Experimental report

27/02/2024

Proposal: **5-24-703**

Council: 10/2022

Title: Melting curve and new phases of hydrogen hydrate in the GPa range: a missing piece of information for planetary modelling

Research area: Physics

This proposal is a new proposal

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Samples: D_2O:D_2

Instrument	Requested days	Allocated days	From	To
D20	3	4	04/04/2023	08/04/2023

Abstract:

Hydrogen hydrates are among the basic constituents of our solar system¿s outer planets, some of their moons, as well Neptune-like exo-planets. The structures that hydrogen-hydrate can form in the 0.1-10 GPa range, as well as their stability at high temperature are fundamental missing piece of information for establishing the presence of hydrogen hydrates against the one of pure components in the interior of those celestial bodies. We propose to determine by neutron diffraction measurements under high pressure on the high flux diffractometer D20:

i) the melting curve of the C2 phase from 2.5 GPa (400 K) to 6.5 GPa (600 K). Those measurements will be complemented by HP Raman scattering measurements of the melting curve but neutrons are needed to properly distinguish ice VII melting from hydrate melting.

ii)the possible existence of other unknown phases in the low temperature/high pressure range

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Melting curve and new phases of hydrogen hydrate in the GPa range: a missing piece of information for planetary modelling

Hydrogen hydrates are among the basic constituents of our solar system's outer planets, some of their moons, as well Neptune-like exoplanets. The structures that hydrogen-hydrate can form in the 0.1-10 GPa range, as well as their stability at high temperature are fundamental missing piece of information for establishing the presence of hydrogen hydrates against the one of pure components in the interior of those celestial bodies. We performed neutron diffraction measurements under high pressure on the high flux diffractometer D20 to determine:

i) the melting curve of the C2 phase from 2.5 GPa (400 K) to 6.5 GPa (600 K)

ii)the possible existence of other unknown phases in the low temperature/high pressure range

Melting curve

1st loading

Sample: D2: 5.7D2O in the SII structure, powder, stored in dewar at liquid Nitrogen temperature

Pressure calibration: a small piece of lead was inserted in the gasket but unfortunately it was not visible in the beam

PE setup: High Temperature setup with sintered diamond anvils and Inconel gasket

Loading procedure: the sample was pelleted under nitrogen vapor to have the same size of the gasket. The filled gasket, stored under liquid nitrogen was loaded in the PE press where the anvils were pre-cooled with nitrogen vapor. The piston was quickly manually screwed and 200 bar load were applied on the anvils to reach approximately 3 kbar pressure on the sample.

Instrument settings: $\lambda = 1.54$ Å

Data acquisition: 2θ scans from -7 to -4 with 0.05 steps

The loaded PE press was aligned in the beam and a first diffraction pattern was acquired. We could observe peaks in the diffraction pattern from the diamond anvils (red squares in fig1), SiC impurities in the anvils (blue squares in fig 1), the Inconel gasket (green squares in fig 1) and some ice VI and likely SII phase of hydrogen hydrate, though rather week. Upon compression of the sample (800 bar on the anvil) we see transformation to Ice VII, but we didn't see enough signal from the hydrogen hydrate so we decided to unload and re-load the PE press.

