EUROPEAN SYNCHROTRON RADIATION FACILITY

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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.

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

https://wwws.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.

ESRF	**Experiment title:** Superionic ammonia and water at high pressures and temperatures	**Experiment number:** HC2185
Beamline: ID27	**Date of experiment:** from: 02/26/2016 to: 03/01/2016	**Date of report:**
Shifts: 15	**Local contact(s):** Gaston Garbarino	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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The report below was submitted confidentially to the User Office on 9 march 2018. The data presented have since been published in the following article:

- Jean-Antoine Queyroux, Sandra Ninet, Gunnar Weck, Gaston Garbarino, Thomas Plisson, Mohamed Mezouar, and Frédéric Datchi « Melting curve and chemical stability of ammonia at high pressure: Combined x-ray diffraction and Raman study », Phys. Rev. B 99, 134107 (2019)

Report:
The purpose of this proposal was to study melting curve of NH3 and H2O. The melting line of NH3 has been fewly investigated[1] while melting curve of water was extensively studied[2–14]. The most recent publications highlight a significant disagreement on melting curve of water and ammonia at high temperature. One issue of studying melting curves is to reach high temperature and to measure them (above 1000K). To reach high temperatures (above 1000K) in water and ammonia studies, indirect heating is commonly performed using an absorber heated with YAG laser except for Kimura. The inconvenience of the absorber heating is that it can react with the sample at high temperature and pressure. To limit any chemical reaction, we used CO2 laser heating to heat our compounds directly.

Experimental methods :
We prepared 3 samples of NH3 loaded cryogenically and 2 samples of H2O. Each sample have a gold ring and no pressure calibrant was used in order to prevent any chemical reaction. Pressure was measured with the EoS of gold. NH3 and H2O samples were heated directly using a CO2 laser. The CO2 laser set-up of EH2 require a long alignement for each DAC (around 3-4h) but we have succeeded in aligning the five DACs. Temperatures were measured by optical pyrometry. The melting was measured by the appearance of a liquid diffuse signal. To obtain these liquid diffuse signals, we used Soller slits in order to reduce drastically the Compton scattering from diamond anvils whose are very important for low-Z elements[15,16].

Results :

For NH3, we explored the P-T diagram between 5<P<40 GPa and 300<T<4000K. We succeeded to measure 3 melting points up to 39 GPa (see Fig. 1). Above 39 GPa diamonds of the 2 DACs in temperature were damaged. One of the hypothesis is that, at this pressure and temperature, we were in the area of a superionic phase and that the fast protons diffusion can creates default in diamond and damage it. Currently, we are trying to find a way to reduce the damage of diamonds.
For H2O, we explored the PT diagram between 27<P<62 GPa and 300<T<4500K. We clearly identified 4 melting points up to 45 GPa (see Fig. 2). Above this pressure we could not see any liquid diffuse signal. The melting points did not correspond with the previous experiments reported[7–11,13]. During heating, one sharp peak appeared near the main bcc reflection. This peak was unexpected however Schwager et al.[12] reported a new phase near this region. This peak disappeared when we returned to room temperature. Analysis is on-going but we believe such results are not due to any artifacts or sample pollutions, because we take a lot of precautions to prevent any chemical reaction in our samples (no ruby, no absorber). A Raman spectroscopy will be planed to obtain vibrational information of this possible new phase.

Conclusions :
This run allowed us to explore the melting curve of ammonia up to 40 GPa around 2500K and for water up to 45 GPa at 1500K. For both compounds, the results are very promising. For ammonia we accumulated data sets which converge to a triple point very close to the last melting point. For water we observed a new compound at high temperature and moderate pressure.

