Structures of Ice VII and Ice VIII to 20 GPa

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The structural pressure dependence of the high-pressure ices VII and VIII has been measured up to 20 GPa by neutron powder diffraction. Measurements of the atomic thermal motion reveal that, while it is strongly reduced by pressure in both phases, the stepwise change in the oxygen thermal motion at the VIII/VII transition is pressure independent within the precision of the measurements. Also, the O-D bondlength in ice VIII changes by less 0.002 Å to 20 GPa. These results suggest that the site-separation of the disordered oxygen atoms in ice VII and the direction of the disorder displacement remain closely similar to those found at 5 GPa.

[Neutron diffraction, Ice, Hydrogen bonding, Disorder]

1. Introduction

The behaviour of ice at high pressures has provoked considerable recent interest. At pressures above 2 GPa only two polymorphs are known to exist up to a least 65 GPa: the disordered (high temperature) ice VII phase and the ordered ice VIII phase. The phase boundary between these two forms has been substantially revised as a result of recent Raman studies [1]. These have shown that at ~10 GPa the temperature of the ice VIII→VII transition starts to decrease from the ~273 K found up to that pressure, and reaches 0 K at ~70 GPa. Recent infrared spectroscopic studies have revealed a transition in ice VII at 66 GPa which has been interpreted as indicating the formation of centred hydrogen bonds [2,3]. It has also been proposed recently that proton-disordered ices have hydrogen bonds with two radically different strengths and the density of states of ices VII and VIII have been compared to test this model [4].

Given this interest, a precise understanding of the relationship between the two structures is essential. However, the detailed nature of the structure of ice VII is a longstanding problem in ice physics.

The structures of both phases are based on two interpenetrating, tetrahedrally hydrogen-bonded oxygen networks [5]. They differ most obviously in that ice VIII is proton ordered while ice VII is proton disordered. Neutron diffraction studies reveal that the intramolecular O-D bondlength in ice VII is ~0.06 Å shorter than that found in ice VIII [5,6], which is too large to be a real change in a strong molecular bond. To account for this, Kuhs et al [5] proposed a model in which the oxygen atoms are disordered over sites displaced $\delta \sim 0.1 \text{ Å}$ along the six $\langle 100 \rangle$ directions from the average site at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, based on anharmonic refinements of the oxygen distribution. Jorgensen and Worlton found no similar direct evidence for oxygen disorder but suggested instead that the deuterium atoms are multi-site disordered about their average site at $(x, x, x; x \sim 0.41)$ [6]. Thus, these two studies differ in their conclusions, and neither model retains both the O-D distance and D-Ö-D angle found in ice VIII.

2. Measurements and results

The development of the Paris-Edinburgh cell since 1989 has greatly increased the pressure range for neutron-diffraction studies [7,8] and has stimulated much new work on the struc-

tures of ice at very high pressures [9-12]. In our recent study of the structure of ice VII [12] we adopted the approach of measuring the changes in atomic thermal motion at the ice VIII↔VII transition; any site disorder in ice VII would appear as an additional component in the apparent thermal motion. This avoids the difficulty of resolving disorder over closely spaced sites directly from powder data. Neutron diffraction is ideally suited to such measurements of thermal motion but accurate studies require reliable corrections to be made for the effects of attenuation by the pressure-cell materials surrounding the sample. The development of the Paris-Edinburgh cell for neutron diffraction has included a considerable effort to put such corrections in place [15].

Fig. 1. Temperature dependence of the thermal motion of ice VIII (open symbols) and ice VII (solid symbols) at 5 GPa. There are two components of the deuterium thermal motion U_{perp} (squares) and $U_{\text{||}}$ (triangles), and the isotropic oxygen thermal motion $U_{\text{iso}}(\text{O})$.

