Experimental report

11/02/2019

Proposal: 5-22-759 **Council:** 4/2017

Title: Structure of refilled metastable water ice XVII

Research area: Physics

This proposal is a new proposal

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Samples: D2O+Ne
D2O+O2
D2O+D2

Instrument	Requested days	Allocated days	From	To
D20	3	3	28/05/2018	29/05/2018
			29/05/2018	01/06/2018

Abstract:

Very recently, by means of X-ray and neutron diffraction, we have studied the crystalline structure of C0-phase H2-filled-ice and ice XVII, a new form of ice discovered by our group. Of paramount interest is the fact that this new ice (obtained by heating C0-phase H2-filled-ice at about 110 K under dynamic vacuum) is so porous that it can absorb again H2 and release it repetitively. After our first diffraction measurements some issues remain still unresolved. This proposal aims to study the structure of this new compound, ice XVII, both empty and with various quantities of refilled D2, Ne and O2, by means of neutron diffraction so to give an answer to the open problems about the effect of the guest on the structure. Data will be analyzed through Rietveld refinement, so to accurately determine the positions of the atoms in the unit cell. This system might have a relevance from the perspective of new materials suitable for H2 storage applications, since it can contain a large amount of H2. Moreover, studying the diffraction of ice XVII refilled with paramagnetic oxygen gas, we aim to investigate the existence of a possible magnetic order due to guest molecules inside the channels.

Report on experiment 5-22-759: D20; 28/5/2018 - 1/6/2018

'Structure of refilled metastable water ice XVII'

Experimental details

Neutron diffraction measurements by D20 were carried out in the 1-153° 2θ range at λ= 1.543 Å on deuterated iceXVII, both empty and filled with several gases (Ne, O_2, D_2). A sample of iceXVII+H_2 was put in an aluminium can and inserted into a cryostat connected to a gas manifold. This was equipped with a vacuum pump, with exchangeable gas cylinders, and with full control of pressure in the sample chamber. At first hydrogen was removed by evacuation at 110 K and 10^{-6} bar, so as to obtain pure iceXVII. Then D_2 was uploaded at 50 K till pressure stabilization to about 1 bar. A series of diffraction measurements of iceXVII+D_2 were performed with 5 K steps down to 20 K. The sample was heated to 115 K, then evacuated and cooled again to 50 K, collecting a diffraction pattern of empty iceXVII. Neon was subsequently charged into the sample, and a pattern of iceXVII+Ne was recorded at 50 K. After a further evacuation at 115 K, oxygen was inserted into the sample at 90 K, and several diffraction measurements were performed at various temperatures down to 4.6 K. Eventually, the sample was evacuated at 110 K and the progressively heated to 175 K, collecting short patterns at intermediate temperatures. After removing the sample, final diffraction measurements were performed on the empty Al can in the pressure cell at several temperatures in the 90 to 20 K range.

The accurate λ value was calibrated by a Rietveld fit to diffraction data collected on the standard material NaCaAlF, fixing all structural parameters to literature values. The λ = 1.543(1) Å result was obtained. The data collection time varied from 5 min for short measurements to about 1 h for long, accurate acquisitions. All collected diffraction patterns contained the FCC (face-centred-cubic) Bragg peaks of Al from the holder can, in addition to those of the sample. The best way to cope with them turned out to be a straightforward subtraction of the intensity profile of the pattern collected on the empty can at the same temperature and with the same measurement conditions. Small 2θ ranges around the Al peaks were then removed from the patterns to avoid numerical noise.

Data were analysed by the Rietveld refinement and difference Fourier synthesis techniques as implemented in the FullProf computing package (Rodriguez-Carvajal). The background intensity was linearly interpolated by a set of fixed points. Bragg peaks were modelled by a linear combination of Gaussian and Lorentzian components (pseudo-Voigt function), with σ and γ half-widths, respectively. The σ and γ parameters varied with the diffraction angle θ as $\sigma = (U \tan^2\theta + V \tan\theta + W)^{1/2}$ and $\gamma = Y/\cos\theta$. The *U*, *V*, *W*, *Y* profile parameters were always refined.

