EUROPEAN SYNCHROTRON RADIATION FACILITY
INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: Structures of the Van der Waals compounds in N_2-Ar and N_2-Xe systems.	**Experiment number**: hc-1890
Beamline: ID09	**Date of experiment**: from: April 22th 2015 to: April 24th 2015 from: July 5th 2015 to: July 7th 2015	**Date of report**: 17/08/2015
Shifts: 12	**Local contact(s)**: Gaston Garbarino and Michael Hanfland	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dominique Laniel* – CEA, Bruyères-le-Châtel, DPTA/SPMC, LHPS

Gunnar Weck* – CEA, Bruyères-le-Châtel, DPTA/SPMC, LHPS

Thomas Plisson* – CEA, Bruyères-le-Châtel, DPTA/SPMC, LHPS

Objectives

The study of N_2-rare gas systems is demonstrating a rich auto-organization of molecular systems under pressure. The first van der Waals compound was observed in N_2-He system, as $(N_2)_{11}He$ [1] and its structure explained by the substitution of N_2 molecules by He atoms at specific sites of the ε-N_2 structure [2]. The first clathrate organized by the quadrupolar interaction has been recently discovered in the N_2-Ne system, as $(N_2)_6(Ne)_7$ [3]. Van der Waals compounds also exist in N_2-Ar and N_2-Xe systems [4]. The aim of this proposal was to determine their associated structures. Intriguing arrangements of N_2 molecules are certainly to be discovered by this study.

April 22th to April 24th 2015

Experimental method

Three membrane diamond anvil cells were equipped with anvils of 150, 400 and 500 µm in culet size, respectively. All cells were loaded with a Xe-N_2 mixture, with xenon concentrations of 7 (2x) and 67 mol%. All samples were brought to the ESRF at pressures lower than 2.5 GPa. Ruby was used as a pressure gauge. Angular dispersive powder X-ray diffraction was performed with a monochromatic beam of energy E = 30 keV at the ID09 beamline. The X-ray diffraction images were collected with an on-line image plate detector (MARCCD). The beam was focussed down to ~ 25 µm.

Results

Samples with xenon concentrations of 67, 7 and 7 mol% were studied up to 6, 25 and 81 GPa, respectively. For all samples, two phases were observed below 5 GPa. One was found to be pure nitrogen while the other was attributed to a xenon-rich solid (see Fig. 1). The xenon-rich solid has the structure of pure xenon (*Fm3m*) but a very slightly different volume. Since its cell volume is not largely above that of pure xenon, it was assumed that nitrogen atoms inserted themselves in the lattice by substituting xenon atoms.

Above 5 GPa, a new phase corresponding to a van der Waals compound was revealed (see Fig. 1 a) and b)). Its Bravais lattice along with its space group and stoichioimetry were determined.

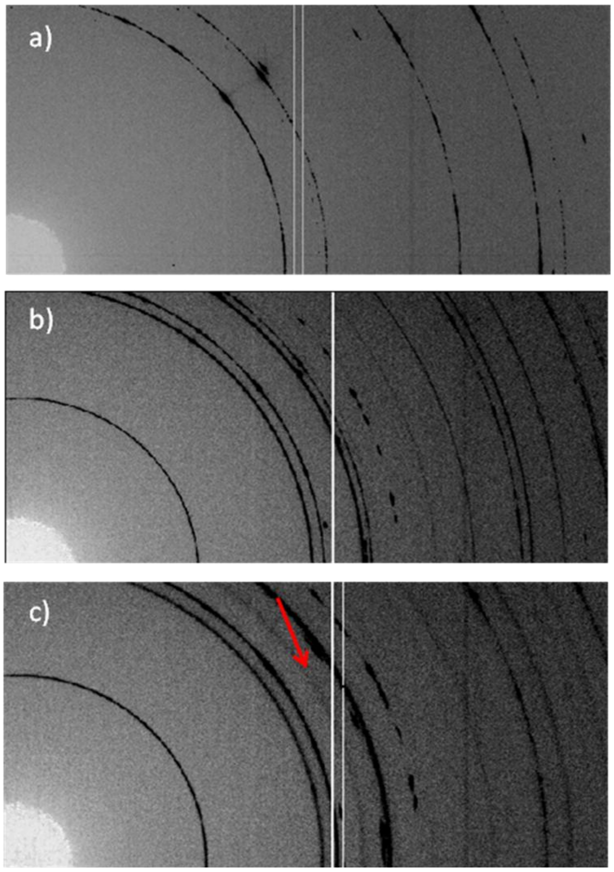

Figure 1: Diffraction patterns, a) 4.8 GPa, only pure nitrogen and the xenon-rich solid can be seen. b) 5.5 GPa, numerous high-quality rings appear, belonging to the van der Waals compounds. c) 10.3 GPa, a phase transition occurs and is characterized by the new diffraction ring evidenced by the red arrow.

