Experimental report

17/09/2018

Proposal:	**5-22-756**	**Council:**	4/2017
Title:	Hydrogen hydrate under high-pressure: filled-ice II structure		
Research area:	Physics		

This proposal is a new proposal

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Samples: D2O-D2

Instrument	Requested days	Allocated days	From	To
D20	2	2	03/04/2018	05/04/2018

Abstract:

Hydrogen hydrate is an inclusion compound in which a hydrogen-bonded crystalline water ice structure accommodates hydrogen molecules in cages or channels. It has been suggested as candidate material for hydrogen storage applications and attracted considerable attention during the last decade. In addition, it is likely to exist in nature since hydrogen and water ice are common constituents of the universe. We recently measured the ambient-temperature equation of state of hydrogen hydrate on D20 up to 4 GPa on the very small sample contained in a Paris-Edinburgh press. Here we propose to measure a larger sample at 1 GPa to determine the atomic positions and guest occupancy of hydrogen hydrate in structure C1.

This experiment was performed in the framework of the ILL/EPFL PhD thesis of Umbertoluca Ranieri [1] and was aimed at investigating the structure of hydrogen clathrate hydrate under high pressure.

We slightly changed the focus of this beamtime (whose proposal had been submitted before the long shutdown of 2017) and investigated the structure of clathrate structure II (sII) hydrogen hydrate and the effect of inclusion of helium in the clathrate structure. This is important information for interpreting the dynamical studies we have performed by inelastic and quasi-elastic neutron scattering on IN5 (exp 6-07-5, exp 6-07-29).

The H_2–D_2O and D_2–D_2O clathrate hydrate samples in phase sII were prepared at the Helmholtz-Centre Berlin (Germany) by exposing deuterated ice spheres at 244 K to H_2 or D_2 gas at 2.8 kbar. High-pressure neutron diffraction measurements at temperatures between 1.7 and 70 K were performed on D20 using a neutron wavelengths of 1.54 Å. Two aluminium-alloy cylindrical gas pressure cells belonging to the ILL (05PG30AL6, 02PG70AL6) were employed to generate high pressures of 2.5 and 5 kbar.

During previous experiments 6-07-5 and 6-07-29, we had employed inelastic and quasi-elastic neutron scattering to characterize the low-temperature dynamics of hydrogen molecules in different hydrate structures at ambient and high pressure, including the dynamics of H_2 and D_2 molecules confined in the large cage of the clathrate structure II. We compressed the samples using helium as pressure transmitting medium and observed in the spectra a spectacular suppression of all inelastic peaks associated with a change in the quantum translational state of H_2 in the large cage. We inferred that this observation was due to inclusion of helium in the large cages of the structure (large cages can host up to four hydrogen molecules but our samples contain only two hydrogen molecules per large cage in average). However, the diffraction patterns obtained on IN5 were not sufficient to confirm this hypothesis.

Hence, we used our D20 beamtime (5-22-756) to measure diffraction patterns of hydrogen hydrate before and after compression with helium at temperatures of 30-45 K, following the same pressure-temperature paths we had followed on IN5, in order to verify *and* quantify the inclusion of helium in the cages of the clathrate structure. During the assigned 2 days of beamtime, we measured diffraction patterns of D_2–D_2O hydrate at the following conditions:

- 1.7 K, ambient pressure (before compression)
- 1.7+70 K, 2.5 kbar (after compression)

We also measured H_2–D_2O hydrate at the following conditions:

- 1.7 K, ambient pressure (before compression)
- 1.7+70 K, 5 kbar (after compression)
- 1.7 K, ambient pressure (after decompression at low temperature)
- 1.7 K, ambient pressure (after decompression and two hours of thermal treatment at 90 K).

Finally, we measured the two empty pressure cells at 1.7 and 70 K.

The D20 experiment confirmed that helium enters the hydrogen clathrate hydrate (on a time scale of typically ten minutes at 30 K) and occupies the large cages of the structure *exclusively.* We took 2 minutes scans and observed the IN5 diffraction pattern of the sample to substantially change within the first ten minutes following the compression and to remain constant afterward. A Rietveld refinement of the measured patterns indicates that about 2 helium atoms occupied the large cages of our sample in average. An example of measured spectrum is reported in Figure 1.

On the other hand, we do not expect that H_2 is able to migrate out of the structure at temperatures below 50 K. Consistently, we noticed that after releasing pressure and thermal treatment at 90 K the diffraction pattern of the sample changed back to the starting pattern of H_2–D_2O hydrate (see Figure 1), indicating that hydrogen molecules do not migrate out of the clathrate structure while the migration of helium into the structure is reversible.

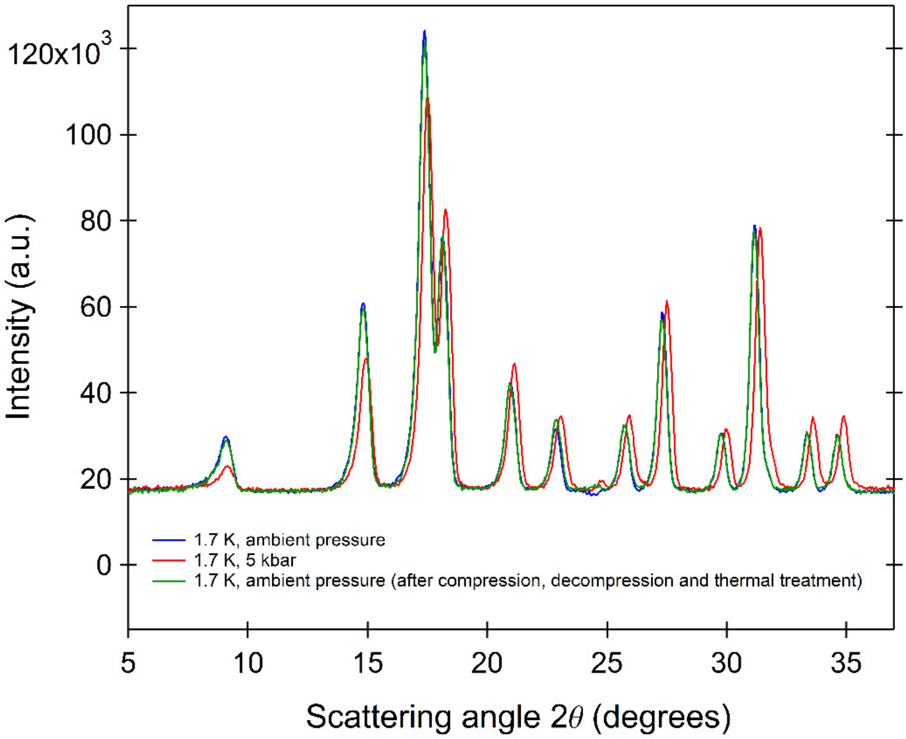

Figure 1: D20 (λ=1.54 Å) powder diffraction patterns of clathrate sII H_2-D_2O hydrate (space group Fd-3m) before compression, after compression to 5 kbar, and after decompression and thermal treatment, plotted over a small region of the recorded scattering angle range.

References

[1] U. Ranieri, PhD Thesis, “Guest dynamics in methane hydrates and hydrogen hydrates under high pressure.” École Polytechnique Fédérale de Lausanne, 2018.