NEW HYDROGEN ORDERED PHASES OF ICE

C.G. Salzmann,1,2 P.G. Radaelli,3,4 A. Hallbrucker,1 E. Mayer1 and J.L. Finney4

1 Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria
2 Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK
3 ISIS Facility, Rutherford Appleton Laboratory, Council for the Central Laboratory of the Research Councils (CCLRC), Chilton, Didcot OX11 0QX, UK
4 Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

1 INTRODUCTION

A full knowledge of the structures of, and transformations between, the many crystalline phases of ice (Figure 1) is important not only in improving our knowledge of the hydrogen bond itself, but also in increasing our understanding of the water molecule in critical chemical, biological, and geological processes.1,2 Understanding the behaviour of water at low temperatures is also of potential importance with respect to the state and dynamics of water in biological systems at low temperatures,3 as well as elsewhere in the solar system.1, 2 High-pressure low temperature phases of ice in particular are thought to be present on the icy satellites of the outer planets as the result of either meteoroid impacts on their surfaces4 or the hydrostatic pressure in the ice shells.5

In the crystalline phases of ice, individual water molecules are tetrahedrally bonded to their neighbours via hydrogen bonding according to the Bernal-Fowler rules.6 A consequence of this connectivity is that each water molecule may adopt six different orientations. In 1935, Linus Pauling showed that the connectivity of the lattice reduces but not altogether suppresses these degrees of freedom, resulting in residual disorder and hence non-zero entropy at zero temperature.7 Thermodynamically, the hydrogen disordered phases of ice should, on cooling, transform via hydrogen ordering into new, thermodynamically more stable phases, with zero entropy at 0 K.1 The basic obstacle in achieving these phase transitions is the slowing down of the reorientation of water molecules with decreasing temperature and a consequent freezing-in of disorder. Addition of dopants can accelerate reorientation in some ice phases. Previous attempts to unlock the geometrical frustration in hydrogen bonded ice structures have focused on doping with potassium hydroxide (KOH). They had success in partially increasing the hydrogen ordering in hexagonal ice (ice Ih) and transforming it into hydrogen ordered ice XI.1, 8-10 Acid dopants, however, had little effect on hydrogen ordering in ice Ih.10
Figure 1 The phase diagram of ice, including liquidus lines of metastable ices IV and XII (long dashed lines) and extrapolated equilibrium lines at low temperatures (short dashed lines). Hydrogen ordered ices XIII and XIV were prepared by isobaric cooling of HCl (DCl) doped H$_2$O (D$_2$O) ice V or XII to 77 K at 0.5 GPa or 1.2 GPa, respectively (indicated by arrows). Cooling of ice XII was started at 190 K, which is 10 K below the temperature where transition to stable ice VI would occur. The temperatures of the hydrogen ordering phase transitions are indicated by grey bars. Transition temperatures for ice V → ice XIII and ice XII → ice XIV are read off from Figure 3 (the pressure dependence of the ordering temperatures is assumed to be small).

We recently reported that hydrogen disordered ices V and XII transform on acid doping with HCl (DCl) into new hydrogen ordered phases, whose structures were determined by powder neutron diffraction, whereas doping with KOH had little effect.\textsuperscript{11-13} These new ice structures were labelled ice XIII for ordered ice V, and ice XIV for ordered ice XII. The space group symmetry of hydrogen disordered ice V is $A2/a$; the monoclinic unit cell contains 28 water molecules,\textsuperscript{14,16} and partial ordering of the water molecules is allowed by this space group. Reduction of the space group symmetry occurs on phase transition from ice V to ice XIII, from $A2/a$ to $P2_1/a$.\textsuperscript{11}

Ice XII is a metastable phase of ice which occurs mainly in the stability domain of ice VI, but also in those of ices V and II.\textsuperscript{17-23} Its structure was first described in 1998 by Lobban et al. who crystallized the tetragonal phase from the liquid at 260 K at a pressure of 0.55 GPa.\textsuperscript{17} Later we reported that pure ice XII can be formed in a controlled and reproducible manner by isobaric heating of HDA in the pressure range 0.7 to 1.4 GPa using appropriate heating rates.\textsuperscript{22-26} Neutron diffraction showed that the structure of ice XII is hydrogen disordered.\textsuperscript{17, 19, 20} In fact, the space group symmetry of ice XII ($I42d$) does not allow any hydrogen ordering and the occupancies of the hydrogen positions are restricted to 0.5.\textsuperscript{27} On cooling ice XII, the disordered structure is frozen-in.\textsuperscript{19-21} However, doping of ice XII with HCl (DCl) induces a phase transition to an orthorhombic hydrogen ordered phase on cooling under pressure.\textsuperscript{11, 13} The new phase of ice has been named ice XIV and has $P2_12_12_1$ space group symmetry. This phase can accommodate varying degrees of hydrogen order and disorder.