Figure 1 shows the temperature dependence of the oxygen thermal motion, $U_{\text{iso}}(\text{O})$, and the components of the deuterium thermal motion parallel, $U_{\text{||}}(\text{D})$, and perpendicular, $U_{\text{perp}}(\text{D})$, to the O-D bond at 5 GPa. As can be seen, there are clear discontinuities of $0.64(5) \times 10^{-2} \text{ Å}^2$ in $U_{\text{iso}}(\text{O})$ and $0.4(1) \times 10^{-2} \text{ Å}^2$ in $U_{\text{perp}}(\text{D})$ at the transition while $U_{\text{||}}(\text{D})$ is unchanged. The lack of change in $U_{\text{||}}(\text{D})$ suggests that the underlying true thermal motion remains unaltered at the transition and this is supported

by neutron-scattering measurements of the density of states [4]. The steps in $U_{\text{iso}}(\text{O})$ and $U_{\text{perp}}(\text{D})$ thus provide the first direct, model-independent evidence of multisite disorder of both O and D atoms in ice VII [12].

The magnitudes of the displacements of O and D were then estimated by refinement with the thermal motion fixed to the mean values found in ice VIII [12]. The displacements from the average sites were found to be $\delta=0.135(10)$ Å for O and $\gamma=0.09(3)$ Å for D. However, it did not prove possible to obtain the molecular geometry found in ice VIII ($\text{O-D}=0.970(3)$ Å; $\text{D-O-D}=107.3(5)^\circ$) with the oxygen atoms displaced along $\langle 100 \rangle$ directions from the average site as proposed by Kuhs et al [5]. Instead, as shown in Figure 2, it was found that an internal molecular geometry closest to that found in ice VIII was obtained for oxygen displacements along $\langle 111 \rangle$ [12]. On the basis that it is unlikely that the strong intramolecular O-D bonds are significantly changed at the transition, we thus conclude that displacements close to $\langle 111 \rangle$ are the most probable.

Fig. 2. Temperature dependence of the O-D bondlength in ice VIII ($\diamond$), and in ice VII for the site-ordered model ($\bullet$) and for disorder models with sites along $\langle 100 \rangle$ ($\blacktriangle$), $\langle 111 \rangle$ ($\blacksquare$) and $\langle 110 \rangle$ ($\blacktriangledown$).

Such a displacement model has important consequences for the hydrogen bond geometry in ice VII [12]. At 5 GPa, the O...O distance in ice VIII is 2.834 Å. Oxygen displacements along $\langle 100 \rangle$ in ice VII give two possible H-bond distances of 2.833 and 2.839 Å which are very close to the ice VIII value. For oxygen displacements along $\langle 111 \rangle$ the only plausible H-bond contacts are one of 2.75 Å and two at around 2.92 Å, which are respectively 0.1 Å shorter and longer than the ice VIII value. These differences are not small and correspond to those produced by changes of ~ 5 GPa at this pressure. Thus it appears that a consequence of $\langle 111 \rangle$ oxygen displacements is that the hydrogen bond geometry of ice VII is significantly different from that found in ice VIII.

The difference in local structure between ices VII and VIII is important for the interpretation of the behaviour of ice at higher pressures. It has been generally assumed that the structure of ice VII is locally like that of ice VIII and that any pressure dependence of the oxygen site separations can be neglected. But, for oxygen displacements along $\langle 111 \rangle$, the pressure dependence of the site separation may make a significant contribution to the pressure dependence of the hydrogen bondlengths, and hence it is important to determine the effect

of pressure on the disorder. Recent developments in anvil design now allow neutron diffraction to be performed at pressures up to ~ 25 GPa using the Paris-Edinburgh cell [13]. We have made use of this to extend our comparative measurements of the structures of ices VII and VIII to 20 GPa using the POLARIS diffractometer of the U.K. pulsed neutron source, ISIS.

Fig. 3. The pressure dependence of the thermal motion of the oxygen atoms in ice VIII (open symbols) and ice VII (solid symbols).

Figure 3 shows the pressure dependence of $U_{\text{iso}}(\text{O})$ in both ices VII and VIII. As can be seen, there is a strong initial decrease in both phases so that $U_{\text{iso}}(\text{O})$ in ice VIII decreases from ~ 1.0 to $\sim 0.4 \times 10^{-2} \text{ Å}^2$ in the range 4-12 GPa. However, the difference between the $U_{\text{iso}}(\text{O})$ in ice VII and ice VIII remains within error the same as the value of $0.64 \times 10^{-2} \text{ Å}^2$ found at 5 GPa. To obtain a more precise determination of the change in $U_{\text{iso}}(\text{O})$ at 20 GPa, measurements were made as a function of

