



	<b>Experiment title:</b> X-ray diffraction of solid ammonia at very high pressure : structure determination and search for the symmetric state	<b>Experiment number:</b> HS-2360
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## Report:

This project is the continuation of our investigation of solid ammonia by single-crystal x-ray diffraction at very high pressures. In the previous run (report HS 2140), we demonstrated for the first time that x-ray diffraction experiments on a single crystal of NH<sub>3</sub>-IV, grown in the sample chamber of a diamond anvil cell, was feasible. This represented a major improvement compared to previous attempts on HP structural investigations of ammonia with x-rays, which were strongly limited by the poor quality of the powder samples [1]. Briefly, this allowed us to:

- 1) end the controversy on the structure of phase IV (stable at 300 K and P>4 GPa) between previous powder x-ray and neutron investigations and unambiguously confirm the space group found by the neutrons experiments on ND<sub>3</sub> [2];
- 2) obtain very accurate data on the P-V equation of state (EOS) up to 95 GPa, which almost doubles the pressure range previously achieved;
- 3) obtain evidence for structural changes at about 12 and 60 GPa.

The aim of this second run was 1) extend the investigation to higher pressures in order to probe for new phase transitions and in particular search for the state with symmetrized hydrogen bonds (see report HS2140) 2) perform x-ray diffraction on ND<sub>3</sub> to uncover the isotopic effects and 3) obtain more structural information on the transitions observed at ca. 12 GPa in NH<sub>3</sub>.

Several diamond anvil cells were loaded with either  $\text{NH}_3$  or  $\text{ND}_3$ . The latter was achieved by filling a sealed volume around the anvils with liquefied  $\text{ND}_3$  (isotopic purity 99.7%). One of the cells was loaded with a  $\text{NH}_3/\text{Ar}$  mixture (20/80) in order to see whether a single crystal of  $\text{NH}_3$  could be grown inside a Ar pressure medium. We observed demixing of argon and ammonia in the liquid and solid phases; however we were unable to obtain a single crystal of ammonia. The other samples were surrounded by a gold liner to improve the hydrostaticity of compression compared to bare rhenium gaskets. We used ruby balls and  $\text{SrB}_4\text{O}_7:\text{Sm}$  powder as pressure calibrants. Single-crystals of (deutero-)ammonia III were grown from the liquid phase at 295 K, 1 GPa. We used the angle-dispersive diffraction (ADX) set-up with a monochromatic beam (0.417 Å) at ID09B. The x-ray spot was focussed down to about 20  $\mu\text{m}$ . The DACs could be rotated along the vertical axis perpendicular to the x-ray beam. Slits machined in the diamond backing plates made out of c-BN allowed  $\pm 25^\circ$  rotation without the beam touching the plates, yielding very clean diffraction images. The use of c-BN allowed us to reach very high pressures compared to the Be backing plates used in standard single-crystal ADX in DAC.

Diffraction images of  $\text{ND}_3$  were obtained at pressure between 1.7 and 60.5 GPa. We collected full-angle rotation images at each pressure and angular-resolved scans (steps of  $0.5^\circ$ ) at 4 GPa (after the III to IV phase transition) and 47 GPa. We used the latter scans to deduce the orientation matrix of the sample. As for the  $\text{NH}_3$  samples studied in the first run, all the reflections observed after the phase III to IV transition could be related by a unique orientation matrix, although the mosaicity of the crystal was rather large (a few degrees). The peaks are best correlated by an orthorhombic cell and the systematic extensions of (h00)  $h=2n+1$ , (0k0)  $k=2n+1$ , (00l)  $l=2n+1$  points to the space group  $\text{P}2_12_12_1$  as found by the neutron experiments [2]. At pressures above 18 GPa, we observed the sudden appearance of new reflections. These reflections have d-spacings compatible with the orthorhombic cell, however cannot originate from the initial crystal. This is reminiscent of our previous observations in  $\text{NH}_3$  at  $P>12$  GPa. Using the scan at 47 GPa, we found that these new reflections could be explained by the appearance of a second crystal with same apparent symmetry. Unfortunately the quality of the crystals at these pressures is not good enough to extract the intensities and solve the structure. It is necessary to improve the hydrostaticity of the pressure medium to get better crystals at these pressures.

Another run was performed on  $\text{NH}_3$  to explore the structure at very high pressures. We started with a sample at 10 GPa and collected diffraction images up to 120 GPa, pressure at which one anvil failed. The unit cell parameters and volume could be extracted to this pressure. No further structural change was observed between 95 GPa, our previous highest pressure and 120 GPa. This means that the symmetric state occurs at higher pressure if at all. However we confirmed the change in compressibility at pressures beyond 60 GPa, indicating a new phase transition.

Contrarily to the conclusions of a Raman study [3], we thus found that the transition to phase V is also present in  $\text{ND}_3$  although at a pressure higher by 6 GPa compared to  $\text{NH}_3$ . As for  $\text{NH}_3$  this transition is accompanied by a change in the slope sign of the  $c/a$  ratio, although the amplitude of the slope change in  $\text{ND}_3$  is smaller. The volume of  $\text{NH}_3$  and  $\text{ND}_3$  were compared as a function of pressure. Interestingly, we find that the isotopic shift  $V(\text{NH}_3) -$

V(ND<sub>3</sub>), which is positive at low pressure as expected, vanishes and become slightly negative at pressures above ca. 15 GPa, ie at the middle of the IV to V respective transition pressures of the two isotopes.

In conclusion, the use of single-crystal samples for x-ray diffraction experiments solved many problems of previous structural studies on ammonia and allowed to unambiguously specify the orthorhombic unit cell and space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> of phase IV. Solution of the structure would require better sample that might be obtained by using rare gas (Ne, He) as pressure medium if possible. We were able to measure the lattice parameters and equation of state with high precision to 120 GPa and measure the isotopic shift between NH<sub>3</sub> and ND<sub>3</sub>. The phase transition at 12 GPa in NH<sub>3</sub> (18 GPa in ND<sub>3</sub> ) was clearly evidenced by the sudden appearance of new reflections that can be interpreted as originating from a second crystal. This is accompanied by a sharp kink in the c/a ratio. We cannot detect a volume discontinuity nor change in the symmetry, which would indicate an isostructural transition. At P>60, we also detect a change in the compressibility of our samples, indicating here again a new transition.

## References

- [1] J. Otto *et al.*, J. Phys. Chem. Solids, **50**,171 (1989); M. Gauthier *et al.*, Proc. of the XV AIRAPT International Conference, Warsaw. World Scientific Publishers (1996).
- [2] S. Klotz *et al.*, Appl. Phys. Lett.,**67**,1188 (1995); J. Loveday *et al.*, Phys. Rev. Lett.,**76**,74 (1996).
- [3] M. Gauthier *et al.*, Phys. Rev. B, **37**, 2102 (1988) ; Ph. Pruzan *et al.*, Int. J. Thermophys., **11**, 259 (1990)