

# Ostwald's rule of stages and metastable transitions in the hydrogen-water system at high pressure

M-E. Donnelly, P. Teeratchanan, C.L. Bull, A. Hermann & J.S. Loveday

## Supplementary Material

### 1 Crystallographic Details for $C_0$

The  $C_0$  phase was found to be best described by the hexagonal space group  $P6_122$  with lattice parameters  $a = 6.2763(5)$  Å and  $c = 6.188(1)$  Å at 0.3 GPa and 175 K. The final Rietveld refinement and the fractional atomic coordinates for  $C_0$  are shown in figure 1 and table 1 respectively. It comprises a similar water network to that reported by Efimchenko *et al.* with two spirals of  $D_2O$  molecules forming a channel between them (see figures 2 and 3), and the hydrogen bonds of the host  $D_2O$  framework are best described by disordered O – D...O bonds. The guest molecules were found to be highly mobile within the structure and were spread out roughly in a spiral at the centre of the cavity. This spiral is thought to be due to the space group and the highly mobile guest  $D_2$  are most likely not at fixed positions within the structure under the conditions studied (0.3 GPa and 175 K). As the guest  $D_2$  are not at fixed positions the structure can be described purely by the symmetry of the  $D_2O$  host network  $P6_122$ . In the temperature range studied down to 80 K no evidence of fixed  $D_2$  positions were observed.

### 2 The structure of $C_{-1}$

The  $C_{-1}$  structure was found to be heavily dependent on the starting material. The work described below details the synthesis and comparison of the  $C_{-1}$  samples made from ice Ih and Isd samples. A more complete analysis is given in [1].

A sample of polycrystalline ice Ih was cooled to 135 K in an Al gas cell and then compressed to 0.3 GPa with  $D_2$  gas. As shown in figure 4 after compression to 0.3 GPa the sample peaks can be seen to shift to lower d-spacing as expected. At this point the sample can be described by pure ice Ih. Slight deviations from expected intensity are observed due to the liquid  $D_2O$  being frozen *in-situ* which created a polycrystalline sample. The sample was then warmed to 150 K and during this the ice Ih reflections shifted to slightly higher d-spacing. This indicated an expansion of the unit cell on heating as expected. At 150 K a small peak could be seen to the right of the (101) and (102) reflections at 3.50 Å and 2.67 Å, respectively. After ten minutes these new peaks had increased in

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C<sub>0</sub> structure at  $P = 0.3$  GPa,  $T = 175$  K  
Space group:  $P6_122$   
 $a = 6.2763(5)\text{\AA}$ ,  $c = 6.188(1)\text{\AA}$ ,  $V = 211.08(3)\text{\AA}^3$   
 $U_{iso}(\text{host}) = 1.4(1) \times 10^{-2}\text{\AA}^2$   
Quality of fit:  $R_{wp} = 4.37\%$

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Atom	Site	x	y	z	F
O <sub>1</sub>	6b	0.7637(6)	0.527(11)	0.25	1.0
D <sub>1</sub>	12c	0.3771(12)	0.0707(17)	0.5317(17)	0.5
D <sub>2</sub>	12c	0.5626(17)	0.3345(16)	0.4578(17)	0.5
D <sub>guest</sub>	6b	0.1067(15)	0.213(3)	0.25	0.82(2)

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Bond	Length ( $\text{\AA}$ )	Bond	Angle (degrees)
O <sub>1</sub> – D <sub>1</sub>	0.958(8)	D <sub>1</sub> – O <sub>1</sub> – D <sub>1</sub>	114.4(11)
O <sub>1</sub> – D <sub>2</sub>	0.977(9)	D <sub>1</sub> – O <sub>1</sub> – D <sub>2</sub>	105.8(8)
O <sub>1</sub> ... O <sub>1</sub>	2.7558(3)	D <sub>2</sub> – O <sub>1</sub> – D <sub>2</sub>	119.9(13)
O <sub>1</sub> ... O <sub>1</sub>	2.7677(1)		

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Table 1: Lattice parameters/volume, thermal parameter of the D<sub>2</sub>O host, atomic coordinates and bond lengths/bond angles of the D<sub>2</sub>O network of the C<sub>0</sub> phase at 0.3 GPa and 175 K. Atom subscripts are used as descriptors and do not refer to molecules in the case of D<sub>2</sub>. As the guest deuterium molecules were modelled in the refinements by one atom with a large variable anisotropic thermal parameters and site occupancy, the D<sub>guest</sub> described here shows the occupancy of that site and so the molecular deuterium occupancy of the guest site is then half of that shown.