Fig. 4. Temperature dependence of the thermal motion of ice VIII (open symbols) and ice VII (solid symbols) at 20 GPa. There are two components of the deuterium thermal motion, $U_{\text{perp}}(\text{D})$ (squares) and $U_{\parallel}(\text{D})$ (triangles), and the isotropic oxygen thermal motion $U_{\text{iso}}(\text{O})$. The hysteresis of the transition reduces with increasing pressure [1] and hence it was not possible to make measurements at overlapping temperatures like those in Fig. 1.

temperature cycling through the transition and figure 4 shows the resulting values of $U_{\text{iso}}(\text{O})$, $U_{\parallel}(\text{D})$ and $U_{\text{perp}}(\text{D})$.

There is a step of $0.61(7) \times 10^{-2} \text{ \AA}^2$ at the transition in $U_{\text{iso}}(\text{O})$ which is within error the same as the value found at 5 GPa. The along-bond deuterium thermal motion $U_{\parallel}(\text{D})$ again shows no change and thus it appears that at 20 GPa the true thermal motion remains unchanged at the transition. The magnitude of the displacement of O from its average site can thus be estimated as at 5 GPa and a value for $\delta=0.13(2) \text{ \AA}$ is obtained — within error the same as at 5 GPa. By contrast, the step in $U_{\text{perp}}(\text{D})$ is reduced to ~zero at 20 GPa, and γ has an upper bound of no more than half its value at 5 GPa.

Figure 5 shows preliminary measurements of the pressure dependence of the O-D bondlength in ice VIII. As can be seen, the rate of change with pressure is very small and the gradient obtained is within error the same as that previously determined to 10 GPa [9]. This rate of change is also consistent with that obtained from recent Hartree-Fock calculations [10].

Using these results for the internal molecular geometry in ice VIII, which give $\text{O-D}=0.973(2) \text{ \AA}$ and $\text{D-O-D}=106.4(5)^\circ$ at 20 GPa, and the magnitude of δ above, it is also possible to make a preliminary exploration of the displacement direction of the O sites. Mean values for O-D of $1.018 \text{ \AA}$ were obtained for oxygen displacements along $\langle 100 \rangle$, $0.989 \text{ \AA}$ for displacements along $\langle 111 \rangle$ and $0.960 \text{ \AA}$ for displacements along $\langle 110 \rangle$. It thus appears that oxygen displacements closer to $\langle 111 \rangle$ than $\langle 100 \rangle$ provide the best internal molecular geometry at 20 GPa. So, both the magnitude and the direction of the displacements from the average site at 20 GPa remain essentially as found at 5 GPa.

Fig. 5. The pressure dependence of the O-D bondlength in ice VIII. The dashed line shows the rate of change of O-D with pressure determined in earlier studies to 10 GPa [9].

3. Conclusions

The conclusion that the magnitude of the oxygen disorder displacement is within error pressure independent is important. It indicates that the differences in H-bond length in ice VII and ice VIII persist up to at least 20 GPa. If this pressure independence were to persist up to centring it would significantly alter our understanding of the centring process. For example, Pruzan [14] calculated (using a pseudo-spin formalism) that centring would occur for an O...O distance of $2.29 \text{ \AA}$ in D_2O ice VII, which corresponds to a pressure of ~100 GPa based on the assumption that O...O can be derived directly as $(3)^{1/2}a/2$ from the lattice parameter, a , of ice VII — an assumption which is valid to a good approximation only if oxygen is displaced along $\langle 100 \rangle$ [11]. As we have seen, for oxygen displacements along $\langle 111 \rangle$, O...O is either $0.1 \text{ \AA}$ shorter or $0.1 \text{ \AA}$ longer than $(3)^{1/2}a/2$ for $\delta=0.13 \text{ \AA}$. If δ were to remain constant up to centring then O...O = $2.29 \text{ \AA}$ would be achieved at either ~80 GPa or

~120 GPa, depending on whether the shorter or longer contact were the hydrogen bond contact. The apparent constancy (or, at least, small rate of change) of δ to 20 GPa thus makes it probable that the detailed nature of the disorder and its pressure dependence are important to the understanding of the bond-centring process.

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