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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 using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now 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:** **Single-Crystal X-Ray Diffraction Study of the Solid Phases in N_2/H_2 Mixtures Under Pressure**	**Experiment number:** HS4585
Beamline: ID09	**Date of experiment:** from: 17/06/2012 to: 01/03/2011	**Date of report:** 08/03/2013
Shifts: 6	**Local contact(s):** M. Hanfland	*Received at ESRF:*

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Background

Pure N_2 and pure H_2 systems have been extensively studied under pressure. These are model systems for studying the effects of pressure on chemical bonding. Interesting phases have been observed, such as the formation of 'black hydrogen' [1] and the formation of non-molecular poly-nitrogen [2]. The observation of the pressure-induced metallization in these two systems remains a challenge, however the study of N_2/H_2 mixtures under pressure is a potentially promising next step toward this goal. Studies of such mixtures open the possibility for a rich array of chemical effects that are not evident by examination of the end-member components alone: existence of stoichiometric compounds; binary chemical reactivity in the solid solutions and possible new routes to the pressure induced metallization of N_2/H_2 systems. Binary mixtures of N_2 and H_2 with rare gases have already been studied, disclosing two van der Waals compounds, $Ar(H_2)_2$ [3], proposed as a new mechanism for the metallization of hydrogen, and $(N_2)_{11}He$ [4], which shows a structural evolution useful for understanding that of pure solid N_2 [5]. The understanding of the interplay between the pressure-induced chemistry and the various microscopic arrangements has the potential to lead to the synthesis of very interesting solids, including metallic forms of N_2/H_2 and/or polymeric forms of nitrogen doped with hydrogen.

We measured the N_2/H_2 binary phase diagram at 296 K by visual observation and Raman spectroscopy (Fig. 1a). Our results suggested the existence of two N_2/H_2 compounds with visually distinct morphologies under optical microscopy (Fig. 1b). The motivation for this proposal was thus to characterize these newly identified compounds.

Objectives

Six shifts were requested and awarded on ID09 in order to characterize single-crystal samples of the two apparent compounds at high pressure and to determine their structure by means of single-crystal x-ray diffraction. In particular, we aimed to examine the following:

- To identify whether the apparent N_2/H_2 compounds shared structural similarities with the corresponding end-member solid structures.
- Evaluate the pressure-volume equation of state of these structures.
- Examine the possible integration of H_2 into the N_2 lattice and any possible pressure-induced reactivity.

Experimental Technique

Three samples were prepared in our laboratory in wide-aperture (35° cone) membrane diamond anvil cells (MDAC). These were equipped with 150 and 300 µm culet Almax-Boehler anvils. Single crystals were grown by pressurization at room temperature from N_2/H_2 mixtures prepared with concentrations of 60% H_2 and 70% H_2, near the condtions under which the compounds were observed in our lab. The ruby luminescence scale was used to determine pressure.

Angle-dispersive single-crystal diffraction was be carried out using a monochromatic beam (~0.4 Å) focused to 15-30 µm. The samples were were rotated about a vertical axis from -29° to 29° to take advantage of the wide cell aperture while not contaminating the CCD with scattering from the experimental apparatus. Images were be collected in steps of 0.5° using the online MAR555 detector.