Here we report the preparation and structures of the two new hydrogen ordered phases of ice named ice XIII and ice XIV. We further show by relative changes of the lattice
parameters that on thermal cycling in vacuo between 80 and 125 K, ordered ice XIII transforms in a reversible manner into disordered ice V, and ordered ice XIV into disordered ice XII.

2 METHODS

Doped ice V samples were prepared from solutions containing 0.01 M DCI in D₂O. The solutions were frozen in a piston-cylinder apparatus precooled to 77 K, and the frozen doped ice heated isobarically at 0.5 GPa to 250 K. Thereafter, the samples were cooled from 250 K at 0.8 K min⁻¹ to 77 K, decompressed, and recovered under liquid nitrogen (cf. Figure 1). The transition to ice II on cooling at 0.5 GPa was never observed, which is in agreement with ref. 16.

DCI doped D₂O ice XII samples were prepared by following a procedure described in ref. 25. First, DCI doped HDA was prepared by compression of D₂O ice Ih doped with 0.01 M DCI at 77 K.²⁸ HDA was then heated isobarically starting from 77 K at 1.2 GPa at ~11 K min⁻¹ to crystallize pure doped D₂O ice XII.²⁵ After cooling from 180 K to 77 K at 0.8 K min⁻¹, the samples were decompressed, and recovered in liquid nitrogen (cf. Figure 1).

The recovered samples were characterised in a cryostat (~50 mbar helium, herein refereed to as in vacuo) by powder neutron diffraction on the GEM instrument at ISIS.

3 RESULTS AND DISCUSSION

For ice V, space group symmetry reduction and thus formation of a new phase (ice XIII) upon cooling of the DCI doped ice V sample under pressure was indicated by the appearance of (31-2) (cf. curve (1), inset in Figure 2(left)) and (110) reflections in the neutron powder pattern of the recovered sample.

![Figure 2](left) Observed, calculated, and difference powder neutron diffraction profiles for the hydrogen ordered ice XIII phase observed at 80 K and in vacuo after cooling from 125 K to 80 K at 0.2 K min⁻¹. Tick marks indicate the positions of the Bragg peaks. Inset: magnification of the region where new reflections were observed: (1) after preparation at 80 K, (2) after heating to 125 K, and (3) after slowly cooling from 125 K to 80 K. (right) Unit cell projection of the refined structure: covalent and hydrogen bonds are indicated by solid and dashed lines, respectively.
The highest-symmetry space group that meets the observed reflection conditions is monoclinic \( P2_1/a \) which is a subgroup of the ice \( V \) space group \( (A2/a) \). \( P2_1/a \) was previously proposed by Kamb and La Placa for ordered ice \( V \) in an abstract,\textsuperscript{29} but their data were never published.

Figure 3(a) shows the changes of the lattice parameters of the DCI doped ice \( V \) sample as a function of temperature. Upon heating ordered ice XIII from 80 to 125 K, stepwise changes of the lattice parameters could be observed between \( \sim 110 \) K and \( \sim 120 \) K which went along with the disappearance of the \((31\,2)\) and \((110)\) reflections (cf. curve (2), inset in Figure 2(left)). This indicates the phase transition from hydrogen order to disorder. The reversibility of this transition to ordered ice XIII could be demonstrated by cooling back to 80 K at \( \sim 0.2 \) K min\(^{-1}\). In fact, slow cooling \textit{in vacuo} even enhanced the ordering process, as demonstrated by larger changes of the lattice parameters and the increased intensity of the \((3\,1\,2)\) reflection (compare curve (3) and (1), inset in Figure 2(left)).

![Figure 3](image)

**Figure 3** Relative changes of lattice parameters from powder neutron diffraction during heating and cooling \((\sim 0.2 \text{ K min}^{-1})\) \textit{in vacuo}: (a) heating of an ice XIII sample from 80 to 125 K, and subsequent cooling to 80 K. The onset temperatures of the order/disorder transition are at \( \sim 108 \) K on heating and at \( \sim 117 \) K on cooling. (b) heating of an ice XIV sample from 80 to 118 K, and subsequent cooling to 80 K. The onset temperatures of the order/disorder transition are at \( \sim 98 \) K on heating and at \( \sim 107 \) K on cooling. Lattice parameters are normalised by dividing with the lattice parameters of the hydrogen disordered phases. Solid lines are guides to the eye.

