

Auxiliary information for "Proton disorder and superionicity in hot dense ammonia ice"

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Experimental methods

Samples of ammonia were cryogenically loaded in membrane diamond anvil cells (MDAC). Pressure was determined with the luminescence of some $\text{SrB}_4\text{O}_7:\text{Sm}^{2+}$ powder using the calibration reported in Ref. [1, 2]. No evidence of chemical reaction has been observed between ammonia and $\text{SrB}_4\text{O}_7:\text{Sm}^{2+}$ at high P-T. The relative uncertainties on pressure measurements, as derived from standard deviation of the fitted luminescence peaks versus wavelength, are typically less than 0.02 GPa at ambient temperature and around 0.15 GPa at 750 K. MDACs made of high-temperature Inconel alloy were used. High temperatures were produced using a ring-shaped resistive heater enveloping the MDAC. During heating, a continuous flow of Ar/H₂ reducing gas mixture is directed into the MDAC. The temperature of the sample was determined thanks to a K-type thermocouple fixed by ceramic cement on the head of one diamond. With these techniques, a temperature uncertainty inferior to 5 K is obtained[3].

Measurements of Raman spectra were performed using a T64000 spectrometer in backscattering geometry, the 514.5 nm line of an argon laser and a CCD detector. X-ray diffraction experiments were conducted at the ID09 beamline of the ESRF synchrotron (Grenoble, France), using a monochromatic ($\lambda = 0.414$ Å) angle-dispersive setup and a mar 345 image plate detector.

Refinement of x-ray patterns

The structures of ammonia II, V (or IV) and III, along with their simulated x-ray spectra at the same volume, are depicted in figure 1. The diffraction patterns of phase II and V are very similar since the positions of the nitrogen atoms in phase V are only slightly displaced (within 0.11 Å) with respect to their positions in the *hcp* structure. The main differences are the existence of weak reflections and the splitting of some reflections in the orthorhombic structure. By contrast, the diffraction pattern of FCC phase III is clearly distinct.

Our experimental x-ray patterns along the 70 GPa isobar show that at the V- α phase transition, a discontinuous jump of the *d*-spacing of the (002) reflection at 743(10) K is observed (see figure 2) and the extinction of some weak reflections occur. We did not observe any new reflection, as one would expect if a mixture of the fcc and *hcp* structures would occur. We have conducted full profile refinements of the x-ray patterns of the α phase at 70 GPa and 743 K, using either the orthorhombic (phase V) and the hexagonal (phase II) structures as input models. The refinements were done with the Fullprof software suite [4]. A two-phase procedure was adopted to take into account the weak diffraction signal from the rhenium gasket. In addition to the zero-shift correction and background coefficients, a minimal set of variables for NH₃ was refined : the scale factor, the lattice parameters, thermal global parameter, three profile coefficients and a preferred orientation model (modified March) coefficient. The final refinements are presented in figure 3A and show that the α phase is better fitted with the orthorhombic rather than the *hcp* structure. In particular, the linewidth of the strongest peaks can only be reproduced with the orthorhombic structure as can be seen in figure 3B. The refinement is moreover improved by omitting the hydrogen atoms in the orthorhombic model, thus keeping only the N atoms as in our *hcp* model. Indeed, this accounts for the observed disappearance of the (120) and (101) reflections whose intensities are strongly correlated with the hydrogen positions. This adds further support to the fact that the α phase is proton disordered.