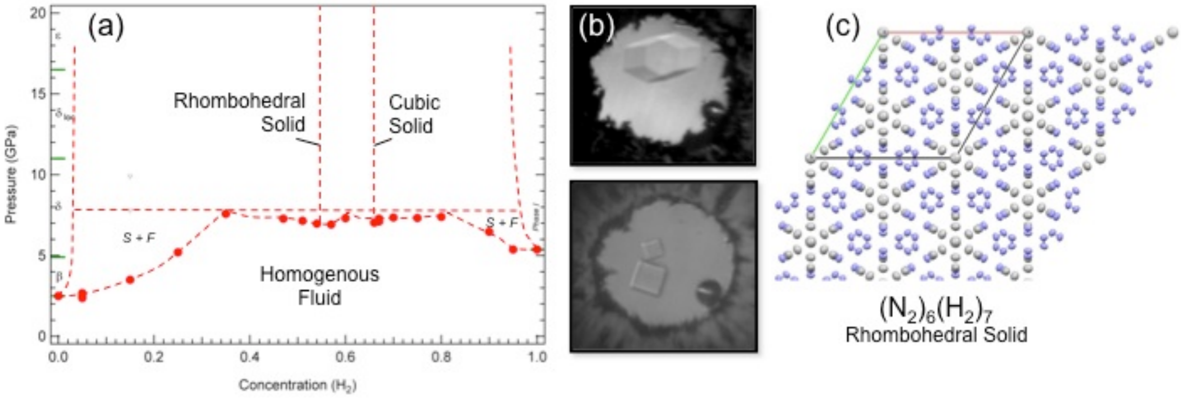

Figure 1: (a) The binary phase diagram for the N_2/H_2 system as measured in our laboratory at the CEA with Raman spectroscopy and visual observation. Two stable compounds have been identified in the solid-state, including a rhombohedral solid at 54% H_2, $(N_2)_6(H_2)_7$, and a cubic solid with a structure close to that of pure N_2 at 66% H_2, $N_2(H_2)_2$. (b) Optical photographs showing the respective morphologies of the single crystals in equilibrium with the fluid. (c) Structure of the rhombohedral solid as determined by single-crystal X-ray diffraction. Molecular nitrogen is represented in blue while molecular hydrogen is shown in grey.

Results

Two of the three samples performed well and yielded good-quality single-crystal diffraction patterns. Though very high-quality data is challenging to collect on such weakly scattering (low-Z) materials, we were able to extract structural information for both of the compounds. We identify them as $(N_2)_6(H_2)_7$ (*R-3m*) and $N_2(H_2)_2$ (*Pm-3m*). In the first case, the structural solutions converge sufficiently well to allow placement of the hydrogen molecules by calculation of the charge distribution and the known stoichiometry (Fig. 1c). In the case of the cubic structure, $N_2(H_2)_2$, peak broadening due to apparent disorder of the N_2 molecules in the lattice complicates the analysis, though it appears likely that the compound shares a structural resemblance to that of pure N_2 at the same pressure.

Though we hoped to carry out equation of state measurements with a third sample equipped for higher pressures, we were unable to carry out these measurements beyond 45 GPa due to a poorly formed crystalline sample. Though we attempted to melt and regrow the crystal in-situ as well as transform the sample to a powder by rapid pressurization, neither attempt resulted in sufficiently high-quality spectra and the remaining beamtime was dedicated to obtaining the best possible structural data below 10 GPa.

Conclusion

The $(N_2)_6(H_2)_7$ compound identified at 54% H_2 concentration presents a novel structure very different from that of pure N_2. As shown in figure 1c, hydrogen molecules (gray) are confined by chain or tube-like arrangements of N_2. This structure thus presents intriguing possibilities for examining the pressure-induced metallization of H_2 by confinement as well as the possible facilitation of poly-N by pre-arrangement of the N_2 molecules in a quasi-linear fashion. Additional studies are underway to characterize these compounds more fully, though the structural data obtained at ID09 has been tremendously important for the synthesis of this project.

References

[1] P.Loubeyre, F. Occelli and R. LeToullec. Nature 416, 613 (2002).

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[3] P.Loubeye, R.LeToullec and J.P.Pinceaux,. Phys. Rev. Lett. 70, 2106 (1993).

[4] W. L. Vos, L. W. Finger, R. J. Hemley, J. Z. Hu, H. K. Mao, and J. A. Schouten, *Nature (London)* **358**, 46 (1992).

[5] S. Ninet, G. Weck, P. Loubeyre, F. Datchi, *Physical Review B*, **83**, 134107 (2011).