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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 at high pressures and temperatures	**Experiment number**: HC1346
Beamline: ID27	**Date of experiment**: from: july 2014 to: july 2014	**Date of report**: 1 mars 2015
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 thermodynamic properties and P-T boundaries of the superionic phase of ammonia. This phase has been observed above 57 GPa and 700 K [1] and is located between the molecular phases and the fluid phases. In this experiment HC1346, we have started to investigate the precise measurements of the melting curve of ammonia as it a good way to access to the superionic phase. Previously, a recent work reported melting points up to ~60 GPa using Raman spectroscopy and indirect YAG laser heating via a Ir coupler, and showed a surprising decrease of the melting temperature above 35 GPa [2]. However, the Raman spectra of the solid and fluid phase at melting are very similar, casting doubt on the ability to detect melting with this method. Moreover, the III/IV transition temperatures reported by these authors are much larger (ΔT=700 K) than those determined by resistive heating [3].

In our experiment, rather than using indirect YAG laser heating via a coupler (NH_3 does not absorb YAG laser), we have used direct heating of NH_3 with a CO_2 laser, thus preventing from any chemical reaction between ammonia and the coupler. Moreover, to detect clearly the melting line, we used the new multichannel collimator in EH2 developed during the long-term project HD463. With this set up, we were able for the first time to observe the x-ray diffraction pattern of liquid NH_3 at high pressure and high temperature. Melting was detected thanks to the appearance or disappearance of the x-ray diffraction of the liquid. In total 4 DACs were loaded in our laboratory with ammonia using a cryogenic method. To measure the pressure, all cells were loaded with ruby and a small piece of gold for which the equation of state is well known. Temperatures were measured by optical pyrometry. Among the 4 loaded cells, only two have been studied because we have had technical problem with the two others DAC dedicated to the high pressure (diamond anvils with 200*300 micron culets) : for one cell, the sample escaped (likely through the anvils) during the laser heating alignement, and for the other one, the gas-input capillary broke when installing the DAC.

Results obtained :

During this run, we could detect melting points of NH_3 up to 30 GPa from the appearance or disappearance of the X-ray scattered diffuse signal of the liquid. For example, figure 1 (c) show the evolution of the XRD pattern of NH_3 across the melting line at 19 GPa. These patterns were collected with an acquisition time of 180 sec. We have removed the Bragg peaks from the solid phase to emphasize the liquid signal. Nonetheless, the diffuse contribution of the solid is still visible and increase with temperature. Remnants of the solid phase are always observed due to the colder layers of sample in contact with the diamond (no thermal insulation layer is used to avoid sample contamination or chemical reaction). There is however a clear difference between the fully solid and solid + liquid patterns, and this can even be more clearly appreciated on the 2D diffraction images where the liquid signal appears as a continuous diffuse halo (see figure 1 (a) and (b)) . This allows a precise determination of the melting line. We have collected 4 (P,T) data for the melting line up to 30 GPa (these data are note presented here because there are not yet published). These point are, within uncertainties, in good agreement with the extrapolation of the melting measurements at moderate temperature obtained with resistive heating [1] and differ from the recent laser heating data of Ojwang et al [2]. At 30 GPa, our measurements of the melting curve incidentally crosses that of Ojwang et al, but we see no evidence for a bending down of the melting line up to 30 GPa as the latter work suggest. We also note that the ordered-disordered solid phase transition could be observed optically in our experiment thanks to the difference in birefringence between the two phases, but the transition temperatures were too low (below 1000 K) to be measured by pyrometry, in agreement with our previous resistive heating measurements [1,3]. We were not able to pursue these measurements to higher pressure because of the technical problems mentionned above. This run can thus be regarded as a half success, due in part to the impossibility of reloading NH_3 on site. We are however confident that we can measure the melting curve of NH_3 to higher pressures, as we have succesfully measured that of N_2, whose scattering power is comparable to NH_3, up to 85 GPa in our last run of HD-463 (see last exp. report of HD-463).

References :

[1] S. Ninet and F. Datchi, ***J. Chem. Phys. 128***, 154508 (2008)
[2] J.G. O. Ojwang et al., ***J. Chem. Phys. 137***, 064507 (2012)
[3] S. Ninet, F. Datchi and A.M. Saitta, ***Phys. Rev. Lett.***,**108**, 165702 (2012)

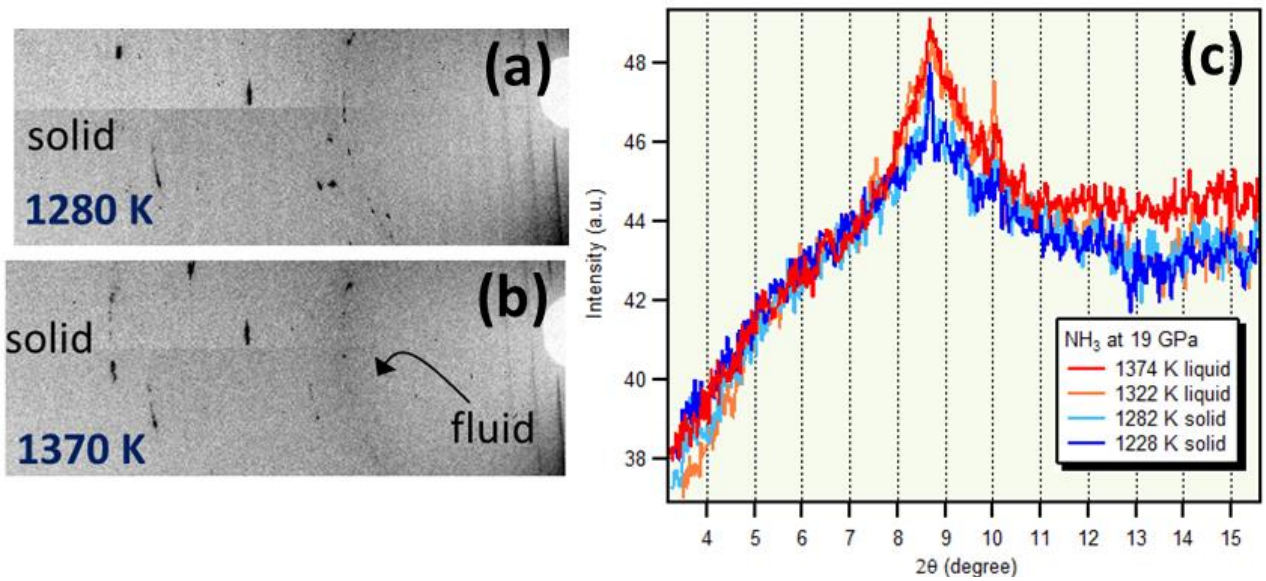

Figure 1 : X-ray diffraction image of NH_3 samples under CO_2 laser heating 19 GPa across the melting line. (a) solid (b) solid + liquid - the liquid signal appears as a continuous diffuse halo (c) evolution of the X-ray diffraction pattern of NH_3 at 19 GPa across the melting line