Experimental report

09/02/2016

Proposal: **5-24-560** **Council:** 10/2014

Title: Hydrogen filled-ices under planetary conditions

Research area: Physics

This proposal is a new proposal

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Samples: D2:6D2O

Instrument	Requested days	Allocated days	From	To
D20	4	4	17/07/2015	21/07/2015

Abstract:

High-pressure hydrogen clathrates can be found in the outer solar system (comets, satellites of the gas giant planets, Mars), and could play a major role as gas storage systems due to the very high H2 ratio 1H2O:1H2 . Up to date, only few structural and some Raman characterizations have been carried on these spatial abundant gas hydrates under HP, while no information is available on the the guest-cage dynamics under pressures in the GPa range. In the frame of our LTP n 57755 we will address the exciting program of characterizing hydrogen diffusive and rotational dynamics in filled ice hydrates under the pressure relevant for ice bodies in our solar system, by QENS studies under high pressure employing a newly developed HP apparatus for QENS. Preliminary to these measurements, precise structural measurements are needed to characterize the filling ratio of the in-situ produced clathrate and monitoring its structural evolution as a function of pressure. Here we apply for 4 days of beamline on the high flux diffractmeter D20 to perform such structural analysis of D2:D2O clathrates directly synthesized in situ in the PE press by means of a new hydrogen loader recently installed at ILL.

The experiment was aimed at investigating the structure evolution of hydrogen hydrate under pressures in the range 0.2-4 GPa by neutron diffraction using the Paris-Edinburgh press. The purpose of the experiment was two-fold: i) clarifying the controversial phase diagram of hydrogen hydrate and ii) establishing an applied pressure versus sample pressure calibration for our setup to be used in further quasielastic neutron scattering studies on IN6.

The D_2O:D_2 sample has been synthesized in laboratory before the experiment. Hydrogen hydrate is only stable below 140 K at ambient pressure. Thus, we loaded it in the PE clamp under liquid nitrogen. Once the clamp was assembled and connected to the compressor, we closed it under a load corresponding to a pressure of a few kbar at the sample chamber. We then quickly installed the clamp in the PE press. The rapidity of this step is crucial as the dissociation temperature of hydrogen hydrate is still below room temperature at a pressure in the kbar range.

In the assigned 4 days, we successfully cryo-loaded three samples and followed their pressure evolutions up to approximately 4 GPa along different isothermal and non-isothermal paths in the range 220-270 K (see Figure1). Ten thermodynamic points were typically measured per sample, for a total of more than 30 points. In addition, the ambient-pressure recovery of the high-pressure phase “filled ice Ic” has been attempted. To allow such a wide investigation of the phase diagram, the acquisition time has been limited to approx. 2 hours per thermodynamic point. The latter is however long enough to obtain diffractograms of reasonable quality (see Figure2).

As a result of a preliminary analysis, our data along an isothermal compression at 275 K reproduced the transition sequence (sII, filled ice II, filled ice Ic) reported for hydrogen hydrate at room temperature in literature [1]. On the contrary, compression above 0.4-0.5 GPa at lower temperatures gave rise to patterns incompatible to any known phase of hydrogen hydrate.

References:

[1] J. S. Loveday and R. J. Nelmes, *Phys. Chem. Chem. Phys*. 10, 937–950 (2008).