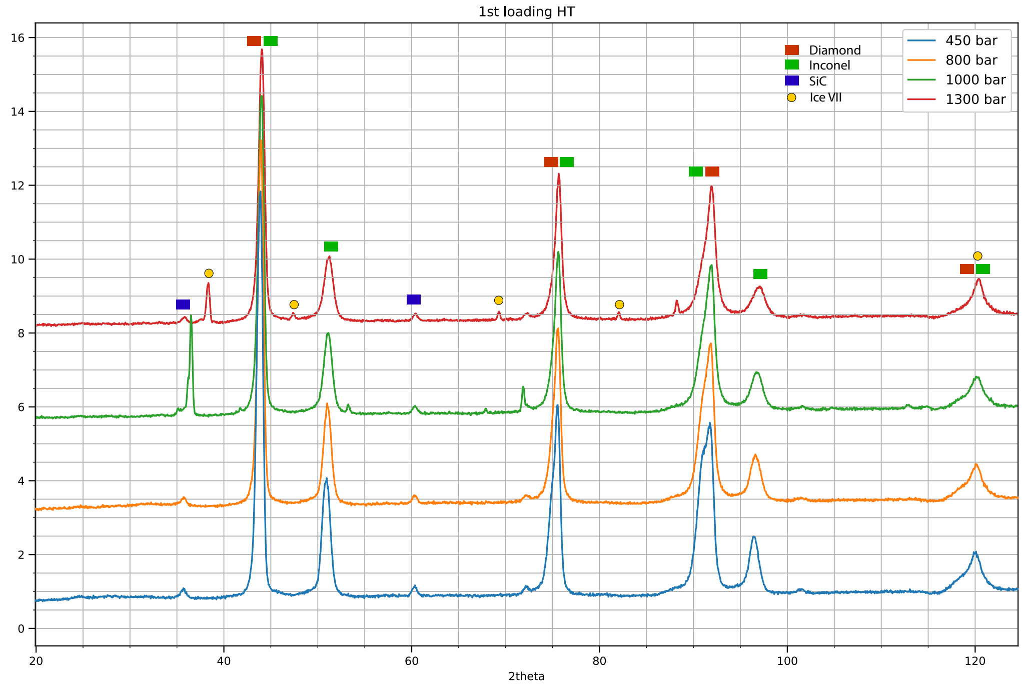

Figure 1: first loading with the HT setup. Compression to 1300 bar.

2nd loading

Sample, loading procedure and instrument set-up same as before.

The PE press was loaded with a starting higher load in order to ensure to be above 5 kbar and don't destabilize the clathrate during the warming up of the anvils. In the first diffraction patterns we see diamond and SiC peaks from the anvils (red and blue squares in fig2) and well visible peaks from the hydrate in phase sII. Upon compression to about 1000 bars we see no major changes in the diffraction patterns. We discovered that the valve for P transmission was inadvertently closed during the press installation. When opened the pressure jumped to about 7 GPa. We decompressed the sample to about 3.6 GPa (180 bar) and started heating. We heated the sample until the melting of Ice VII at about 400 K. C2 hydrate sample melting was contemporarily.

