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| | Experiment title: Phase diagram and equation of state of hydrogenous and deuterated ammonia up to the megabar range | Experiment number: |
| Beamline: ID30 | Date of experiment: from: 03/03 to: 04/03 | Date of report: 25/07/03 |
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| Names and affiliations of applicants (* indicates experimentalists): *F. Datchi, Lab. PMC, Univ. Pierre et Marie Curie, Paris, France. *M. Gauthier, Lab. PMC, Univ. Pierre et Marie Curie, Paris, France. *B. Canny, Lab. PMC, Univ. Pierre et Marie Curie, Paris, France. *S. Ninet, Lab. PMC, Univ. Pierre et Marie Curie, Paris, France. *F. Decremps, Lab. PMC, Univ. Pierre et Marie Curie, Paris, France. | | |

Report:

Ammonia, like water, belongs to the important group of molecular ices with major abundance in the solar system. Jovian planets like Neptune and Uranus are mostly composed of these ices (H_2O , NH_3 , CH_4) under extreme conditions of pressure and temperature. Hence there exists a natural interest in studying these compounds at high pressure. Moreover, ammonia presents a fundamental interest in condensed-matter physics, in common with water ice, due to the presence of hydrogen bonds. These are weaker in ammonia than in water since 3 H atoms instead of 2 share an electronic lone pair. Whereas the symmetric state of water ice, the so-called ice X, has been observed experimentally, that of ammonia, also expected at high density, hasn't yet. In a general manner, the phase diagram of ammonia is very poorly known. Some questions remain about the structure of phase IV stable above 4 GPa. Also, do phases V and VI, that have been suggested from Raman experiments at respectively 15 and 60 GPa [1], but not confirmed by X-ray [2], really exist ?

This was the aim of this experiment to answer these questions. X-ray diffraction has been performed on NH_3 on ID 30. Previous x-ray works on ammonia under pressure were all hampered by the problem of making a good powder. As a matter of fact, ammonia has a strong tendency to recrystallize, which makes it very difficult. We decided to overcome this problem by doing single-crystal diffraction. If it is relatively easy to obtain a single crystal in the phase adjacent to the liquid at 300 K (phase III, $P=1$ GPa), there remained to be shown that the crystal would survive the III-IV first order transition at 4 GPa (phase IV not being accessible from the liquid). Diffraction images obtained at the ESRF showed that despite the

transition the crystal remained of good-enough quality to perform the experiment. Actually, although the angular width of the reflections were relatively broadened (about 1-2° after the transition), the reflections were all related to the same orientation matrix, i.e. to the same crystal.

Experiments were performed on ID 30 using the monochromatic ($\lambda=0.3738 \text{ \AA}$) angular-dispersive single-crystal diffraction set-up. The experimental volume of several membrane diamond anvil cells (MDAC) were filled with liquid ammonia at 5 bar and 5°C with the help of a loading device designed in our laboratory. The MDAC has a large x-ray aperture (74°) thanks to the use of x-ray transparent diamond seats (made out of B₄C or c-BN). The x-ray beam was focussed down to $\sim 10 \times 10 \text{ \mu m}^2$. Pressure was measured with the luminescence from a ruby ball. Reflections were collected with a plane detector (MAR3450 or Bruker CCD 6500). Three different samples were compressed up to 31.5, 50 and 95 GPa respectively.

In contrast to previous x-ray works on powder, our results confirm the primitive orthorhombic structure (space group P2₁2₁2₁) of phase IV obtained by neutron diffraction experiments on ND₃. Weak reflections allowing to distinguish the primitive structure from a centered one could be observed for the first time with x-ray. Up to 47 reflections were used to determine the cell parameters a, b and c . The specific volume was then measured with an accuracy better than 0.2% up to a compression factor $V/V_0=0.39$ (Fig. 1).

Several observations were made that suggest structural changes at about 13 GPa. First, for the two samples that reached the highest pressures (and which had similar sizes), we observed the sudden appearance of new peaks coupled to the extinction of others. These new reflections can nevertheless be indexed in the same space group and no volume discontinuity is detected. Second, the intensity of the (hkl) reflections such that $h+k=2n+1$ increase by an order of magnitude from 5 to 15 GPa. Third, the ratio c/a and c/b increase slightly up to 13 GPa and then falls sharply up to 20-25 GPa where they stabilise to a lower value. These observations suggest an isostructural phase transition with no volume discontinuity, that is most certainly of second or higher order.