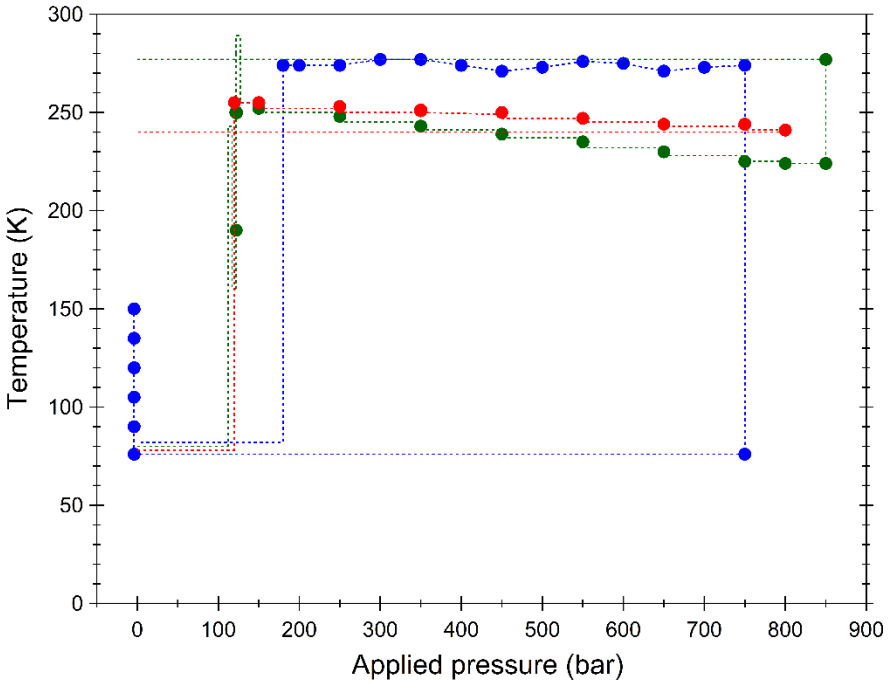

Figure1: *Thermodynamic paths, temperature as a function of the applied pressure, followed during the beamtime 5-24-560. Each colour corresponds to a different sample loading. Round points indicate approximately 2 hours measurements. For each loading, the applied pressure axis can be converted to sample pressure using the lead powder we mixed to the sample powder as pressure gauge.*

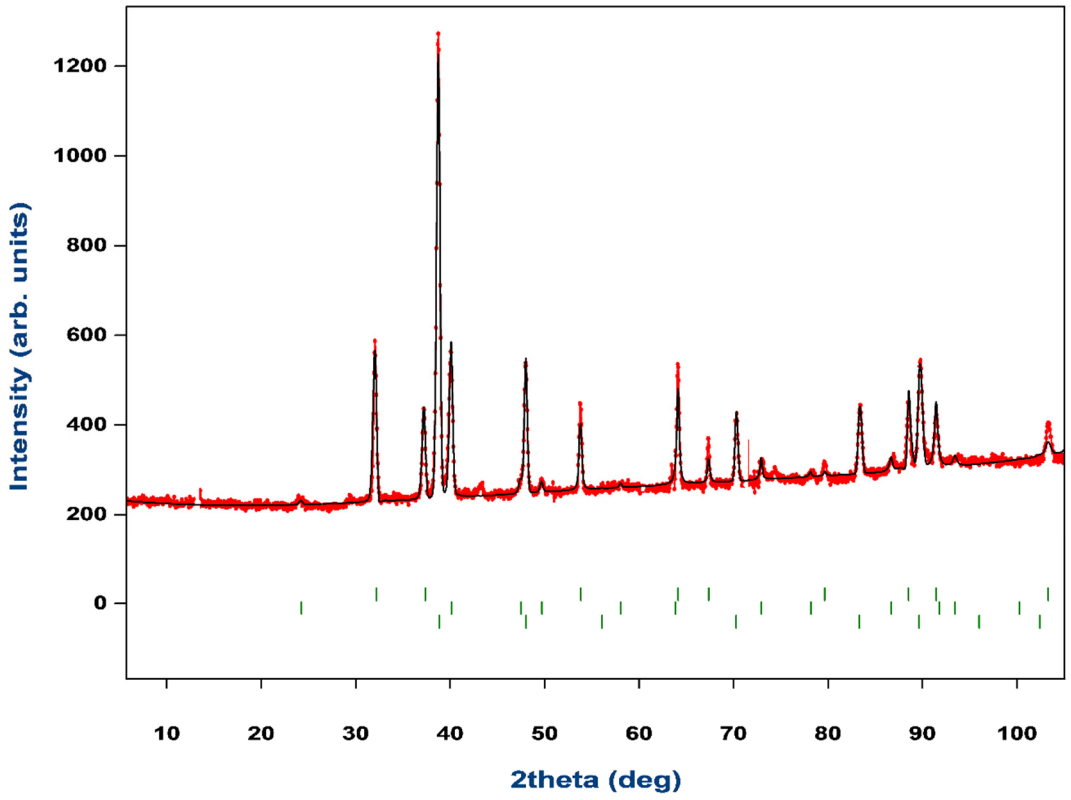

Figure2: *Diffractogram of hydrogen hydrate as measured in 2 hours during the beamtime 5-24-560 at 4.2 GPa and 275 K, as an example. Its Rietveld refinement (including the phases filled ice Ic, ice VII and lead) is also shown.*