The structural parameters of ordered ice \( V \) (ice XIII) were refined by using the General Structure Analysis System (GSAS) program,\textsuperscript{30} by using the values for disordered ice \( V \) as
a starting point. The refinement of the ordered structure after slow cooling \textit{in vacuo} (cf. Figure 2(left)) revealed the formation of highly ordered molecules as the refined occupation probabilities of the deuterium positions converged within the errors to either 0 or 1 (cf. Table 1 in ref. 11). The unit cell of this hydrogen ordered cell is shown in Figure 2(right). It comprises 28 water molecules with 7 crystallographically distinct oxygen atoms (cf. Table 1 in ref. 11). This makes the $P2_1/a$ structure of ice XIII even more complicated than that of ice V, and thus the most complicated structure among the known crystalline phases of ice.

The ice XIII $\leftrightarrow$ ice V phase transition \textit{in vacuo} was also followed by using Raman spectroscopy.\textsuperscript{12} On heating ice XIII from 80 to 120 K, pronounced spectral changes occurred and the spectrum recorded after heating to 120 K is that of hydrogen disordered ice V (refs 31, 32, and Figure 3, curves 6, in our ref. 12). Subsequently, the sample was slowly cooled from 120 K to 80 K at 1 K min$^{-1}$. The spectrum recorded at 80 K was again that of ordered ice XIII which spectroscopically demonstrated the reversibility of the ice XIII $\leftrightarrow$ ice V phase transition, a result that is consistent with the changes in the lattice parameters shown in Figure 3(a).

The ordering effect in DCI doped D$_2$O ice XII is visualized most clearly by the splitting of the tetragonal (310) reflection to (130) and (310) orthorhombic reflections (cf. curve (1), inset in Figure 4(left)). The highest symmetry orthorhombic space group that meets the observed reflection conditions is $P2_12_12_1$ which is a subgroup of $I4_2d$. The unit cell of ordered ice XIV, which contains 12 water molecules with three crystallographic distinct oxygen atoms (cf. Table 2 in ref. 11), is shown in Figure 4(right). Strain may prevent the sample from becoming completely ordered in a similar manner to the transition of ice Ih to ice XI.$^{33}$

![Figure 4](image)

\textbf{Figure 4} (left) Observed, calculated, and difference powder neutron diffraction profiles for the hydrogen ordered ice XIV phase observed at 80 K and \textit{in vacuo} after the preparation. Tick marks indicate the positions of the Bragg peaks, the lower tick marks representing a small ice IV impurity. Inset: magnification of the region where peak splitting was observed for the ordered ice XIV phase: (1) measurement at 80 K after preparation, (2) after heating to 118 K, and (3) after cooling from 118 K to 80 K at $\sim$0.2 K min$^{-1}$. (right) Unit cell projection of the refined structure: covalent and hydrogen bonds are indicated by solid and dashed lines, respectively.
Heating of the ordered ice XIV sample from 80 to 118 K in vacuo showed, similar to ordered ice XIII, stepwise changes of the lattice parameters between ~95 K and ~115 K (cf. Figure 3(b)). This was accompanied by the disappearance of the orthorhombic splitting which indicates the phase transition from ice XIV to disordered tetragonal ice XII (cf. curve (2), inset in Figure 4(left)). Reversibility of the phase transition was found on cooling. However, the changes of lattice parameters, which correspond to the degree of reordering, are less pronounced if compared with the ice V ↔ ice XIII phase transition. For lattice parameter \( a \), no significant changes could be observed, and lattice parameters \( b \) and \( c \) were found to change back by only 35% and 29%, respectively, of the original stepwise changes observed on heating (cf. Figure 3(b)). The orthorhombic splitting of the 310 reflection could also not be found anymore. Instead only broadening of the 310 reflection could be seen (compare curve (3) and (2), inset in Figure 4(left)). Subsequent cooling under pressure was, however, capable of achieving full reversibility (not shown). Cooling under pressure therefore produces a more ordered ice XIV than cooling in vacuo. We speculate that a strain effect may prevent the sample from becoming highly ordered.\(^\text{11}\) The existence of strain was deduced from asymmetric peak shapes of the 130 and 310 reflections found in a higher resolution powder neutron diffraction measurement (not shown). The line shapes we observed are strongly reminiscent of those encountered in a variety of materials undergoing martensitic phase transitions. We therefore speculate that regions of incomplete ordering are stabilised by a combination of overall tensile strain and anisotropic strain, due to the different shape anisotropy of the two phases.

Very recently, Tribello et al. identified two hydrogen ordered configurations (ice XIV\(^*\) and ice XIV\(^{**}\)) very close in energy to the ground state by using DFT calculations.\(^\text{34}\) They showed furthermore that the difference in energy between these metastable phases and the ground state decreases even further with decreasing pressure. These results suggest that the structure after cooling in vacuo might contain an increased fraction of one or more of these metastable states. This scenario could also explain the differences in hydrogen ordering of ice XII between 1.2 GPa and in vacuo. A more detailed analysis and discussion of the neutron diffraction data will be presented elsewhere.

