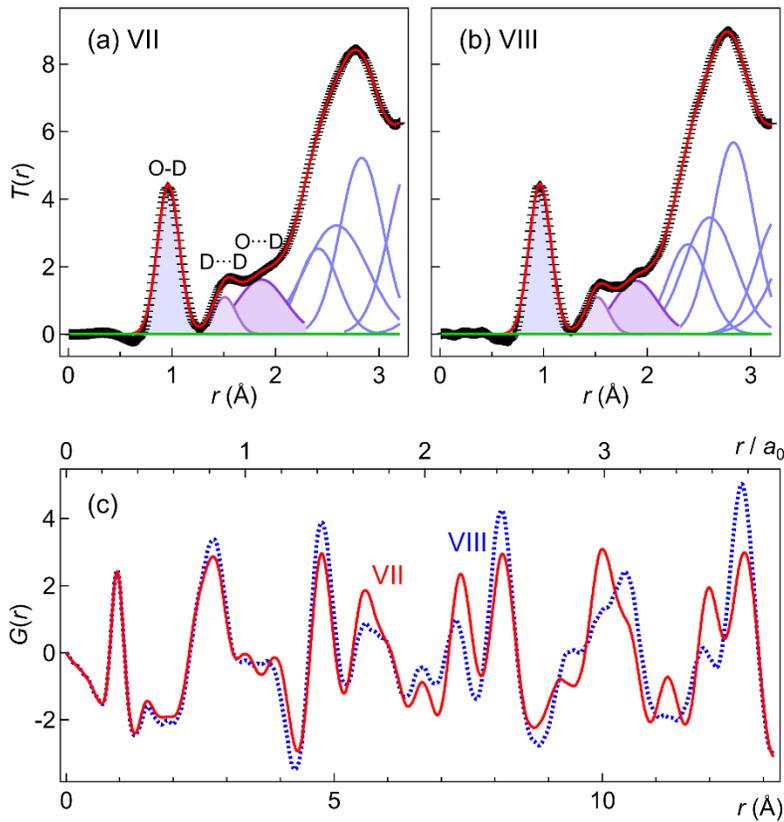
Figure 1. Crystal structure of ice VII. (a) Interpenetrating diamond-like hydrogen-bonding networks colored by red and light blue. Balls on the nodes correspond to oxygen while hydrogen is omitted for clarity. (b) Close-up view of water molecules in the same hydrogen-bonding network. Large red and small pink balls correspond to oxygen and hydrogen, respectively.



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Figure 2. Distribution of scattering-length density in ice VII derived from (a) single-crystal data and (b) powder diffraction data both at 298 K and 2.2 GPa. (c) and (d) are cross sections of (a) and (b) on (110) plane, respectively. The oxygens and deuteriums are illustrated as those in the single-site model with O-D = 0.97 Å, as in the water molecule, and $\angle\text{DOD} = 109.47^\circ$ for comparison. Density decreases from red to blue color.

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Figure 3. Total correlation functions $T(r)$ of (a) ice VII and (b) ice VIII at 274 K and 2.2 GPa. Each peak was fitted using Gaussian functions (blue curves). The black cross indicates measured data and the red line corresponds to a profile reproduced from peak fitting. The initial five peaks at $r < 2.5$ Å are located at the expected positions derived from the Rietveld analysis whereas four peaks up to 4.4 Å were set to be at the maximal positions of the profile. (c) Pair distribution functions $G(r)$ of ice VII and VIII were obtained at 274 K and 2.2 GPa. Abscissa on top is normalized interatomic distance by lattice parameter $a_0 = 3.346632$ (13) Å of ice VII determined from the Rietveld analysis.

1 **Table 1.** Summary of interatomic distances derived from Gaussian peak fitting of correlation
 2 function $T(r)$ and Rietveld refinement with reported values.

		VII $_{T(r)}$	VIII $_{T(r)}$	VII $_{Riet}$	VIII $_{Riet}$	VIII	VIII
	unit			This study		ref. 10)	ref. 11)
$r(O-D)$	(Å)	0.9662 (5)*	0.9658 (5)*	0.9163 (5)	0.9681 (8)	0.968 (7)	0.973(11)°
$r(D...D)$	(Å)	1.510 (5)*	1.521 (6)*	1.4963 (10)	1.5498 (14)	1.543 (14)	1.532(12)°
$r(O...D)$	(Å)	1.86 (13)*	1.89 (26)*	1.9820 (5)	1.9304 (8)	1.911 (9)	1.920(10)°
$\angle DOD$	(°)	102.8 (4)*	103.9 (6)*	109.47	106.34 (11)	105.6 (11)	103.8(15)°
ρ	(GPa)	2.2	2.2	2.2	2.2	2.4	2.8
T	(K)	274	274	274	274	10	269

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5 * Errors estimated from the SD of peak fitting for $T(r)$ are given in parenthesis.

6 ° Errors estimated from the refinement procedures are given in parentheses. Riet, Rietveld.

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