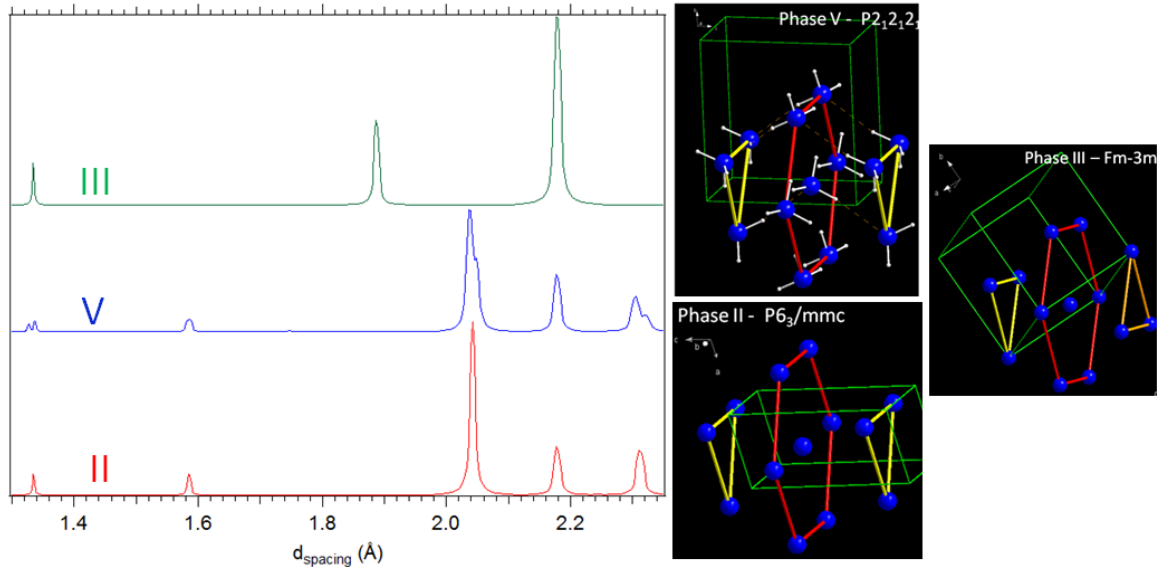


FIG. 1: Simulated x-ray spectra at constant volume (left) and structural representations (right) of phases II, V and III of NH_3 . The blue and white spheres are respectively nitrogen and hydrogen atoms. The hydrogen positions are not represented in the plastic phases II and III, as they are disordered over many possible sites. The red, yellow and orange line underline that phase V has a pseudo-HCP, (ABA)-type stacking as in phase II, whereas cubic phase III has an (ABC)-type stacking.

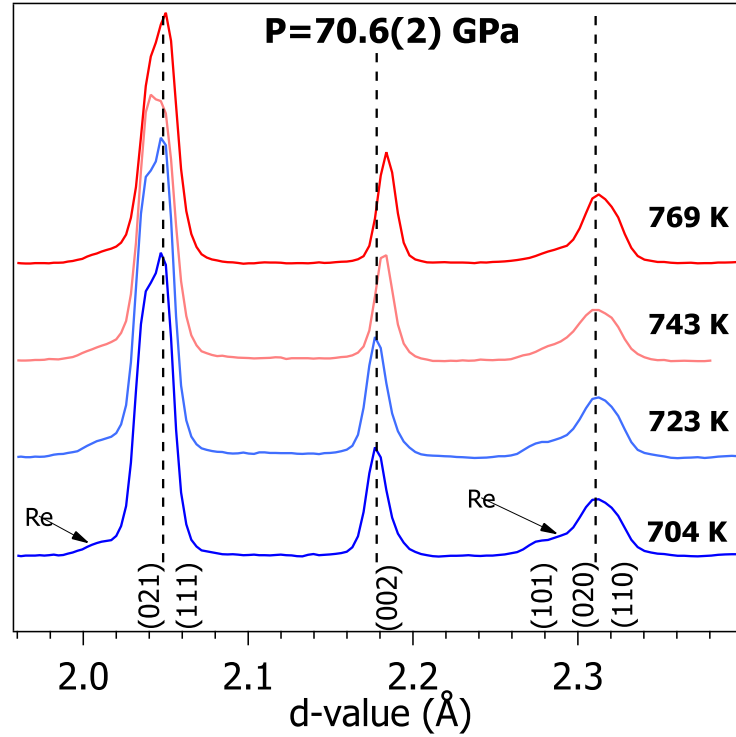


FIG. 2: Detail of the X-ray spectra along the isobar 70.6 GPa showing the strongest first reflections. The (hkl) indices are for the orthorhombic structure and the dashed lines are guides to the eye. "Re" designates the diffraction lines from the rhenium gasket.