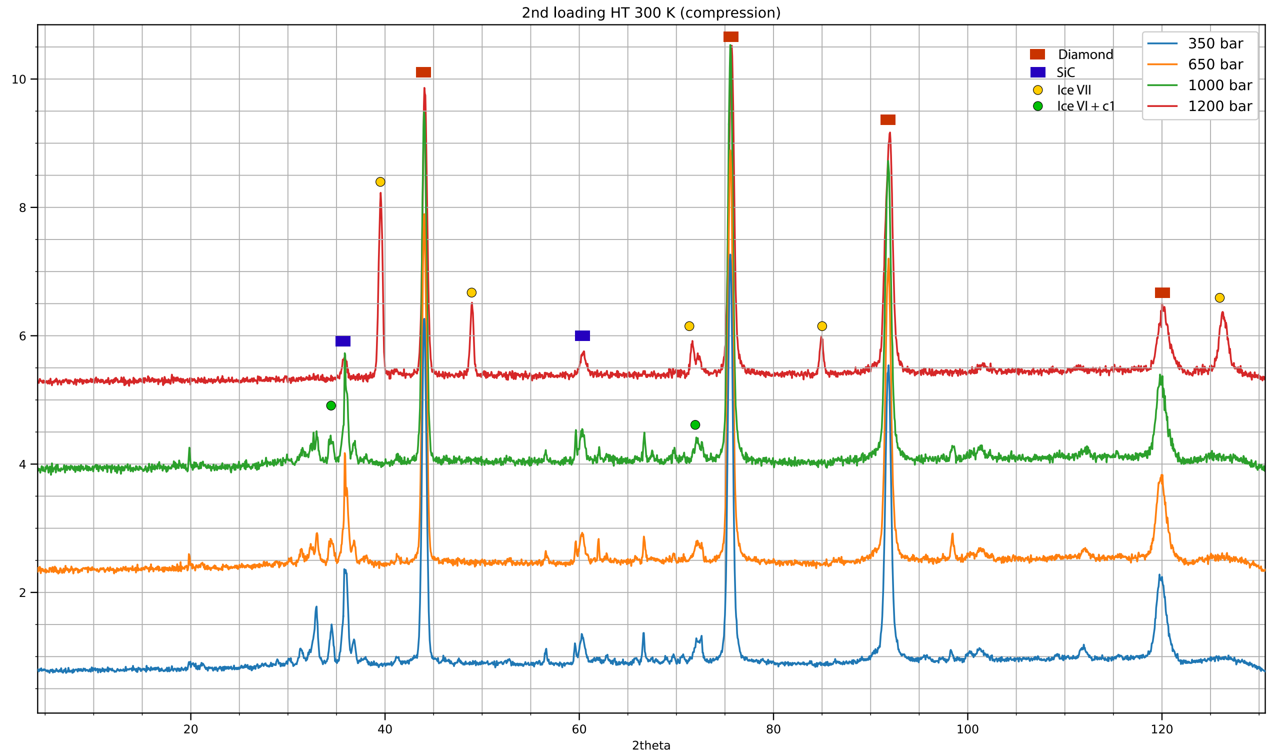

Figure 2: Second loading with the HT setup. Compression to 1200 bar.

Low temperature phases

Sample: D2: 5.7D2O in the SII structure, powder, stored in dewar at liquid Nitrogen temperature
Pressure calibration: a small piece of lead was inserted in the gasket
PE setup: Low temperature setup with clump for cryoloading the sample. TiZr gasket
Loading procedure: the sample was pelleted to have the same size of the gasket. A clamp was loaded at liquid nitrogen temperature and then inserted in the PE press. We put 300 bar load on the anvils. The PE is then inserted in the cryostat.
Instrument settings: $\lambda = 1.54$ Å
Data acquisition: 2θ scans from -7 to -4 with 0.05 steps

After sample loading we acquired diffraction patterns at RT. In this case we only see peaks from the sample. We compressed to 1100 bar, about 5 GPa from the sample. At this pressure we see peaks from Ice VII and from the C2 phase.

