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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

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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.

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 $(N_2)_4(Ne)_5$ van der Waals compound: a new path to polymeric nitrogen.**	**Experiment number**: HC-1077
Beamline: ID09	**Date of experiment**: from: 07/10/2013 to: 08/10/2013	**Date of report**:
Shifts: 6	**Local contact(s)**: M. Hanfland	*Received at ESRF:*

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Report

Introduction :

The solid phase diagram of pure nitrogen has been extensively studied and has revealed a rich physics. In particular, the destabilization of the triple bond was observed and two non-molecular phases have been identified: i) at ambient temperature, an amorphous phase (η) is reported above 150 GPa. The pressure evolution of its band gap suggests that metallization begins at 280 GPa [3]. ii) By coupling pressure and temperature (110 GPa and a temperature above 2000 K) nitrogen transforms into polymeric phase with the cg-N structure [1]. We are searching different routes to synthesize polymeric forms of nitrogen; more specifically through the compression of nitrogen van der Waals compounds (stoichiometric compounds with other simple molecules). Up to now, three such van der Waals compounds are known. $(N_2)_{11}He$ has been discovered some years ago [4]. Its structure could be refined and its structural changes under pressure studied up to its amorphization [2]. Recently, our group has discovered two van der Waals compounds by studying N_2/H_2 mixtures, $(N_2)_6(H_2)_7$ and $(N_2)(H_2)_2$ [5]. The structures of these compounds have been successfully characterized at ID09. In particular, the $(N_2)_6(H_2)_7$ compound exhibits a chain-like structure of N_2 molecules with trapped H_2. That is a very unusual structure but the chemical reactivity of N_2 and H_2 under pressure leads to the formation of ionic N-H bonds compound and hampered the polymerization of nitrogen.

By exploring the phase diagram of the N_2-Ne mixture, we evidenced a van der Waals compound. The existence of such a compound had been previously suspected [6]. The aim of this experiment was to determine the structure of this compound, which results to be the same as the structure of $(N_2)_6$ $(H_2)_7$, i.e a rhombohedral structure with large unit cell and formation of chains of N_2 molecules. However, Ne, unlike H_2, is expected to be chemically neutral and should prevent any chemical reaction with N_2, leaving the possibility to observe a different path for the polymerization of nitrogen at high pressure.

Experimental details:

Two samples were prepared, consisting in wide aperture (35° cone) membrane diamond anvil cells (MDAC) in Almax-Boehler configuration, equipped with 300 μm culet diamonds. In the first cell, a pure single crystal of the van der Waals compound was grown at room temperature, from a mixture with a neon concentration of 54%. A ruby luminescence gauge was used to determine pressure.

Angle-dispersive single-crystal diffraction was carried out at ID09 using a monochromatic beam (~0.4 Å) focused to ~15 μm. The sample was rotated about a vertical axis and images were collected in steps of 0.5° over the entire aperture of the DAC using the online MAR555 detector.

In the second sample, a single-crystal was grown from a mixture at a different concentration (45% neon concentration). A part of the sample was filled with a demixing that we analyzed. For this sample, we recorded time integrates images, and we increased the pressure up to 27 GPa.

Results :

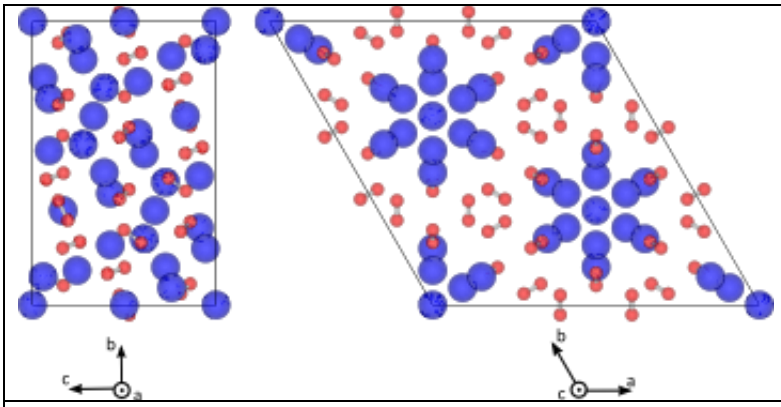

Fig1: Structure representation of the $(N_2)_6Ne_7$ compound. Neon and nitrogen atoms are represented in blue and red respectively. Left: view along the a axis (100 direction). Right: view along the c axis (001 direction).

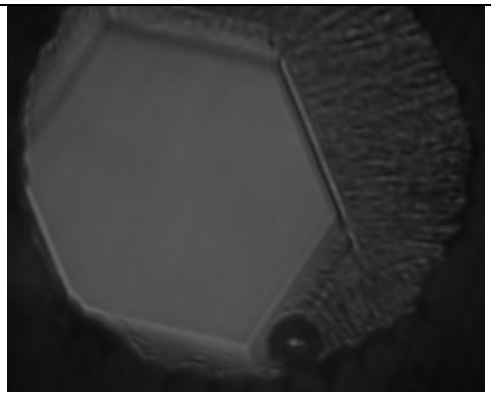

Fig2: Photograph of the second sample. The single-crystal is visible. The remaining part of the sample is filled with a demixing.

Despite the weak scattering of these low-Z elements and the small size of the samples, we were able to collect good-quality diffraction patterns and extract structural information about the compound. It was possible to determine the space group R-3m (hexagonal) and the cell parameters: a = 14.3995 A and c = 8.0939 A at 8.0 GPa and 298 K, using the CrysAlisPro software. The atomic structure has been successfully solved with direct methods implemented in SIR2011 and refined using ShelXL. It is presented in Fig1. It is the same structure as in N_2-H_2, which can be explained by the fact that Ne and H_2 have similar van der Waals interaction potentials.

The analysis of the demixing revealed the presence of the compound and pure nitrogen. We did not find any evidence for the second compound suggested in [6]. This work was recently published in Physical Review Letters [7].

References:

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[5] D. Spaulding, ESRF report, Article in preparation.
[6] M. Kooi, J.Schouten, Phys.Rev. B, **60**, 12635 (1999).
[7] T.Plisson, G.Weck, P.Loubeyre, Phys. Rev. Lett. **113**, 025702 (2014)