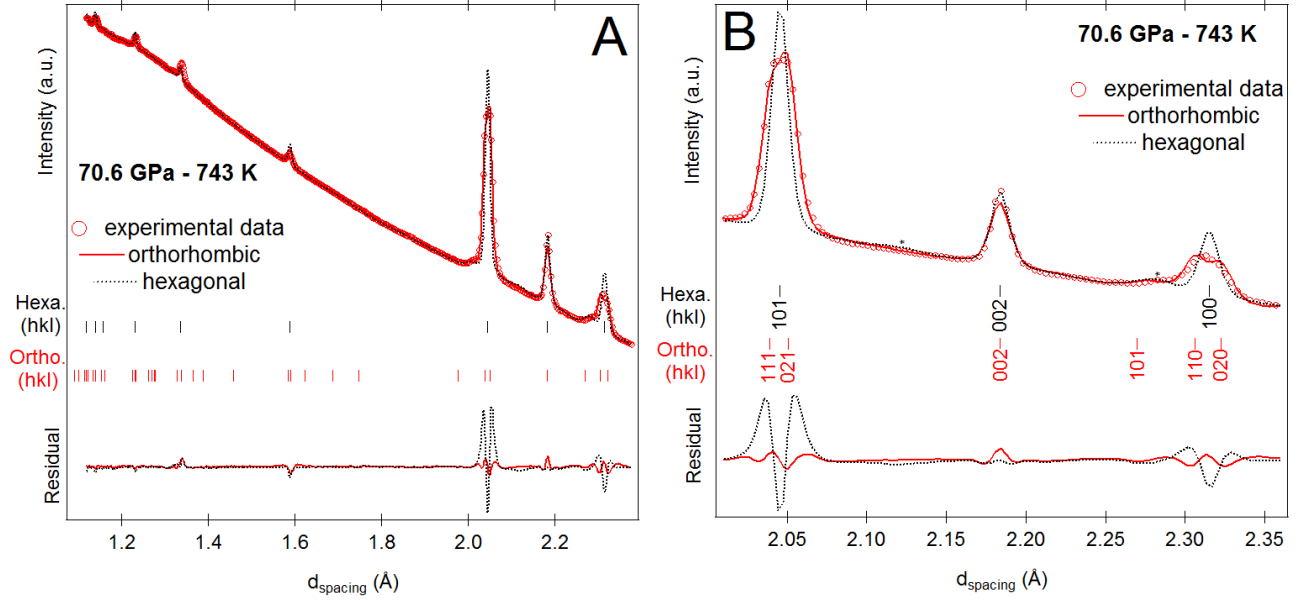


FIG. 3: A - X-ray diffraction spectra of NH₃ at 70.6 GPa and 743 K. Red circles: experimental data (Y_{obs}); black line: full profile refinement in the hexagonal $P6_3/mmc$ structure ; red line: full profile refinement in the orthorhombic $P2_12_12_1$ structure ; sticks: predicted position of Bragg reflections (up: in the hexagonal structure - down: in the orthorhombic structure) ; the difference ($Y_{obs} - Y_{calc}$) is plotted at the bottom. B- Zoom of the refinement on the main reflections. The indexation (hkl) of the reflections in the hexagonal and orthorhombic structures are respectively indicated in black and red.

Entropy variation

In solid ammonia (I,II,III, IV and V), each nitrogen provides 6 hydrogen bonds - three as donor and 3 as acceptor. As the positions of H atoms are fixed in the ordered phases I, IV and V, the number of possible configurations for NH₃ molecules is 1. In the disordered phase, the positions of the hydrogen atoms are not fixed but each nitrogen atom always forms three covalent NH bond (to respect the NH₃ stoichiometry) and three H-bond with three others molecules. By considering that the sites along the six NN directions are equally accessible for each hydrogen, there is $\binom{6}{3}=20$ possibilities to place 3 hydrogen in these 6 sites. By considering that only one H is present between two N, the occupation factor of each site is 1/2 for each hydrogen. This restriction decreases the number of configuration to $\Omega = \binom{6}{3}(\frac{1}{2})^3$. As the configurational entropy is defined by $S = R \ln \Omega$, we can evaluate the configurational entropy variation between a totally ordered phase and a disordered phase of NH₃. The calculated entropy variation is 0.91R. This value is in very good agreement with the experimental values determined along the ordered-plastic (V-III) transition line ($1R \pm 0.4$).