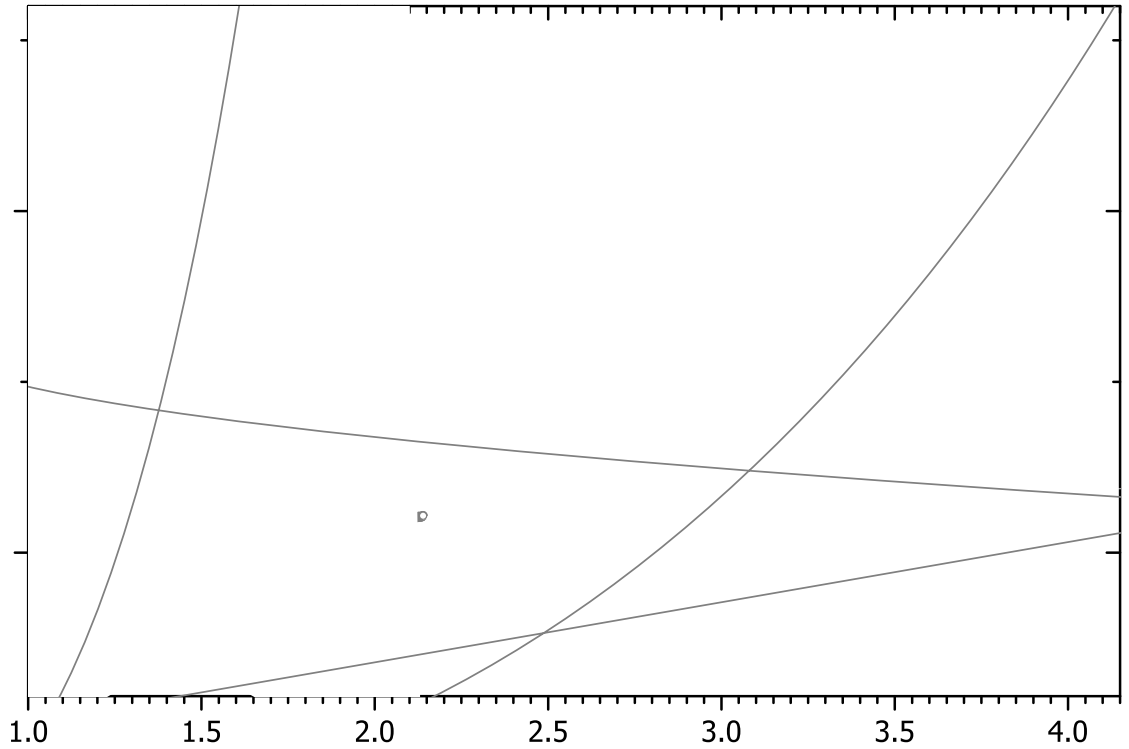


Figure 1: Fit of the refined model of  $C_0$  to neutron diffraction data collected at 0.3 GPa and 175 K. Open circles show the observed data, the black line the fit of the model refined to the data, and the bottom curve shows the difference between observed data and the refined model diffraction pattern. Tick marks indicate the position of reflections from the  $C_0$  structure (bottom) and Al (middle and top).

intensity. This was also accompanied with a decrease in intensity of all ice Ih peaks and the growth of two new peaks at 3.59 Å and 4.00 Å. It was noted that all reflections that indexed as  $(00l)$  in pure ice Ih had new reflections grow in to the left of them (smaller d-spacing), whilst all others had reflections grow to the right (larger d-spacing). With these changes the  $D_2$  gas pressure decreased dramatically. This indicates either a transition to an extremely dense phase or the inclusion of gas into the ice. Over a period of five hours these new peaks grew in intensity whilst those from ice Ih decreased. After five hours no further changes occurred even when the sample was left for a further five hours.

