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ESRF

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.

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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.

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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.

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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.

ESRF	**Experiment title:** **Superionicity in ammonia monohydrate at high pressure and temperature**	**Experiment number**: HC2483
Beamline: ID27	**Date of experiment**: from: 22 june 2016 to: 28 june 2016	**Date of report**: 19-09-2016
Shifts: 12	**Local contact(s)**: G. Garbarino	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The aim of this proposal was to study the phase diagram, structures and possible superionicity of ammonia monohydrate (AMH) at high pressures and temperatures. Despite their high relevance for planetary physics, in particular giant icy planets, our knowledge of the properties of ammonia/water compounds are limited to low temperatures (<300 K). In our last proposal HC-1646, we have investigated the solid phases of AMH up to 80 GPa at temperatures from 5 to 300 K. We have evidenced the presence of OH^- and NH_4^+ species at pressures as low as 8 GPa for T≤300 K[1], but the compound does not fully ionize up to 80 GPa contrarily to what DFT predicts [2]. We could explain this discrepancy on the basis of structural data of AMH samples obtained during run HC1646 and DFT calculations. Indeed, we showed that the ionization of AMH occurs in a body-centered cubic (*bcc*) structure, previously observed in [3], where water and ammonia are randomly distributed over the lattice sites, and that this substitutional disorder hinders a complete ionization [1]. The presence of the predicted fully ionic phase P4/nmm is also observed but as a minor phase. We have also investigated the diffusion of the proton at high temperature by *ab initio* calculations. The latter predict that AMH becomes superionic at much milder P-T conditions than the pure ices, as the calculations of the proton diffusion coefficient is 10^{-6} $cm^2.s^{-1}$ at 500 K. The purpose of this experiment was to investigate the structure of AMH at temperatures between 300 and 700 K up to 40 GPa and find evidence for the sueprionic phase.

Results obtained :

We have studied 4 different samples of AMH. The samples were loaded and compressed at ~80 K to pressures greater than 7 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 pressure was measured in situ with a ruby ball or with the EOS of gold.

The first sample (sample A) was heated at 8 GPa up to the melting temperature (~550 K) prior to the ESRF experiment in order to grow a single crystal and cool it down to room temperature. The x-ray diffraction pattern collected at ESRF from this sample shows that its structure is different from that of the DIMA phase or of the ionic P4/nmm phase. We will call this phase the "post HT phase". We have recorded the x-ray diffraction pattern of this compound up to 30 GPa and then on decompression down to 7 GPa. This

phase was found stable in this pressure range. We then heated this compound up to the melting line at 6 GPa-450 K and made a new single crystal. The data collected at high pressure-high temperature shows that the sample is a high quality single crystal and that the Bragg peaks are best indexed by a *bcc* structure. A third single crystal was grown at 8.5 GPa, which also presented a *bcc* strcuture. The sample was then slowly cooled down to ambient temperature where a new set of x-ray diffraction images was collected. The sample remained a single crystal and the XRD images looked similar to those obtained earlier for the "post HT phase". The diffraction pattern of this phase is much more complex than the one of the high temperature *bcc* phase, analysis of the data is still on going.

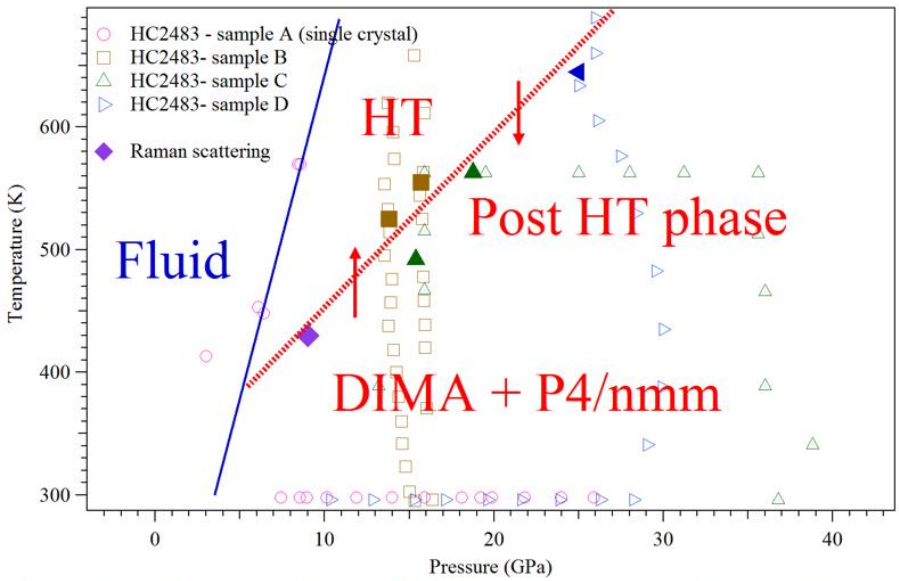

Figure 1 : Phase diagram of AMH at high temperature. The pink, brown, green and blue open symbols show the different experimental (P,T) data explored with four different samples. The transition line between the DIMA/bcc or bcc/"post HT phase" is depicted with the dotted red line.

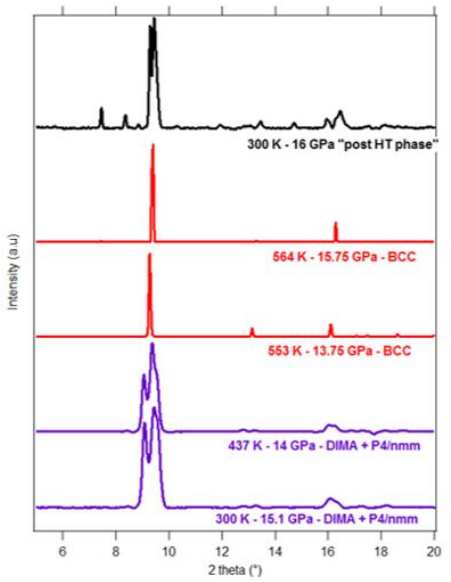

Figure 2 : XRD pattern at various temperature along an isobar (15.00(1.25) GPa) : these data were collected on sample B.

The three other samples were prepared in powder form. The phase transitions from the DIMA (or DIMA+P4/nmm) phase to the high temperature (HT) *bcc* phase and from the HT to the "post HT phase" were observed in the three samples at different pressures and temperatures, as reported in Fig. 1. This data set allows us to draw a phase transition line between the DIMA+P4/nmm mixed phase and the HT phase or from the HT phase to the "post HT phase" as depicted in figure 1. This transition line agrees well with our Raman scattering data showing a phase transition at around 9 GPa and 420 K.

In conclusion, the present experiments show that the DIMA phase of AMH transits to a HT phase of *bcc* structure on annealing at any pressures between 8 and 30 GPa. Futher, the samples do not revert to the DIMA phase on cooling but to a "post HT phase" with a complex XRD pattern. Our ab initio calculations predict that *bcc* AMH is superionic at 500 K, which could explain the observed transition line. This is also supported by the observed changes in the Raman spectrum.

References :

[1] C. Liu, A. Mafety, J.A. Queyroux, C. Wilson, K. Beneut, G. Le Marchand, B. Baptiste, P. Dumas, G. Garbarino, F. Finocchi, J.S. Loveday, F. Pietrucci, A.M. Saitta, F. Datchi and S. Ninet, submitted (2016)
[2] G. I. G. Griffiths et al, J. Chem. Phys. 137, 64506 (2012)
[3] J. S. Loveday and R. J. Nelmes, Phys. Rev. Lett. 83, 4329 (1999)
[4] C. W. Wilson et al., J. Chem. Phys. 142, 094707 (2015)