Report on exp. HS 3381

Motivations:

Several experiments have already been done on pure nitrogen and have reported a sequence of molecular-molecular phase transition below 120 GPa: the rhomboedric ε-phase of nitrogen transforms at 60 GPa in the ζ-phase (orthorhombic); this phase is stable up to 110 GPa and is followed by a monoclinic κ phase [1]. The destabilisation of the triple bond has been experimentally observed and two non molecular phases have been identified:

- At ambient temperature, an amorphous phase η above 150 GPa is reported. The pressure evolution of its band gap suggests that metallisation begins at 280 GPa [2].
- by coupling pressure and temperature, nitrogen transforms into polymeric phase with the cg-N structure [3].

All these experiments were performed in non hydrostatic conditions. The aim of the present experiment was to use a new route to synthesize a non molecular phase of nitrogen by compressing a single-crystal of the Van-der-Waals compound $(N_2)_{11}He$ in hydrostatic conditions.

Experimental Method:

One membrane diamond anvil cells with high X-ray aperture ($2\theta_{max}$ = +/- 37°) was loaded in our laboratory with a 3% mol N_2 of N_2/He mixture at ambient temperature and high pressure (800 bars). A single-crystal of $(N_2)_{11}He$ (see photograph 1), embedded in helium hydrostatic pressure transmitting medium, was grown in the middle of the experimental chamber. At 97 GPa, the typical size of the sample was 50 μm in diameter with a single crystal of 20 μm in diameter. We performed angular dispersive X-ray diffraction with a monochromatic beam at the ID9 beamline. The X-ray diffraction images were collected with an on-line image plate detector (MAR3450). The beam was focussed down to 20 μm in diameter. The sample was compressed up to 97 GPa.

Results:

The figure 2 shows a diffraction pattern of the single crystal at 18.3 GPa. All the diffraction peaks can be related to the same orientation matrix (hexagonal unit cell). A systematic extinction has been observed: (00l) with l odd. The dimensions of this unit cell are close to those of the ε-phase of N_2. The diffraction peaks have been followed up to 97 GPa and a phase transition (characterised by a splitting of some diffraction peaks) has been observed at 30 GPa. All new d-spacings can't be indexed in the primary hexagonal unit cell. The observed splitting exhibits analogy with the ε-ζ phase transition of nitrogen but is observed at lower pressure (60 GPa in pure nitrogen). The determination of the unit cell of the new phase is in preparation.

The essential output are:

- the $(N_2)_{11}He$ VdW compound is stable up to 100 GPa
- the phase transition at 30 GPa maps the $\varepsilon \rightarrow \zeta$ phase transition of pure nitrogen
- the single-crystal data should allow to refine the structure of the VdW compound.

Fig 1: Coexistence of single crystal of $(N_2)_{11}He$ with rich fluid He – 300 K; 11.5 GPa

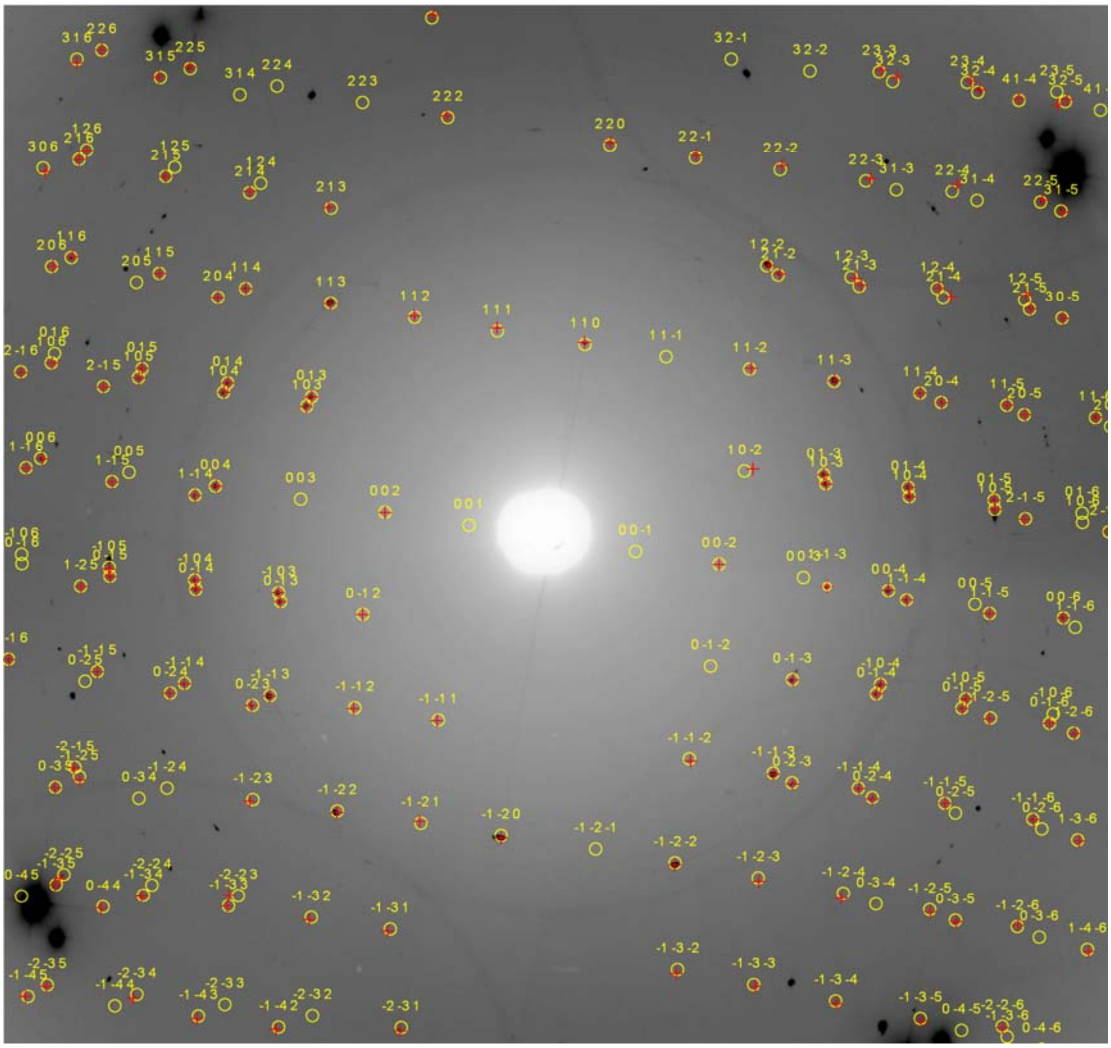

Fig 2: Diffraction image: Single-crystal $(N_2)_{11}He$ (18.3 GPa) - yellow circles: predicted peaks; red crosses: observed peaks

References:

[1] E. Gregoryanz, *J. Chem. Phys.*, **126**, 184505 (2007) and cited references
[2] E. Gregoryanz et al, *Phys. Rev. B*, **64**, 502103 (2001)
[3] M.I. Eremetz et al, *Nature Materials*, **3,** 558 (2004)