Another sample of the  $C_{-1}$  structure was synthesised from ice Isd. Although, the initial starting material was a good powder of ice Ih, this good powder of ice Ih was compressed to form other structures in the  $D_2$ - $D_2O$  system (such as  $C_0$ ) before recovery to ambient pressure for the subsequent experiment. Analysis of the ice before compression (and formation of  $C_{-1}$ ) showed that it was mainly composed of ice Ih with some ice Ic due to the ice being recovered from high pressure phases [2, 3]. This mixture was determined to be ice Isd due to the presence of a region of ‘raised intensity between 3.43 and 3.86 Å’ [2]. After compression to 0.28 GPa at 120 K the reflections from ice Ih were observed to shift to lower d-spacing as expected (figure 5). As the sample was warmed the  $D_2$  gas pressure was held constant and not allowed to decrease below 0.275 GPa to ensure full conversion

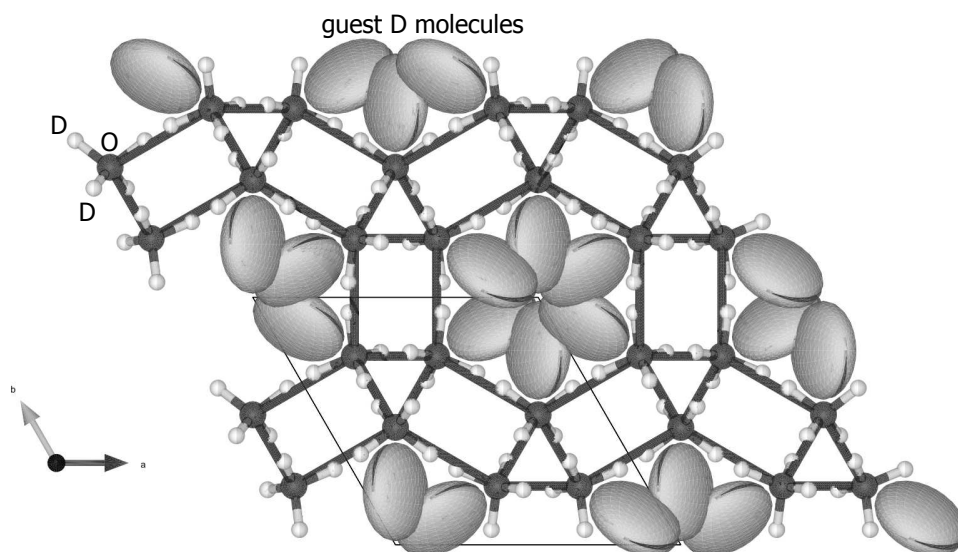


Figure 2: The refined  $C_0$  crystal structure down the  $c$ -axis.

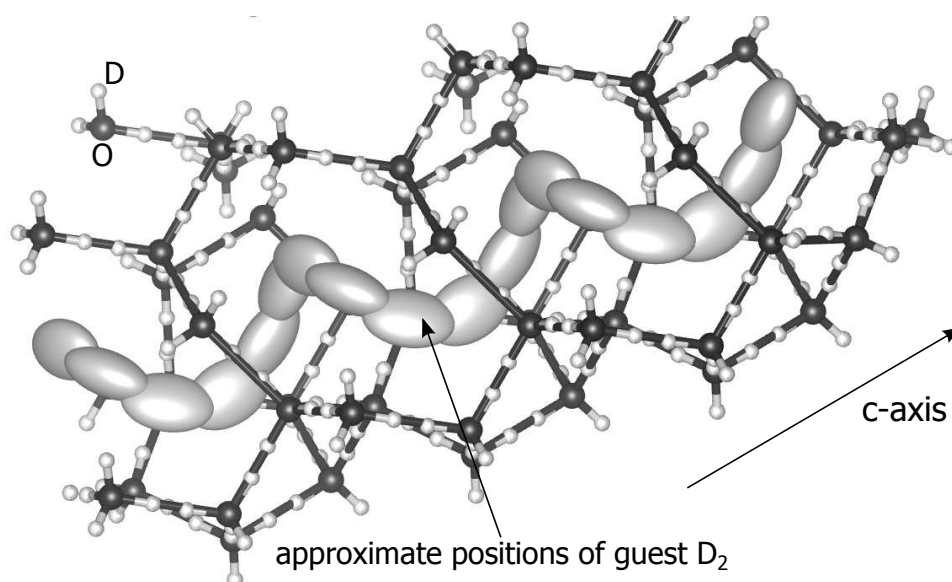


Figure 3: The refined  $C_0$  crystal structure along the  $c$ -axis. The spiral of ellipsoids in the centre of the cavity represent approximate positions for the guest  $D_2$  molecules and the spiral shape is most likely an effect of the space group (discussed further in the text).