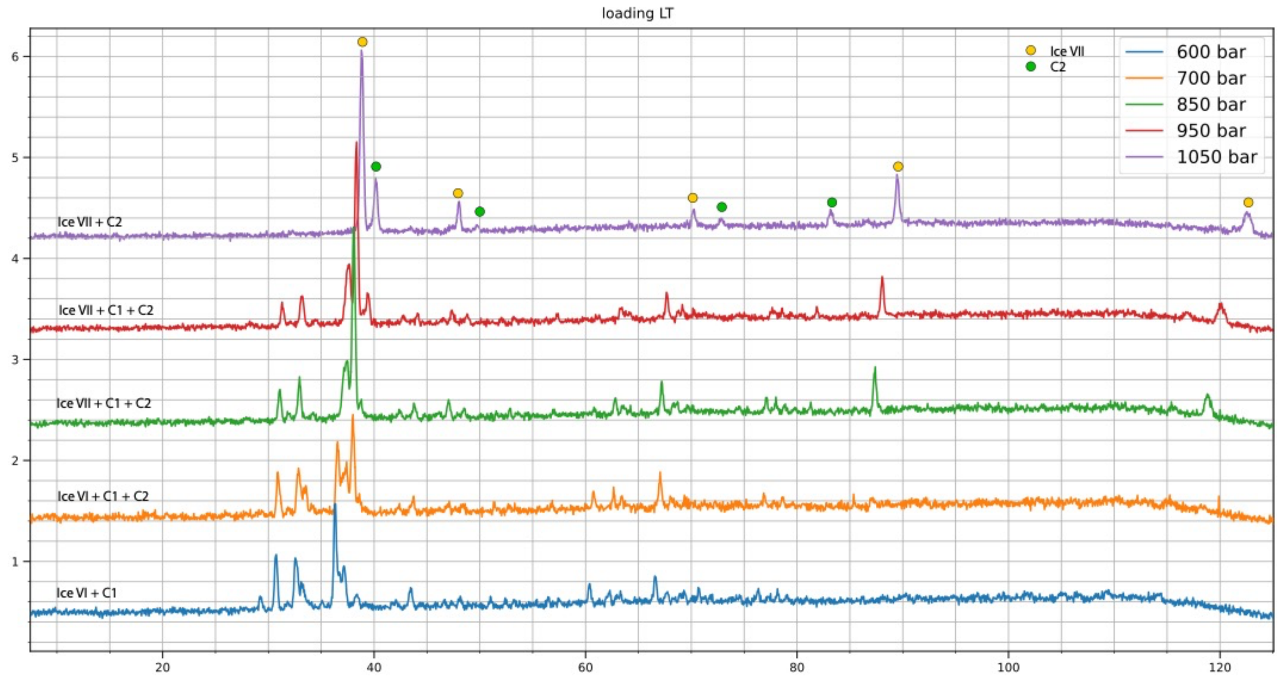

Figure 3: Loading with the LT setup. Compression to about 5 GPa

At 5 GPa we started cooling down to 5 K and acquired diffraction patterns at 80 K, 46 K, 30 K, and 5 K. A selection of temperatures is reported in figure 4. We see no major changes in the diffraction pattern except from the transition from ice VII to ice VIII. No evidence of tetragonal distortion in the C2 hydrate phase down to the lower temperature.

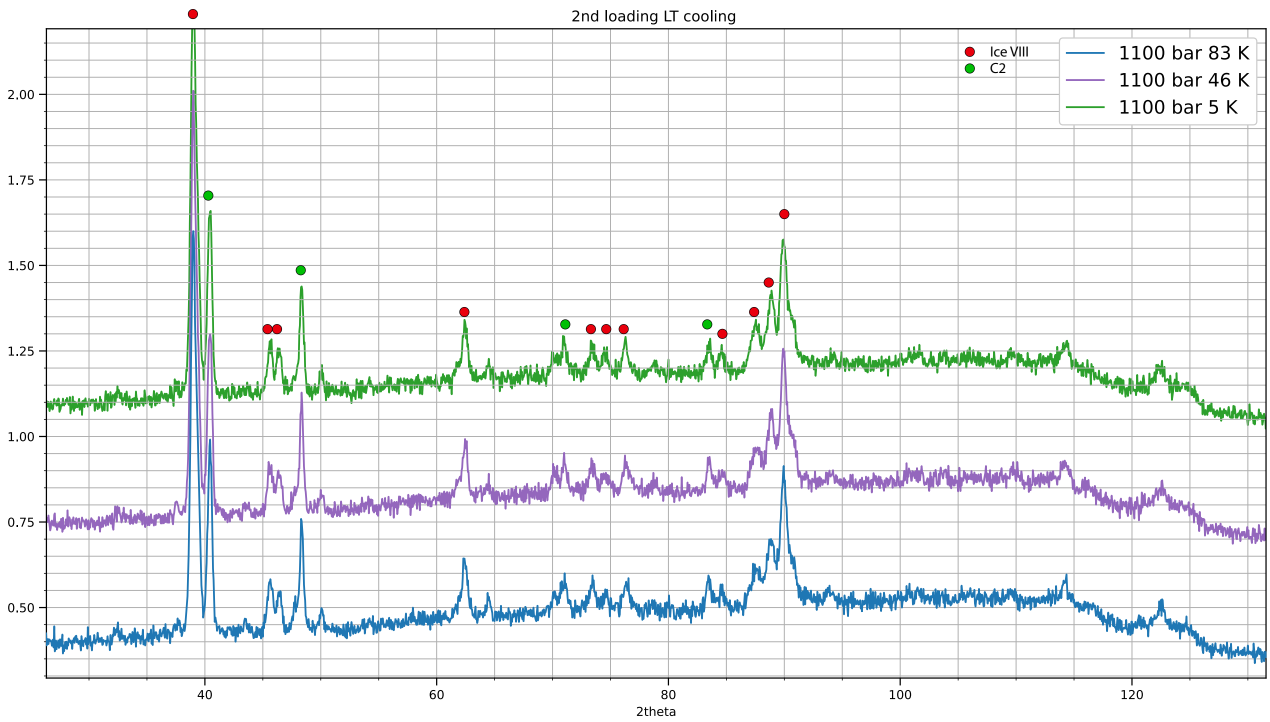

Figure 4: Cooling at 5 GPa.