The reversibility of the ice XII ↔ ice XIV phase transition was also investigated by using Raman spectroscopy.\(^\text{12}\) On heating ice XIV from 80 K to 110 K, the Raman spectra developed to those of disordered ice XII (refs 26, 35, and spectra at 110 K in Figure 2 of ref. 13). Subsequent cooling at 0.5 K min\(^{-1}\) led to the weak reappearance of ice XIV lattice modes demonstrating the reversibility of the hydrogen disorder ↔ order phase transition. However, the only weak reappearance of the ice XIV lattice modes shows, consistent with what we have shown here for the changes in lattice parameters (Figure 3(b)), that hydrogen ordering of ice XII is difficult at low pressures.

The remarkable effect of HCl (DCl) as dopant in accelerating the reorientation of water molecules and hydrogen ordering at low temperatures needs to be discussed. At high temperatures, water ices can explore their configurational manifold thanks to the presence of mobile point defects that locally lift the geometrical frustration constraints.\(^\text{1, 11, 12, 16, 36}\) The two types of thermally-induced point defects uniquely found in ices are (a) rotational defects in which either two (D defect) or no (L defect) hydrogen atoms are found between neighbouring oxygen atoms, and (b) ionic defects (\( \text{H}_2\text{O}^+ \) and \( \text{OH}^\cdot \)) (cf. refs 1, 11 for discussion). With decreasing temperature, reorientational ordering of water molecules is hampered by the decreasing number and mobility of these point defects. Except for disordered ices III and VII, intrinsic point defects are not sufficient to permit phase transitions from the hydrogen disordered phases to their hydrogen ordered phases. Extrinsic point defects can be introduced by doping ices with impurities, such as in the
partial conversion of hydrogen disordered ice I h to hydrogen ordered ice XI facilitated by KOH doping.\textsuperscript{1, 8-10} KOH doping is expected to generate L and OH\textsuperscript{−} defects, whereas HCl doping is thought to produce L and H\textsubscript{2}O\textsuperscript{−} defects.\textsuperscript{1} Both powder neutron diffraction and Raman spectroscopy show that only HCl (DCI) doping induces the phase transitions of disordered ices V and XII to ordered ices XIII and XIV,\textsuperscript{11-13} whereas KOH doping had only a minor effect on hydrogen ordering in ices V and XII (cf. Figure 2 in ref. 11, and Figure 3, curve 5, in ref. 12). Thus, the remarkable effect of HCl doping in comparison to that of doping with KOH seems to be caused by H\textsubscript{2}O\textsuperscript{−} defects.

In calorimetric studies of KOH doped ice V, endothermic peaks observed by Handa et al.\textsuperscript{37} on annealing had been attributed previously to an order-disorder phase transition. Subsequent studies of undoped or KOH doped ice V could not confirm a phase transition.\textsuperscript{11, 12, 38, 39} Thus, the previous evidence for partial hydrogen ordering in undoped ice V,\textsuperscript{16, 27, 37, 39} or in KOH doped ice V,\textsuperscript{37, 38} must have been obtained within the ice V phase, which allows considerable hydrogen ordering.\textsuperscript{14-16}

4 CONCLUSIONS

Two new hydrogen ordered phases of ice were prepared by cooling the hydrogen disordered ices V and XII under pressure. Previous attempts to unlock the geometrical frustration in hydrogen-bonded ice structures have focused on doping with KOH and have had success in partially increasing the hydrogen ordering in ice I h and its transition to ice XI. By doping ices V and XII with HCl (DCI), we have prepared hydrogen ordered ice XIII and ice XIV, and we analysed their structures by powder neutron diffraction and Raman spectroscopy. The formation of ice XIII from HCl doped ice V is the first successful example of fully ordering a frozen-in disordered ice phase by using a dopant. The phase transitions between the disordered phases ice V and ice XII, and their corresponding phases ice XIII and ice XIV, are reversible \textit{in vacuo}. At low pressures, these phases are all metastable. Therefore these are, to our knowledge, the first reported examples of reversible phase transitions between two \textit{metastable} ice polymorphs \textit{in vacuo}.

The remarkable effect of HCl (DCI) doping on the reorientation dynamics of hydrogen disordered ice V and ice XII came as a surprise, and it demonstrates that we know very little about the types of extrinsic defects and also the mechanism important for accelerating reorientation in the various disordered phases of ice. These results suggest a way forward in trying to clarify the mechanisms involved. The use of HCl (DCI) doping represents a major step forward in releasing the geometrical frustration that locks in disorder in hydrogen bonded systems, and opens up the possibility of finally completing the phase diagram of ice. In this context, very recent measurements on DCI doped ice VI also show hydrogen ordering, and the refinement of the consequent ice XV is currently under way.

References

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