Further, the measured volume at $P>60$ GPa significantly deviates from its extrapolation from lower P values given by any EOS model (Vinet, Holzapfel, Birch-Murnaghan). In the mean time, we observe another decrease in c/a after a stable regime. This could also indicate a phase transition. Note that the pressures where we observe structural changes are well correlated with those obtained in Raman experiments [1]. However, we can exclude the cubic structures suggested in Ref. 1, as well as the symmetrization of the H-bonds.

A more detailed analysis of the structure is required to uncover these subtle changes. However this requires more extensive data and this will be proposed for a new run. Also, we lacked time to investigate ND₃. This should also be part of the next run as it would be interesting to see if the observed changes in NH₃ are present in ND₃. As a matter of fact, a Raman investigation saw no change up to 40 GPa, in contrast to NH₃. This might suggest that the 13 GPa transition is linked to the quantum nature of the proton.

References :

1. M. Gauthier *et al.*, *Phys. Rev. B*, **37**, 2102 (1988).
2. J.W. Otto *et al.*, *J. Chem. Phys. Solids*, **50**, 171 (1989).
3. J.S. Loveday *et al.*, *Phys. Rev. Lett.*, **76**, 74 (1996)
4. Ph. Pruzan *et al.*, *Int. J. Thermophys.*, **11**, 259 (1990)

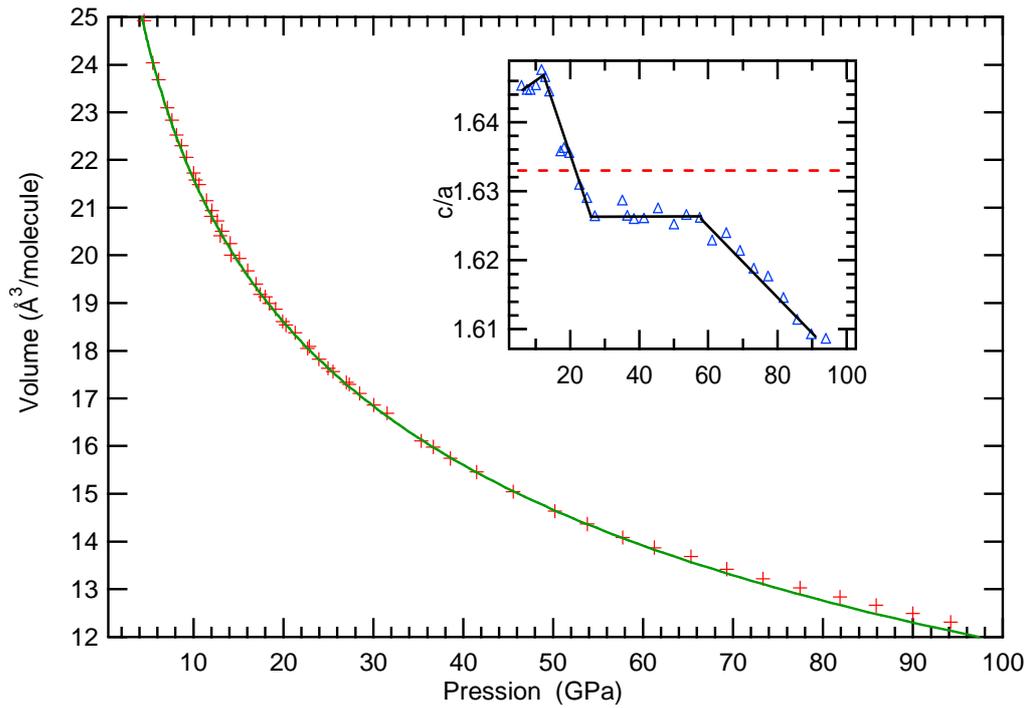


Figure 1 : Equation of state of ammonia determined by x-ray diffraction. Crosses represent data points and the solid line, a fit to the data from 5 to 60 GPa with the Vinet model ($V_0=31.5 \text{ \AA}^3/\text{molecule}$, $B_0=10.1 \text{ GPa}$, $B_0'=5.4$). This unveils a smaller compressibility at pressures above 60 GPa with respect to the expected behaviour. The variation of the c/a ration, shown in the insert, shows 4 regimes : 1) a slight increase up to 13 GPa ; 2) a rapid fall up to 25 GPa, 3) a stable regime up to 60 GPa and 4) another decrease up to 95 GPa. The dashed line shows the ideal value for the hcp structure.