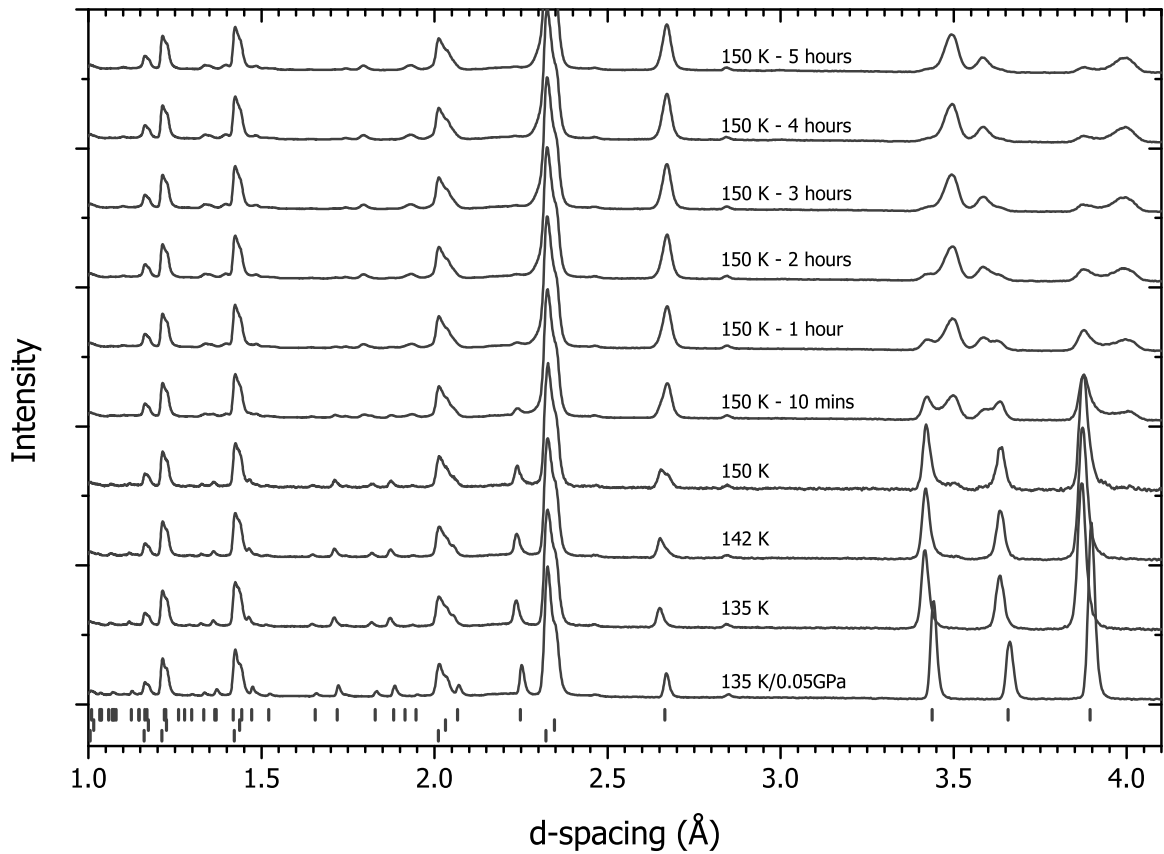


Figure 4: Diffraction patterns collected of a sample of polycrystalline D<sub>2</sub>O ice Ih on compression to 0.3 GPa with D<sub>2</sub> gas and subsequent heating from 135 K to 150 K. The diffraction patterns collected at 150 K show the time dependence of the transition from ice Ih to the new phase C<sub>-1</sub>. Tick marks indicate the position of reflections from ice Ih and all other reflections are from the new phase, with the exception of reflection at 2.8 Å which is from the lead seal of the gas cell.