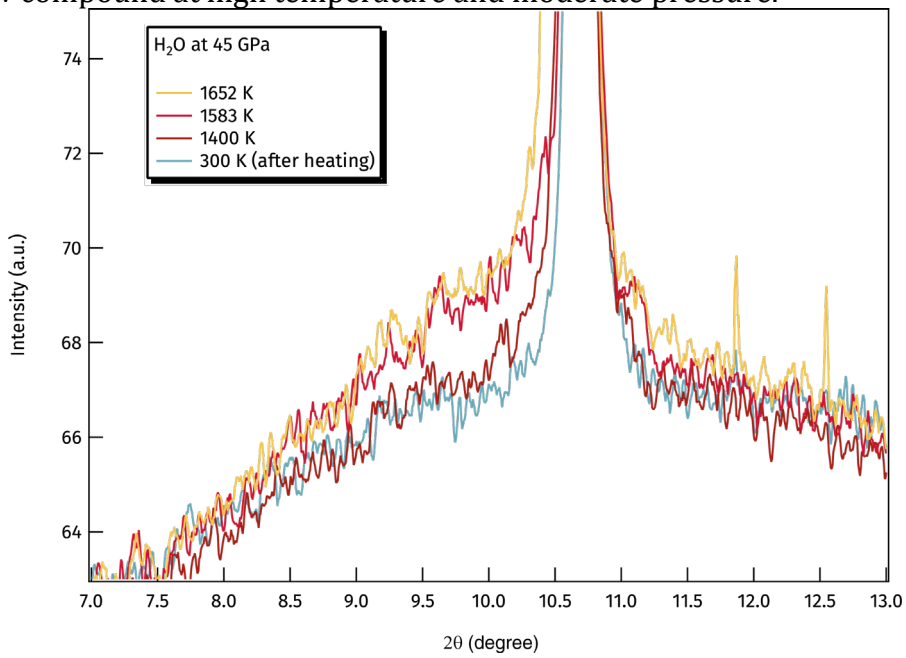

Figure 1 : Patterns of water at 45 GPa and different tempertures. Melting point is T = 1492 ± 100 K

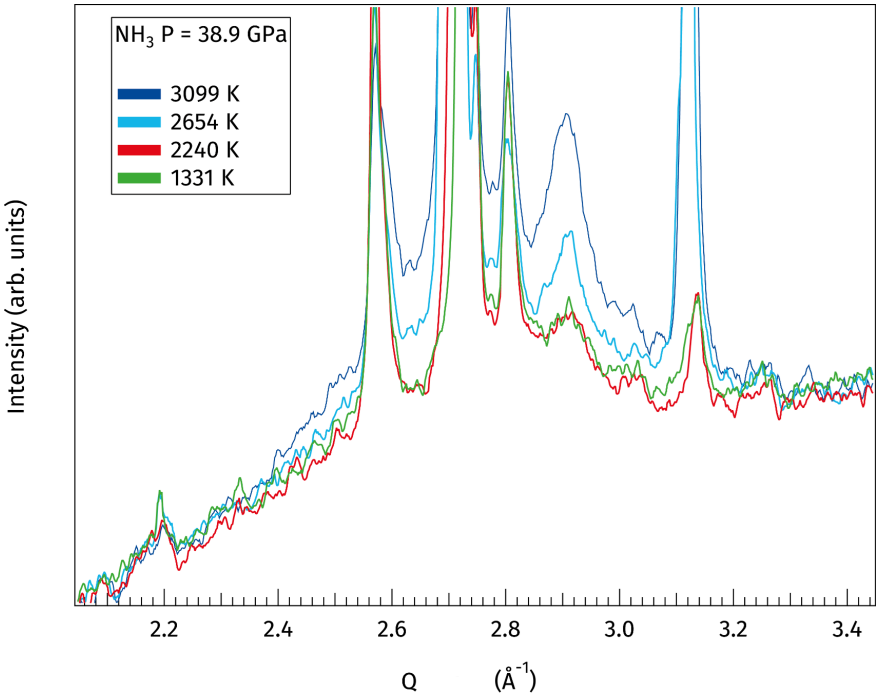

Figure 2 : Patterns of ammonia at 39 GPa and different tempertures. Melting point is T = 2447 ± 207 K

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