ESRF	**Experiment title:** XRD of water ice above 200 GPa under variable P-T conditions: revealing a structural complexity at planetary interiors pressures.	**Experiment number**: HC5078
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Report:

Scientific background and objectives

H_2O presents a fascinating phase diagram, exhibiting numerous crystalline structures, amorphous phases and fluid polymorphism depending on thermodynamical conditions. Among ices, superionic (SI) phases that are stable at extremely high pressures and temperatures has attracted great attention due to their unusual fluid-like proton diffusion within a fixed oxygen lattice. Besides its fundamental interest, the high protonic conductivity in SI ice is expected to instigate the unusual non-dipolar and non-axisymmetric magnetic fields of giant ice planets (e.g. Neptune and Uranus), motivating detailed studies of their stability fields and physical properties.
Early theoretical and numerical predictions have proposed SI ice phases sharing the same bcc oxygen sublattices as ice VII and X, but also with a close-packed fcc O sublattice [1,2]. The fcc-SI ice phase was first experimentally reached in 2019 by multi-shock compression at P-T conditions of 170-400 GPa and 2000-4000 K [3]. More recently, two static studies based on in-situ sychrotron X-ray diffraction (XRD) in the laser-heated diamond anvil cell (DAC) aimed to disclose more finely the stability fields of the fcc SI phase [4,5]. These two works shows a large discrepancy on the bcc-fcc transition line reaching 1500 K at 150 GPa, ours showing the larger stability field of the fcc phase in agreement with previous shock data and calculations (HC3952, ref. 5).
In refs 4 and 5, indirect heating using a YAG laser absorber loaded in the DAC along with the sample was implemented to efficiently heat the ice sample while collecting XRD data, the two studies differing in the absorber material used (boron-doped diamond {BdD} in our case).
Recently, we implemented a new sample geometry that uses *two* opposite boron-doped diamond (BdD) absorbers encapsulating the warm dense ice sample inside the heated BdD capsule. This new ice sample confinement, first used using our run HC4677, have allowed to obtained excellent quality data thanks (i) to the more homogeneous heating and (ii) to the more significant hot volume probed in the DAC than when using a single absorber. The present experiment aimed at pursue and extend our measurements following this strategy, by following the bcc-fcc transition line and finely measure thermodynamical properties of the fcc ice. Since no static equation of state (EOS) data was available for ice at ambient pressure beyond 170 GPa, we also aimed at measuring the 300 K compression curve of ice X within a DAC equiped with toroidal anvils [6] to reach highest pressures.

Experimental details and results

Four diamond anvil cells were studied as synthetized in table 1.

Sample	Anvil culets diameter	Details	Objectives
#1	34 µm (toroidal anvils)	The two toroidal anvils were prepared by focused ion beam (FIB) machining The gasket hole measured 14 µm. A small piece of gold was loaded alond with the ice sample for pressure determination using gold EOS.	- Measure the ambient temperature EOS of ice up to 300 GPa.
#2	50 µm	Central circular pits were FIB-machined to provide space for the two BdD absorbers in the DAC cavity. 1.5-2 µm-thick Al_2O_3 layers were deposited on each anvil for thermal insulation. The two absorbers were carefully glued in each pits by using a very thin layer of UV-curing glue.	- Probe the bcc-fcc boundary line up to 250 GPa. - Finely measure thermodynamical properties of the fcc-SI phase. - Collect data on the 300 K EOS with frequent sample annealing.
#3	75 µm	Same as #2	- Probe the bcc-fcc boundary line and measure thermodynamical properties of the fcc-SI ice at 200 GPa.
#4	150 µm	Same as #2	-Probe the bcc-fcc boundary line and measure thermodynamical properties of the fcc-SI ice up to 120 GPa.

Table 1: H_2O samples studied during HC-5078.

After H_2O loading, all samples were characterized by Raman spectroscopy at our laboratory. Samples were brought at the ID27 beamline of the ESRF to collect *in-situ* XRD data at ambient and high temperatures using the double-sided YAG-heating set-up available at the beamline. Temperatures values were measured by optical pyrometry.

A large number (~250) of ambient temperature XRD diffraction pattern were collected on sample #1 between 1 GPa and 230 GPa, the pressure at which one diamond anvil broke. XRD patterns from both the ice sample and the gold pressure gauge were taken at each pressure changes. These measurements extend the knowledge of the ice EOS ~50 GPa higher than previously published data. Large non-hydrostatic stresses in the sample #1 were observed. Furthermore, at the highest pressures values, only the first X-ray reflexion was sufficiently strong to be followed. Hence, we decided to collect 300 K density measurements on sample #2 during pressure increase: BdD absorbers allowed to perform frequent annealing up to 2000 K to relax non-hydrostatic stresses. Data are currently under analysis to compare the two compression curves.

In sample #2, #3 and #4, heating ramps were performed while collecting in-situ XRD patterns at various pressure conditions. Care was taken to balance the temperature at each side of the sample and keep it stable during XRD measurements. Small temperature increments of ~100 K were performed. Frequent XRD cartographies were collected to investigate sample inhomogeneities. Sample #2 reached 220 GPa and ~2700 K when the anvils broke inducing a pressure drop to ~ 60 GPa. Samples #3 and #4 were keeped at their last investigated pressures (200 GPa and 80 GPa) for further analysis. These measurements allowed to confirm our previous measurements up to 200 GPa, and are currently under deeper analysis.

XRD measurements during heating ramps have allowed to investigate the thermal expansion of the fcc-SI phase. During several quasi-isobaric ramps at different pressure conditions, we have been able to observe a strong variation of fcc-SI phase volume, manifesting a thermal expansion bump (Schottky bump). Such feature was reported as a direct signature of the superionic transition [7]. Thus, density measurements are able to directly probe superionic states at extreme P-T conditions. A manuscript reporting these results is in preparation.

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