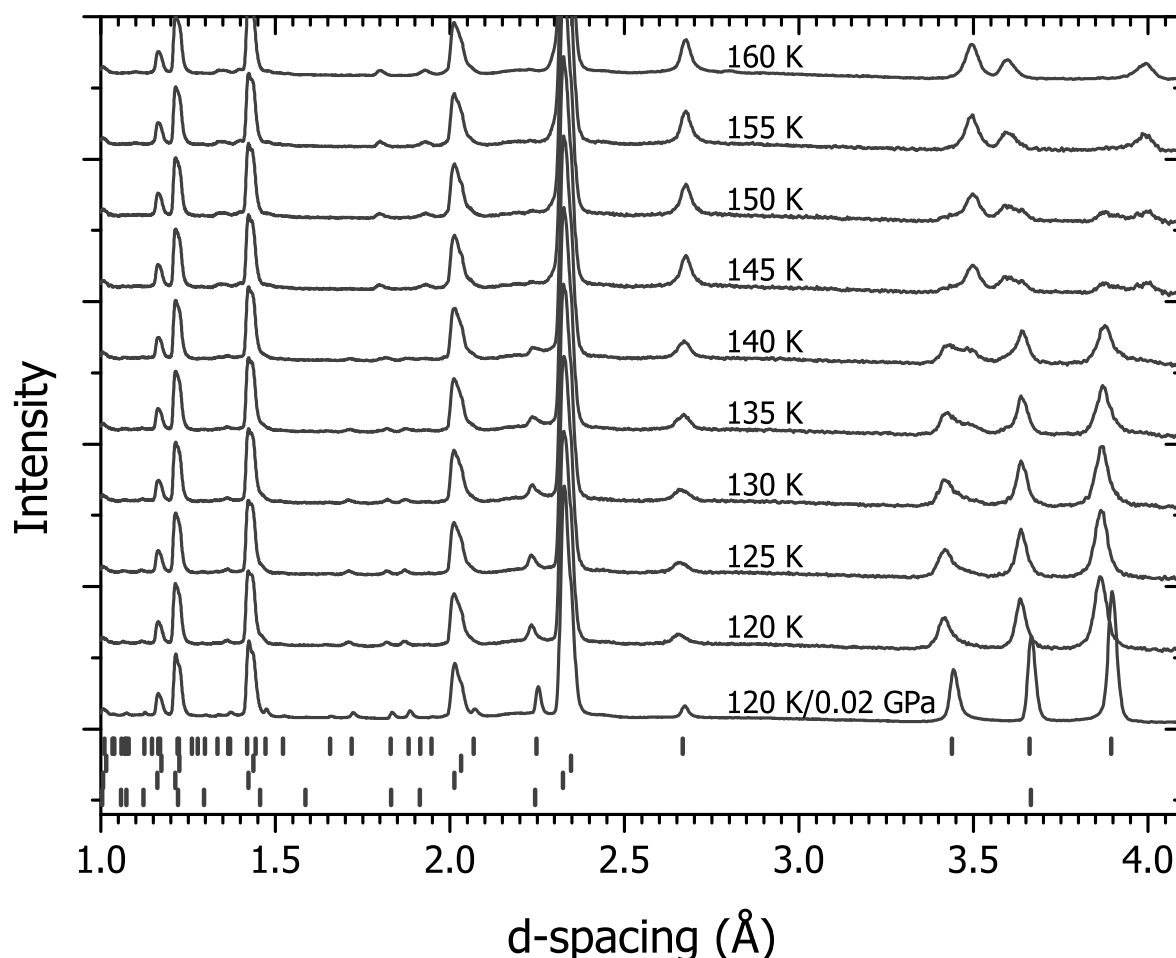


Figure 5: Diffraction patterns collected of a sample of  $D_2O$  ice Isd on compression to 0.28 GPa with  $D_2$  gas and subsequent heating from 120 K to 160 K. At 140 K the clear transition from ice Isd to  $C_{-1}$  is observed. Tick marks indicate the position of reflections from ice Ih (top), both unit cells used to fit the Al from the gas cell (middle), ice Ic (bottom) and all other reflections are from the new  $C_{-1}$  phase.

of the ice. At 130 K the reflections from ice Ih started to decrease in intensity. This was accompanied by the appearance of two new peaks to the right of the (101) and (102) reflections at 3.51 Å and 2.67 Å, respectively. A similar behaviour was observed at the onset of transition in the polycrystalline ice Ih sample discussed above. As the sample is warmed further these two peaks grow in intensity whilst the (101) and (102) peaks decrease in intensity (figure 5). Until 140 K it is only these two peaks that appeared to be changing. Above 140 K the (002) peak is observed to move to lower d-spacing (opposite to the direction of the other peaks) and decrease in intensity. Above 140 K there was also a decrease in intensity of the (100) peak (at  $\sim 3.9$  Å) and the appearance of a new peak at 4.00 Å. As the sample was warmed further the peaks from pure ice Ih decreased in intensity whilst those from the new phase increased. By 160 K the sample had completely converted.