Results and discussion

The $P6_122$ crystal structure of empty ice XVII was confirmed by results of Rietveld refinements at several temperatures. When neon was inserted into the ice XVII framework, the space group did not change (Table 1). By the technique of Fourier difference maps it was possible to locate the Ne atoms inside the [001] channels present in the structure. The most interesting outcome is that Ne atoms are not located in the centre of the channel, similarly to what reported in the case of Ne-filled iceII, but they are disordered over a set of peripheral positions closer to the O atoms (Fig. 1). In this way Ne-O contacts as short as 3.04 Å are attained, providing a weak attractive interaction of dispersive character which justifies the stability of the iceXVII+Ne system. The average occupancy of Ne atoms leads to a fraction of 0.25 Ne/D_2O molecule at 20 K.

Table 1. Agreement indexes and lattice parameters from Rietveld refinements of deuterated iceXVII (pure and filled with neon, oxygen and deuterium) at 50 and 20 K. Fractional atomic coordinates and displacement factors are not reported for shortness.

	IceXVII	IceXVII+Ne	IceXVII+Ne	IceXVII+O_2	IceXVII+O_2	IceXVII+D_2	IceXVII+D_2
T (K)	50	20	50	20	50	20	50
Space group	$P6_122$	$P6_122$	$P6_122$	$P6_1$	$P6_1$	$P6_1$	$P6_1$
R (%)	3.45	5.22	4.20	5.65	5.25	4.64	4.22
R_w	5.14	7.16	5.84	7.87	7.57	5.99	5.53
R_B	3.19	3.62	2.53	4.18	4.20	3.90 5.47(α-N_2)	3.98 3.98 4.36(β-N_2)
a (Å)	6.34231(8)	6.3287(1)	6.3343(1)	6.3310(2)	6.3365(2)	6.3423(2)	6.3439(2)
c (Å)	6.0711(1)	6.1385(2)	6.1181(1)	6.2163(3)	6.2225(3)	6.1599(3)	6.1592(3)

