Experimental report

30/03/2020

Proposal: **5-15-624** **Council:** 10/2018

Title: Single crystal neutron diffractionstudy of a novel MgCl2-hydrate under pressure to 1 GPa by using a newly designed pressure cell

Research area: Physics

This proposal is a new proposal

Main proposer: **Stefan KLOTZ**

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Samples: MgCl2x6D2O

Instrument	Requested days	Allocated days	From	To
D9	10	10	10/02/2020	18/02/2020

Abstract:

The proposed single crystal neutron diffraction experiment aims to determine full structural parameters including hydrogen positions in a high pressure form of a salt hydrate. The sample under investigation is a high pressure phase of MgCl2 hydrate which was recently discovered by Komatsu and co-workers (Univ. Tokyo) using single crystal x-ray diffraction. The crystal structure without hydrogen positions was solved by x-ray diffraction, and the structure may have disordered water molecules involving "switching hydrogen-bonding networks", which is the main interest of this study. We will use a newly developed high pressure cell which overcomes many difficulties previously encountered in single crystal neutron diffraction under pressure.

Experimental report "In-situ single crystal neutron diffraction study of ice VII under pressure" (proposal nr. 5-15-624)*

Instrument: D9

Date: 10.-18.2. 2020

Experimental team: Stefan Klotz, Keishiro Yamashita, Kazuki Komatsu, Oscar Fabelo, Maria Teresa Fernandez Diaz (main proposer: S.K.)

Ice is a purely hydrogen-bonded material and pressure-induced changes of its physical properties are hence intrinsically related to the nature of the H-bond. This proposal focused on ice VII (*) which is stable over an enormous pressure range, i.e. from 2 GPa to 60 GPa at room temperature. This wide stability provides unique opportunities for studying H-bond phenomena across a significant density change, such as quantum tunnelling, symmetrisation of H-bonds, anomalous proton dynamics, to give a few examples. The previous studies on the crystal structure of ice VII were carried out by powder neutron diffraction methods with their intrinsic limitations due to peak-overlap. Single-crystal methods would allow to address important open issues of H- and O-site disorder in this phase, but no single crystal studies have been reported so far. This is mainly due to the technical difficulty to grow a single crystal in a high-pressure chamber above 2 GPa with sufficient size for neutron diffraction measurement. We recently developed a method which enables to grow single crystals of mm-size starting with a mixture of water and alcohol. In a test experiment in June 2019 we demonstrated that it is indeed possible to observe Bragg intensities from an ice VII single crystal at D9 by using a new type of compact high-P cell [1].

The cell is an opposed-anvil type device using large anvils made of nano-polycrystalline diamond (NPD). Its load frame is made of bulk metallic glass (BMG) cylinder with tungsten carbide pistons to transfer the force generated by a screw-mechanism~~.~~ [1]. It is small enough (mass: ca. 1 kg) to mount it on the standard Eulerian cradle of D9 (Fig. 1). Since none of the cell components is single-crystalline, the Bragg reflections from the sample can be easily identified. Both NPD and BMG are highly transparent to neutrons. Test runs on D9 (Ju~~ne~~ly 2019) with a small single crystal of NaCl inside the cell confirmed that the attenuation by the cell is negligible for most configurations and that peak indexing is straightforward.

The measurements at D9 were a full success. A single crystal of ice VII was grown at 2.0 GPa with a size of 0.8 × 0.8 × 0.4 mm^3 (Fig. 2) and Bragg intensities observed up to high-Q values (~11.4 Å^{-1}). A total of 48 reflections were observed with 26 symmetrically unique ones. Such high-Q reflections are not easily visible by powder diffraction method. A preliminarily structure analysis gives a reliability (R) factor of approximately 5.5 %. The detailed data analysis is being carried out at the moment.
We take the occasion to thank ILL staff for their support which was crucial for the success of this experiment.

*) In agreement with the D9 instrument team, the title/aim of the original proposal was changed since the scientific issue had been solved in the meantime, i.e. the original proposal became obsolete.

[1] Yamashita et al. High Press. Res. 40(1), 88, 2020.

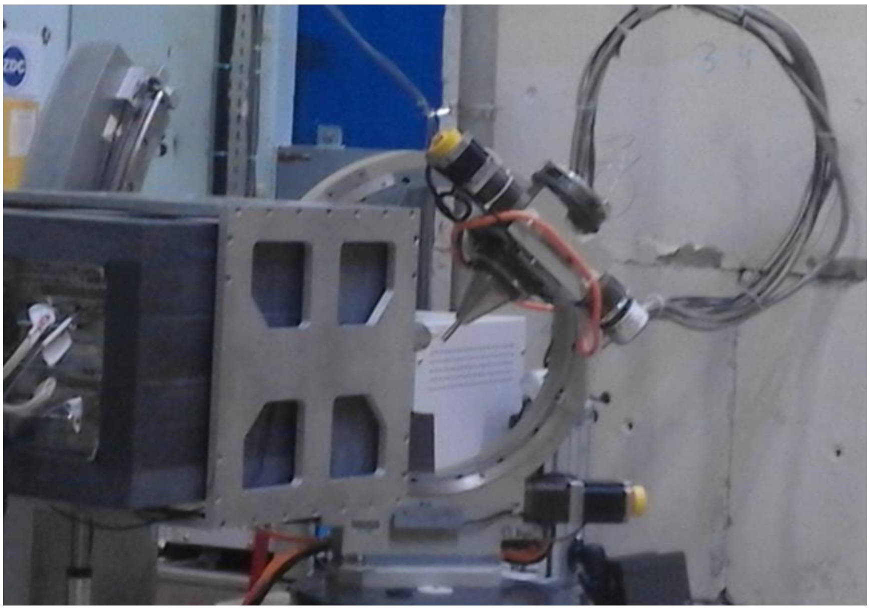

Figure 1. Pressure cell mounted on the D9 Eulerian cradle at ILL. The sample is located inside the tip of the metallic tube. The conical item is part of the screw mechanism which generates the force on the anvils. See ref. [1] for details.

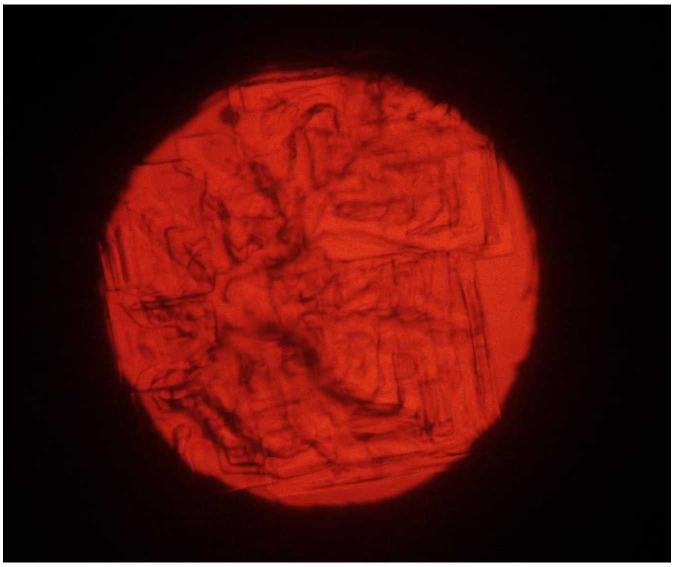

Figure 2. Single crystal of ice VII at 2.3 GPa inside the pressure cell. The diameter of the gasket hole is approximately 1 mm. The red colour is due to an optical filter. Neutron diffraction confirmed that the sample is fully single-crystalline despite its irregular surface appearance.

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