The synthesis of a sample of ‘empty’  $C_{-1}$  was also attempted, following a similar procedure used to form ices XVI and XVII [4, 5]. This was done to confirm whether the host  $D_2O$  framework is based on ice Ih or not. The sample of  $C_{-1}$  synthesised at 0.3 GPa was cooled to 85 K and then recovered to ambient pressure (figure 6). On recovery from 0.3 GPa

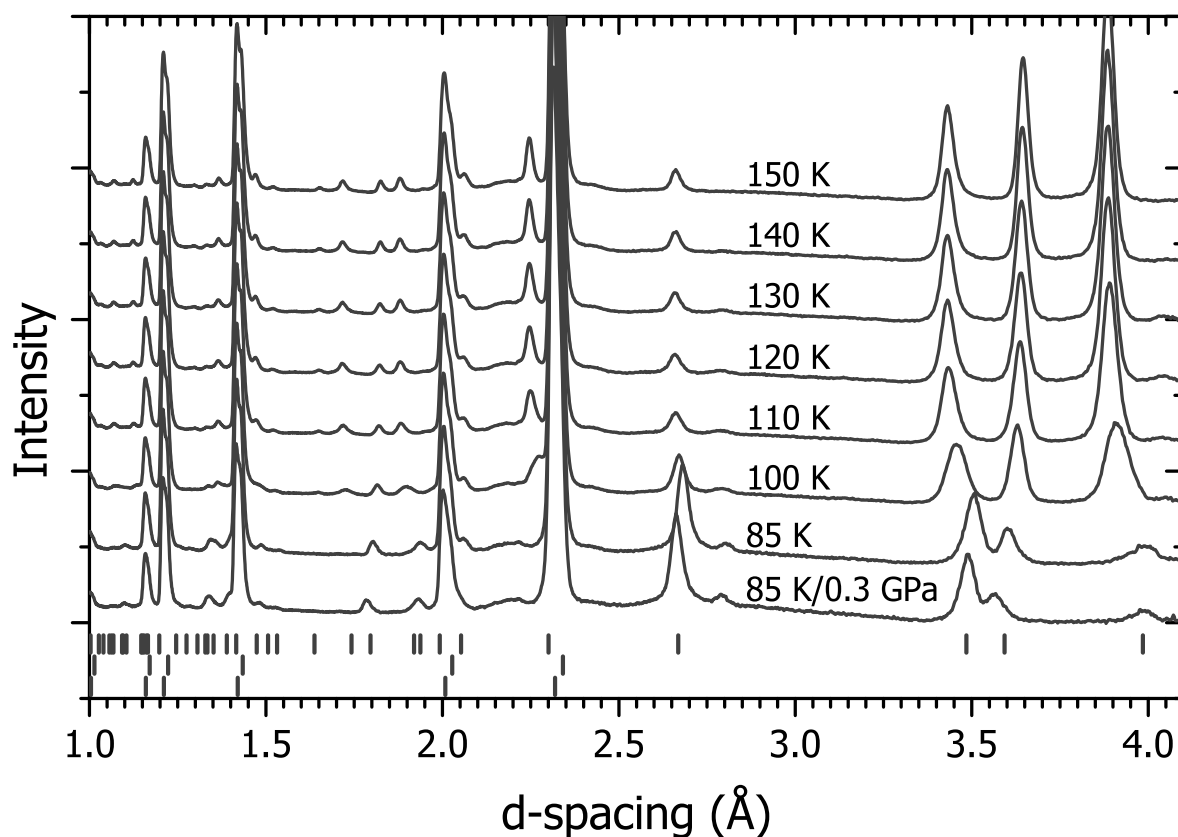


Figure 6: Diffraction patterns collected of a sample of  $D_2$ - $D_2O$   $C_{-1}$  on recovery to ambient pressure and subsequent warm up. The bottom diffraction pattern is the sample at 85 K at 0.3 GPa before recovery to ambient pressure. All other data was collected at ambient pressure. Tick marks indicate the positions of reflections from  $C_{-1}$  (top) and Al (middle and bottom).

to ambient pressure the sample reflections were observed to move to higher d-spacing as expected. Upon heating from 85 K the sample immediately started to transform back to an ice Ic/Ih mixture. By 120 K the sample had fully transformed from  $C_{-1}$ . A comparison of the diffraction patterns collected on the recovered  $D_2O$  ice and the ‘starter’ ice can be seen in figure 7. This showed that the diffraction patterns collected on the starter and recovered ice were extremely similar, and the only differences observed were the presence of a larger background in the starter material as a result of the presence of  $D_2$  atmosphere, and an increase in the peak width in the recovered ice as a result of the higher temperature. In general ice I recovered from high pressure clathrate or ice structures usually contains a larger cubic component than the starting ice and the recoverability of the same starter ice here is noted as being odd [2, 3]. This ‘recoverability’ of the initial ice Ic/ice Ih mixture may be evidence that the host  $D_2O$  network in  $C_{-1}$  is not that different from pure ice Ih/Ic and the inclusion of molecular deuterium into the structure results in a reversible distortion to the host  $D_2O$  network.

