ESRF	**Experiment title:** Determination of nitrogen's phase diagram up to 400 GPa	**Experiment number**: HC-4881
Beamline: ID27	**Date of experiment**: from: May 31st 2022 to: June 3rd 2022	**Date of report**: 11.08.2022
Shifts: 9	**Local contact(s)**: Gaston Garbarino	*Received at ESRF:*

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Report:

Objectives

This proposal's goals were to uncover nitrogen's phase diagram between 180 and 400 GPa, discover novel polymeric phases and solve their structure with single-crystal X-ray diffraction (SC-XRD). These experiments also aimed at challenging current theoretical models and unveiling novel forms of polynitrogen arrangements, providing a rare, but crucial, example of the behavior of simple homoatomic systems at ultrahigh pressures.

It must be emphasized that these planned experiments were very ambitious—though realistic—both regarding the samples' preparation as well as the beamline's performance. Regarding the latter, it must be emphasized that such experiments had not yet been attempted.

Results

To accomplish the objectives of this proposal, three toroidal diamond anvil cells (DAC), each with a culet size of 40x300 μm (DAC1), 40x300 μm (DAC2) and 60x300 μm (DAC3), were carefully prepared. This anvil geometry is now routinely used at the CEA to reach static pressures above 300 GPa. The DACs were loaded with N_2 and precompressed to a pressure of ~150 GPa before arrival to the ESRF. Exceeding this pressure would have led to the nitrogen sample becoming completely opaque, preventing the alignment of ID27's YAG lasers employed for sample laser heating. However, with the nitrogen sample being transparent at 150 GPa, the YAG lasers could be properly prealigned on the sample before further pressure increase.

At the beamline, upon running the single-crystal calibrant DAC and later the nitrogen toroidal DACs, a number of stability issues with the beamline were found. Amongst minor problems, sample motors and pinhole drift were also observed, precluding high-quality data to be obtained. Figure 1 shows two consecutive X-ray diffraction mappings of the sample which illustrates the effect of the sample drifting about 5 microns vertically and 2 microns horizontally in just a few minutes. This, combined with the requirement of a submicron beam and the submicron size of the nitrogen crystallites of interest for single-crystal data acquisition, prevented the collection of good quality data. The staff of ID27 was extremely helpful in trying to solve these issues, spending even good portions of the nights with us at the beamline. However, as it was found out after our beamtime, the problem—*i.e.* too large temperature fluctuations inside the experimental hutch—was outside the realm of moderately quickly solvable issues. We have been informed that this problem has now been fixed.

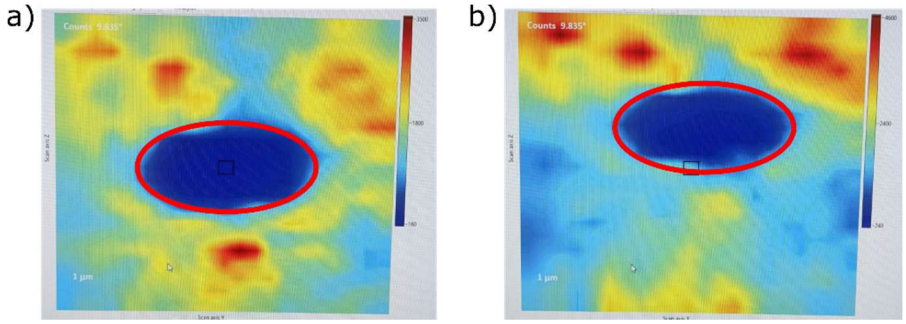

Figure 1: Two X-ray diffraction maps of the same sample after laser-heating at 300 GPa, with a) obtained immediately before b). The red oval represents the nitrogen sample. While the two maps should have been identical, due to sample motors drifting, between the two measurements the sample moved by about 5 microns vertically and 2 microns horizontally in the span of a few minutes.

Nonetheless, pressure was increased on the DACs and data was still collected, providing some insight into nitrogen's phase diagram. DAC1, DAC2 and DAC3 were respectively compressed to 295, 292 and 194 GPa. While the diamond anvils of DAC1 broke before laser-heating could be attempted, DAC2 and DAC3 were laser-heated to temperatures above 2000 K at their maximum pressure. In DAC2, we did not observe any diffraction signal originating from the nitrogen sample. This DAC was kept at this pressure and planned to be further characterized at the CEA with Raman spectroscopy. In DAC3, still close to 200 GPa after laser-heating, clear diffraction spots were observed. Part of these reflections was found to belong to the nitrogen sample and could be indexed to the known bp-N phase.[1] This, in itself, is a very interesting result as, hitherto these measurements, the bp-N phase stability range was only known to extend up to about 160 GPa (see Figure 2). Other single-crystal reflections—mainly found at the interface between the nitrogen sample and the rhenium gasket and thus assumed to belong to a new Re-N compound—could not be indexed to a unit cell. Further measurements will need to be performed to solve the crystal structure of this compound.

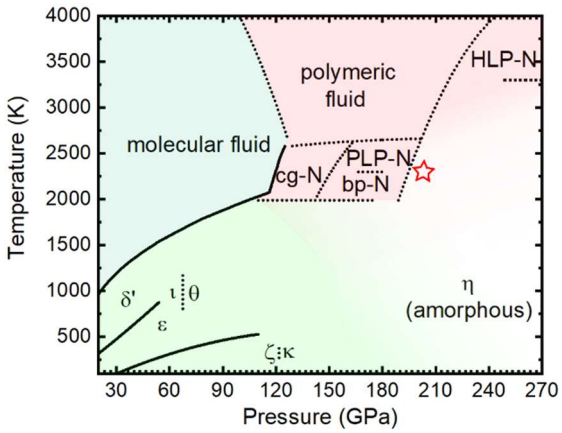

Figure 2: Known phase diagram of nitrogen before the experiments performed during HC-4881. The red star represents the synthesis of the bp-N phase near 200 GPa and above 2000 K. This datapoint extends the phase stability region of the bp-N phase from the previous known limit of 160 GPa to ~200 GPa.

With this beamtime, we demonstrated our capability to reach multi-megabar pressures on pure nitrogen, successfully laser-heat such tiny samples and collect single-crystal X-ray diffraction on these polycrystalline samples. Now that the ID27 beamline has been further tested—and with issues related to the temperature-induced drift of the motors fixed—we are confident that, with further beamtime, we will be able to unveil the phase diagram of nitrogen up to 400 GPa and solve the structures of the phases to be discovered. Additional measurements on the presumed Re-N will also be required.

References

1. Laniel, D. *et al.* High-pressure polymeric nitrogen allotrope with the black phosphorus structure. *Phys. Rev. Lett.* **124**, 216001 (2020).