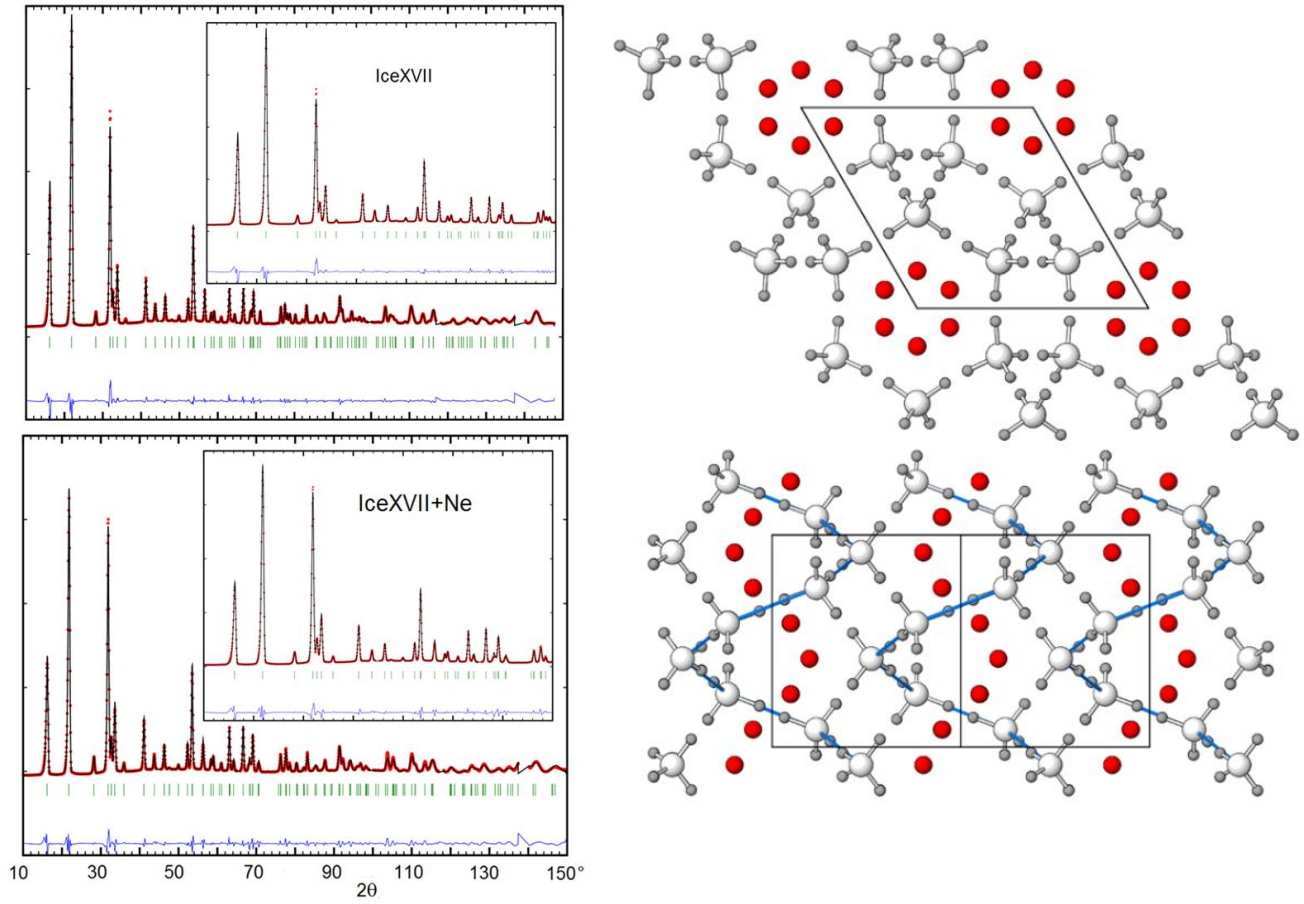

Fig. 1. Neutron diffraction powder patterns of deuterated iceXVII (left, above) and iceXVII+Ne (left, below) at 50 K (λ = 1.543 Å). $P6_122$ crystal structure of Ne-filled deuterated iceXVII, projected onto the (001) (right, above) and (110) (right, below) planes. The spiral-arranged sequences of hydrogen bonds are emphasized with blue lines in the below picture.

In the case of iceXVII+O_2, again the O atoms of the oxygen molecule could be located by Fourier difference maps. However, a better Rietveld fit could be obtained in space group $P6_1$ with respect to $P6_122$, as removal of the twofold symmetry axis allowed to relax the intramolecular O-O bond length conveniently to 1.20 Å. Oxygen molecules are statistically distributed over disordered positions in the [001] spiral-like channels (Fig. 2). The average occupancy of O atoms leads to a fraction of 0.23 O_2/D_2O molecule at 20 K.

