

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: <i>Structural evolution of the ionic phases of ammonia monohydrate at high pressure</i>	Experiment number: HC1646
Beamline: ID27	Date of experiment: from: 28 octobre 2014 to: 04 novembre 2014	Date of report: <i>Received at ESRF:</i>
Shifts: 12	Local contact(s): G. Garbarino	
Names and affiliations of applicants (* indicates experimentalists): Sandra NINET – IMPMC – Paris Frédéric DATCHI – IMPMC- Paris Jean-Antoine QUEYROUX – IMPMC – Paris Cailong LIU – IMPMC – Paris		

Report:

Despite its high relevance for planetary physics, in particular giant icy planets, the properties of ammonia/water compounds are totally unknown above 10 GPa. The aim of this proposal was to study the structural properties (EOS and structure) and P-T boundaries of the 1:1 compound (ammonia monohydrate or AMH) over a wide range of pressure at low and ambient temperature. Previously, a theoretical work predicted a full ionization of AMH in a tetragonal structure only composed of NH_4^+ and OH^- ions [1]. Using infrared spectroscopy, we have detected a molecular/ionic phase transition and the presence of OH^- and NH_4^+ species above 8 GPa at ambient temperature [4]. However, the signature of NH_3 and H_2O molecules were still present. The structure and stability of this partially ionic phase at high pressure and low temperature was unknown.

Results :

We have studied 4 different samples of AMH. The samples were loaded and compressed at 80 K to pressures greater than 10 GPa before warming up to room T in order to keep the 1:1 composition [3]. The Raman spectra of all samples confirmed the presence of ionic species after loading. The first sample was decompressed from 27 GPa at 300 K to determine the phase transition sequence between the ionic and molecular phases. Figure 1(a) shows the evolution of the integrated x-ray pattern from 15 GPa at 300 K. Down to 8.2 GPa, the x-ray pattern can be indexed by a bcc structure, as reported for AMH-VI (the disordered molecular alloy, or DMA, phase) [2]. Below this pressure, we observed a sequence of phase transitions at the same pressures as observed by infrared spectroscopy: at 7.15 GPa, the bcc peaks broaden and decompose into several peaks at 6.7 GPa. At 5 GPa, the pattern can be indexed with AHH-II and another, unidentified phase. At 4 GPa, the spectrum can be interpreted by the coexistence of AHH-II and ice VII, as in Ref. [3]. At 3.1 GPa, the sample is fluid.

Figure 1(b) shows a high quality pattern collected at 12 GPa. As can be seen in the inset of figure 4(a), the x-ray pattern of the ionic phase differs from the predicted ionic tetragonal structure. A Rietveld refinement using the BCC structure proposed for AMH-VI [2] provides a very good fit, suggesting that the ionic phase can be described by the same substitutionally and rotationally disordered structure as AMH-VI. The same x-ray pattern is observed up to 80 GPa, from 5 to 300K, showing that this phase is stable in this

large P-T range. We determined the EOS of AMH from 2 samples up to respectively 35 GPa and 80 GPa at ambient temperature.

We have also explored the phase diagram of AMH at low T below 15 GPa. Our goal was to determine the influence of the followed thermodynamic pathway on the structure of the AMH sample. The results are depicted in figure 2. On cooling a sample of AMH-VI at 13 GPa (purple thermodynamic pathways in figure 2), no phase transition was observed down to 2 GPa at 200 K. At this pressure, the pattern changed: new peaks appear, some of which can be indexed with AMH-II but not all. Phase III is never observed. On recompression, the x-pattern is gradually modified when reaching the stability range of AMH-IV but its structure remains unknown. The bcc DMA phase appears again at 6.4 GPa -270 K, where it coexists with the low pressure phase. Finally, at 7.4 GPa-300 K, the pure bcc phase is observed. With another sample, we cooled the liquid at 0.2 GPa (green thermodynamic pathways in figure 2). We did not observe the crystallization in AMH-I down to 80 K but obtained an amorphous phase which persisted up to 10 GPa at 80 K. The crystallization in the DMA phase was again observed by warming the sample above 200 K at 12 GPa.