In both samples, the diffraction pattern can still be indexed by a hexagonal unit cell with lattice parameters:  $a = 4.6084(3)$  Å,  $c = 7.1582(6)$  Å (ice Ih derived sample) and  $a = 4.6016(5)$  Å,  $c = 7.1895(9)$  Å (ice Isd). With a volume of around  $131.8$  Å<sup>3</sup>. Unfortunately full Rietveld refinement of the structure was unsuccessful. This was due to either the

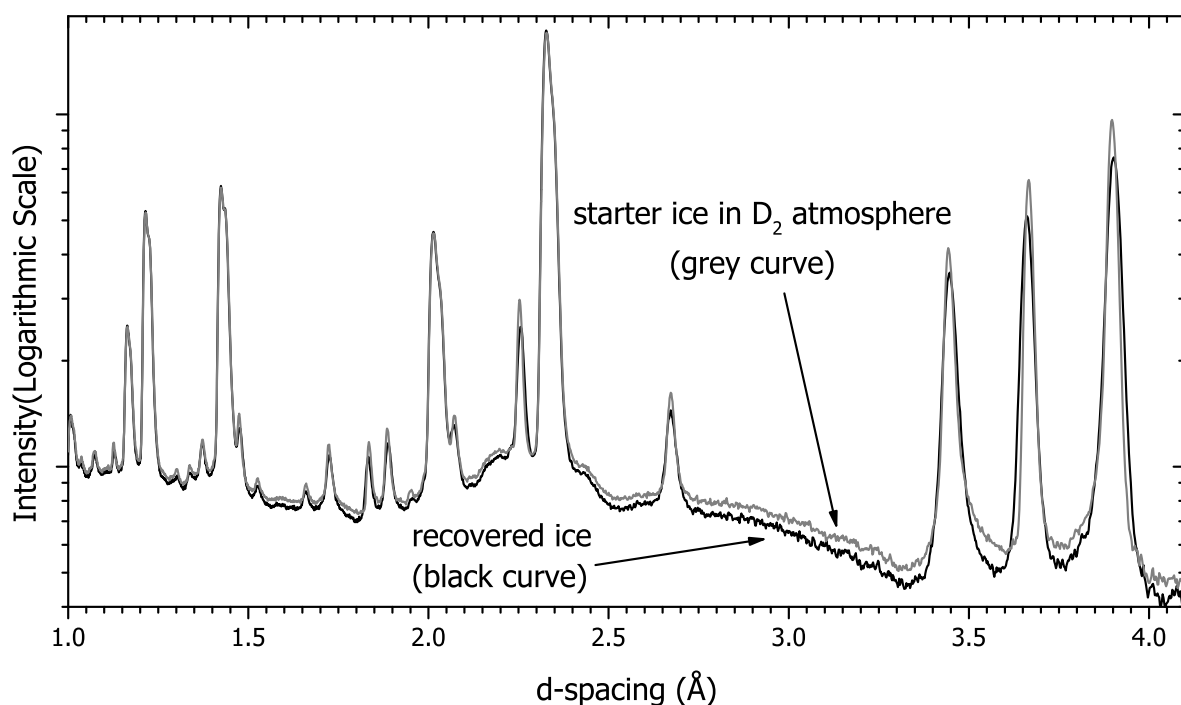


Figure 7: Comparison of the diffraction patterns collected on the recovered ice (at 160 K) and the starter ice (at 120 K). The difference in background intensity is from the presence of a  $D_2$  atmosphere in the starter material.

polycrystalline nature of the sample in the case of the sample synthesised from ice Ih, or to the difficulty in separating the cubic and hexagonal contributions to the diffraction pattern due to overlapping reflections, and determination of the deuterium uptake of the cubic/hexagonal fractions and boundaries in ice Isd.

## References

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