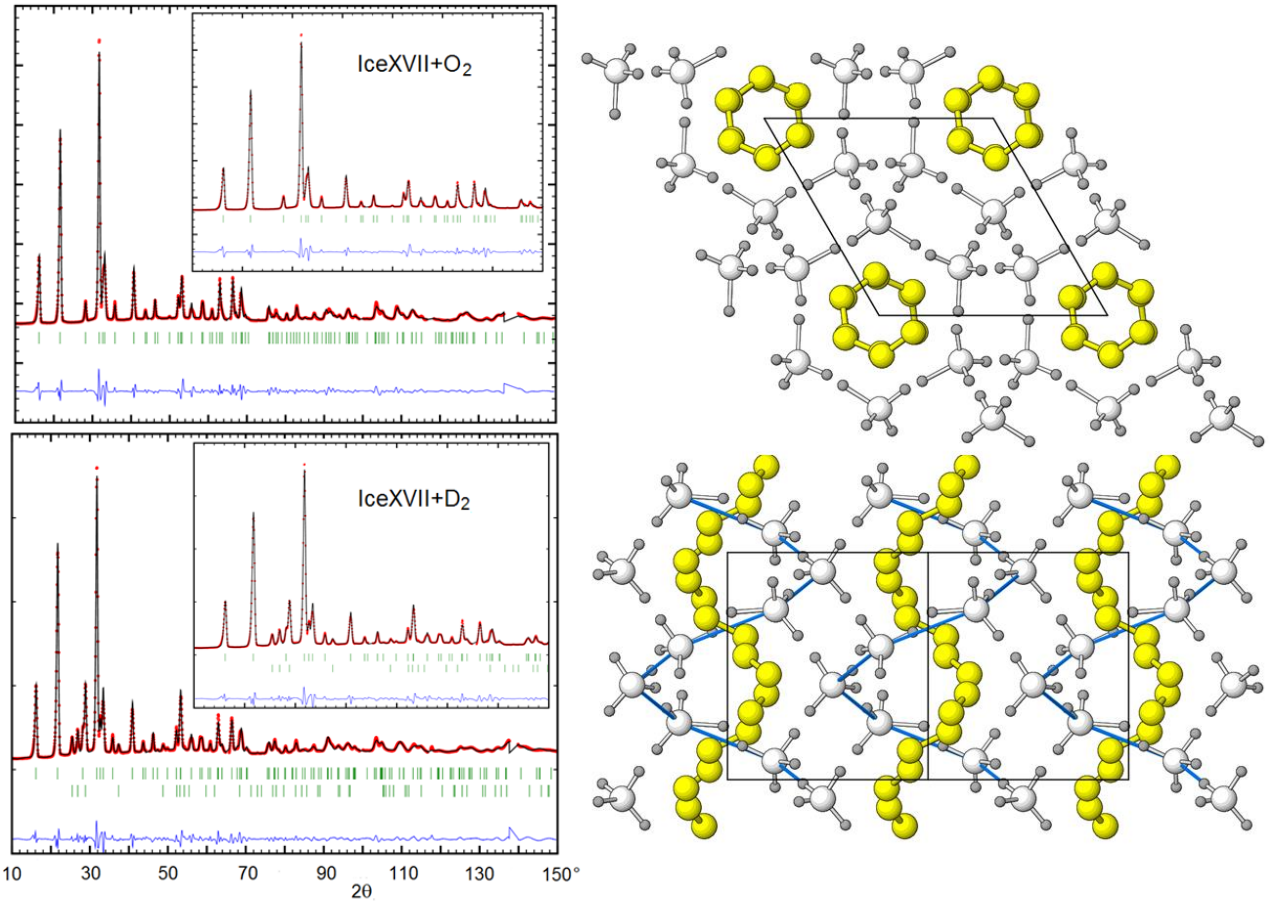

Fig. 2. Neutron diffraction powder patterns of deuterated iceXVII+O_2 (left, above) and iceXVII+D_2 (left, below) at 50 K (λ = 1.543 Å). $P6_1$ crystal structure of O_2-filled deuterated iceXVII, projected onto the (001) (right, above) and (110) (right, below) planes.

As for iceXVII+D_2, again best results of the Rietveld refinement were attained in the $P6_1$ space group. The complete analysis of data is however still in course.

At the end of the last outgassing treatment of the sample, on heating it slowly in vacuum and collecting 5 minutes patterns at 5 K intervals, a surprising phenomenon was observed. The hexagonal $P6_122$ iceXVII structure underwent a phase transformation to the cubic one of ice Ic in the 155 to 160 K range. A long data collection at 160 K showed that the Ic phase obtained was very pure, with no extra peaks, at variance with common literature reports of Ic ice contaminated by Ih ice structural features. Thus, we believe to have found a way of synthesizing pure ice Ic in substantial amounts. We plan to investigate this phenomenon and related properties of pure Ic ice in future experiments.

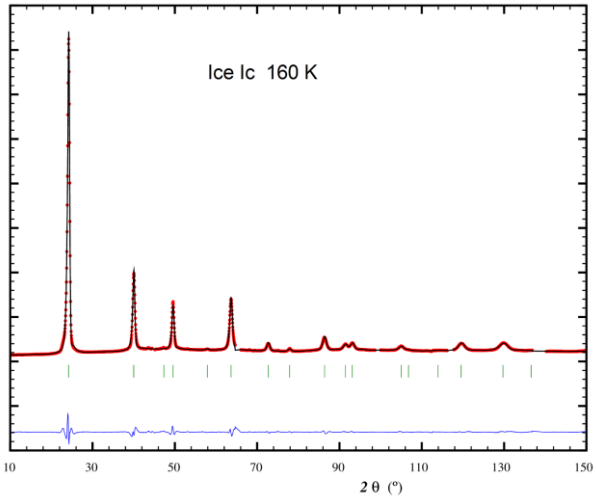

Fig. 3. Powder pattern with Rietveld refinement of the structure of cubic ice Ic (R = 2.5, Rw = 4.1, RB = 0.8 %).