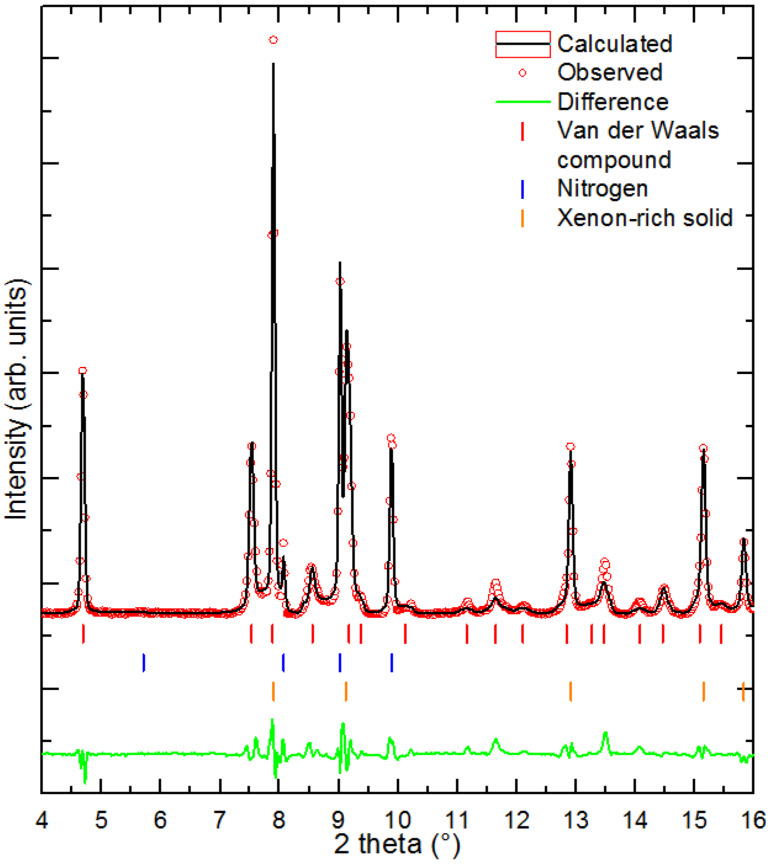

Figure 2: Rietveld raffinement of the diffraction pattern taken at 10.3 GPa. It validates the Bravais lattice, space group, stoichiometry of the van der Waals compound and allowed the determination of the atomic positions of nitrogen and xenon.

A phase transition occured in the van der Waals compound at ~ 10 GPa (Fig. 1c)). Again, the Bravais lattice was determined along with the space group. The stoichiometry of the compound persisted through the phase transition. From the Rietveld refinement shown at Fig. 2, the Wyckoff position of the xenon and nitrogen atoms in the high pressure phase was resolved. This phase was found stable up 81 GPa; the highest pressure reached.

July 5th to July 7th 2015

Experimental method

Three membrane diamond anvil cells were equipped with anvils of 100, 300 and 400 µm in culet size, respectively. All cells were loaded with a Xe-N_2 mixture, with xenon concentrations of 7 (2x) and 30 mol%. In order to validate the structural parameters previously determined, single crystals of the van der Waals compound low pressure phase were grown. Xe-N_2, with 7 mol% of xenon, solidifies at 2.5 GPa whereas the van der Waals compound is stable only above 5 GPa. Therefore high temperatures acheived by resistive heating were necessary to have the solid Xe-N_2 compound in equilibrium with the liquid phase and grow a single crystal. Too high temperatures are required to similarly produce a single crystal of the van der Waals compound high pressure phase. Therefore, once the necessary single crystal diffraction images of the low-pressure phase were taken, pressure was increased above 10 GPa with the cells heated. The samples transitioned to the high-pressure phase while at high temperatures, with the hopes of minimizing crystal damage. Ruby and gold were used as pressure calibrants. Angular dispersive X-ray diffraction with a monochromatic beam of energy E = 30 keV was performed at the ID09 beamline. The X-ray diffraction images were collected with an on-line image plate detector (MARCCD). The beam was focussed down to ~ 25 µm.

Results

The single crystal X-ray diffraction of the low pressure phase (see Fig. 3) allowed us to confirm the previously determined lattice and space group. The full structural resolution has not yet been completed at this stage of the analysis. Despite occuring at high temperatures, the phase transition from the low to the high pressure phase significantly damaged the crystal. Data quality is not sufficient for a complete structural resolution of the high pressure phase.

The cell equipped with anvils of 100 µm in culet size allowed to reach a pressure of 154 GPa. The high pressure phase of the van der Waals compound was still stable at that pressure.

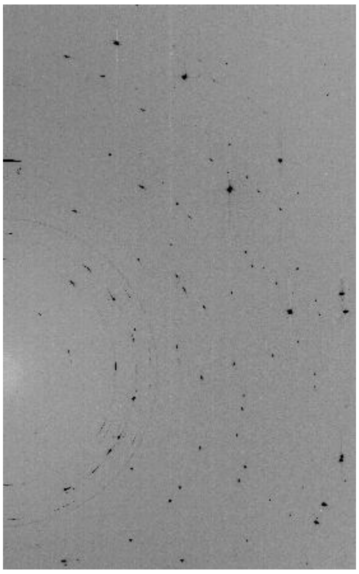

Figure 3: Diffraction pattern obtained from a single crystal of the van der Waals compounds of Xe-N_2 at 8.2 GPa. The cell was rotated by ± 32° during the acquisition. The faint diffraction rings and diffraction spots belong to the xenon-rich solid and the van der Waals compound, respectively.

The structural studies of Xe/N_2 van der Waals compound was more demanding than expected and so no beamtime could be devoted to the structural studies of Ar/N_2 compounds. That will be performed by the application of a continuation proposal.

References

[1] M. Eremets, A. Gavriliuk, I. Trojan, D. Dzivenko, and R. Boehler, *Nature Materials* **3**, 558 (2004).
[2] S. Ninet, G. Weck, P. Loubeyre, and F. Datchi, *Phys. Rev. B* **83**, 134107 (2011).
[3] T. Plisson, G. Weck and P. Loubeyre, *Phys. Rev. Lett.* **113**, 025701 (2014).
[4] M. Kooi and J. Schouten, *Phys. Rev. B* **60**, 12635 (1999).