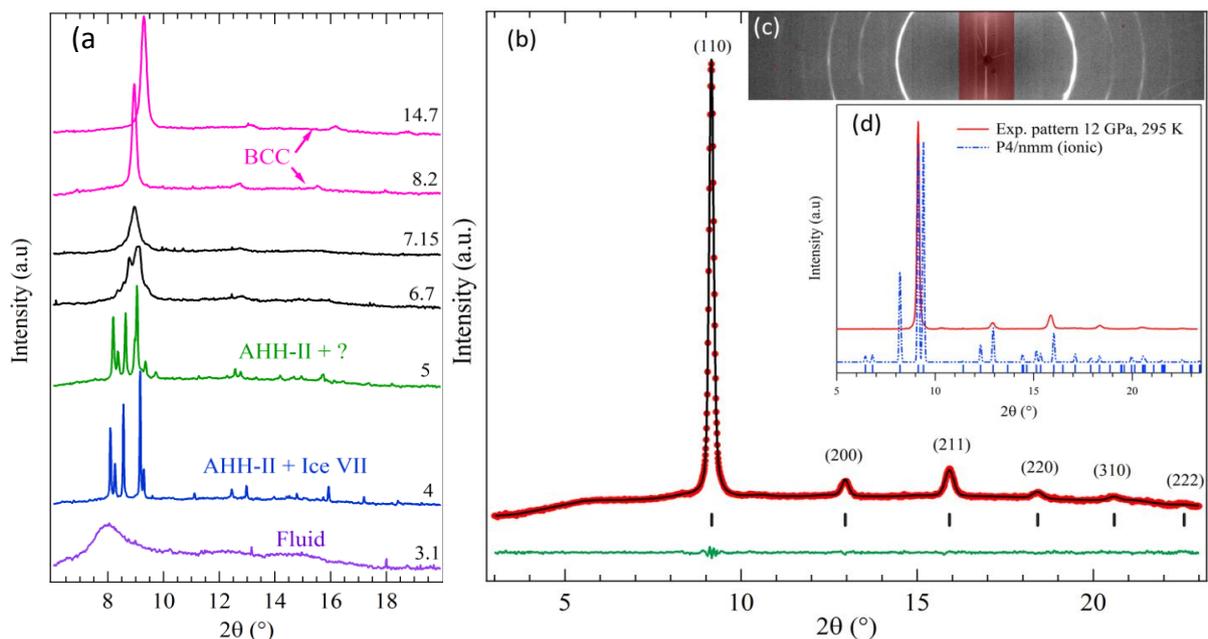


Figure 1 : (a) X-ray evolution of AMH with pressure (b) X-ray diffraction data and Rietveld profile refinements of AMH at 12 GPa. The symbol are experimental data. The red continuous line is the calculated pattern. The difference between the observed and calculated profiles is shown at the bottom with a green curve. In this refinement, the structure is described in the $Im\bar{3}m$ space group : N and O are in position 2a (0,0,0) with a occupation 1/2 and H atoms are distributed on 16f positions (x,x,x) with $x=0.18234$ and occupation of 5/16. Unit cell parameter : $a=3.307$ Å. The inset compares the experimental (red) and calculated (blue curve) X-ray profile of the Pnma ionic structure.

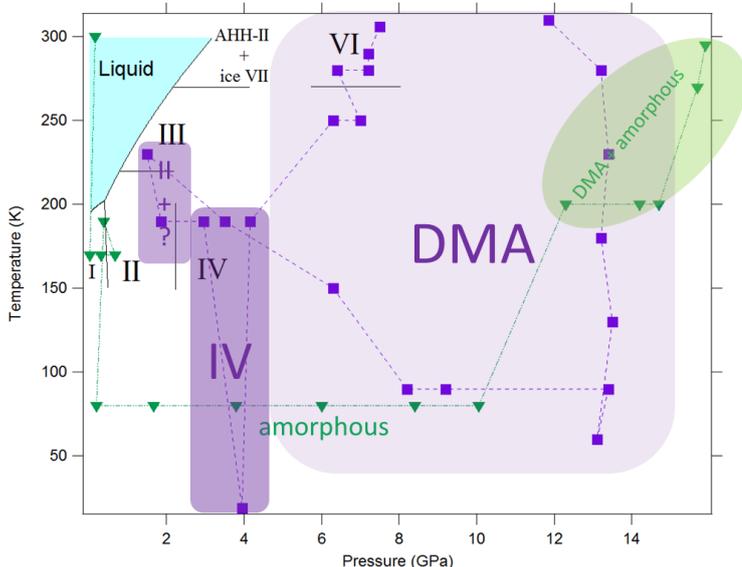


Figure 2 : Phase diagram of AMH at moderate conditions. The green and purple symbols show the different experimental (P,T) data explored with two different samples. We observe that cooling liquid AMH (green curve) at low pressure (0.2 GPa) prevents the crystallisation into phase I and IV.

Conclusions:

This run allowed us to determine the structure of AMH over a large range of P-T conditions: 0.2-80 GPa, 5-300 K. Above 7.5 GPa at room T, the x-ray pattern is always best described by the bcc structure of AMH-VI. The ordered P4/mnm ionic structure predicted by DFT is never observed, even at low T. This shows that the substitutional disorder is maintained even in the partially ionic sample. Following this run, we performed new ab initio calculations which confirm that ionicity is compatible with the disordered structure. Publication of these results is underway [4].

References :

- [1] G. I. G. Griffiths et al, J. Chem. Phys. 137, 64506 (2012)
- [2] J. S. Loveday and R. J. Nelmes, Phys. Rev. Lett. 83, 4329 (1999)
- [3] C. Wilson et al, J. Chem. Phys. 136, 094506 (2012)
- [4] C. Liu, S. Ninet, F. Datchi, et al. (in preparation)