Our simulations show that in the superionic phase, the formation of the NH_4^+ and NH_2^- ionic species is allowed, such that the number of possible configurations increases and is :

$$\Omega = \Omega(NH_2^-) + \Omega(NH_3) + \Omega(NH_4^+) = \binom{6}{2}\left(\frac{4}{6}\right)^2 + \binom{6}{3}\left(\frac{1}{2}\right)^3 + \binom{6}{4}\left(\frac{2}{6}\right)^4 \quad (1)$$

The new configurational entropy variation is 2.24R. The entropy variation measured at the V- α transition ($4R$ (+/- 2R)) is in good agreement with this value and thus suggests the existence of dissociation in the α phase. Note that for the above expression to be correct, there should be equal probability to form NH₃ molecules and NH_4^+ or NH_2^- ions, which can only be true in the superionic phase. Note also that our model neglects the additional vibrational entropy coming from the vibrational modes of the NH_4^+ or NH_2^- ions, which should make the calculated entropy variation in even closer agreement with the experimental one.

Theoretical methods

We used the Quantum-ESPRESSO package [5], which is based on Density Functional Theory (DFT) and implements a pseudopotential/plane-wave scheme. Ultrasoft pseudopotentials were adopted to describe the electron-ion

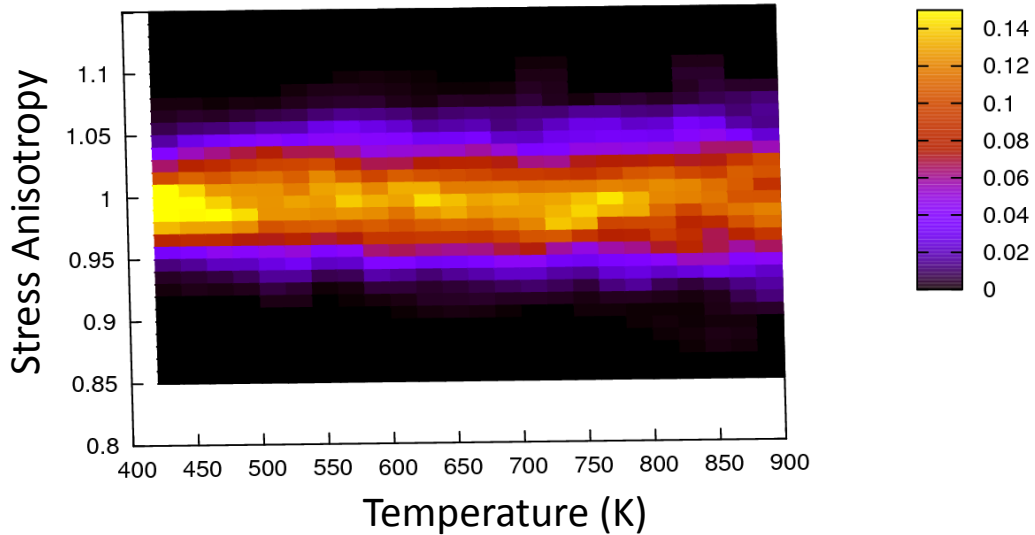


FIG. 4: Distribution of the instantaneous calculated values of the stress anisotropy with respect to temperature across the superionic transition. The color scale is in arbitrary units.

interaction within the Perdew-Burke-Ernzerhof gradient corrections scheme. Born-Oppenheimer molecular dynamics was employed to carry out finite-temperature simulations, with a timestep of 0.38 fs . Tests performed at high temperature ($T=850 \text{ K}$) and pressure ($P \sim 70 \text{ GPa}$) using a smaller timestep of 0.19 fs give indistinguishable trajectories. As in all standard DFT ab initio molecular dynamics approaches, in our calculations atomic nuclei evolve according to classical dynamics; as such, the quantum nature of the proton is not taken into account. A kinetic energy cutoff of 35 Ry was used on the wavefunctions. Brillouin zone integrations were performed at the Γ point. The orthorhombic structure (phase V) was described with a supercell containing $4 \times 2 \times 2$ unit cells, i.e. 64 NH_3 molecules, while the cubic structure (phase I) was described with a supercell containing $2 \times 2 \times 2$ unit cells, i.e. 32 NH_3 molecules. The experimental positions of the orthorhombic phase V and cubic phase I were used to set up the simulation boxes of 64 and 32 molecules respectively. At each thermodynamic point the simulation times were of the order of at least 10 ps . Our calculations are performed at constant volumes, and the experimental discontinuity on the volume should be in principle reflected in a variation of the calculated pressure at the phase V-superionic phase transition, and in particular of its stress anisotropy, that we define as $\epsilon = \frac{2\sigma_{zz}}{\sigma_{xx} + \sigma_{yy}}$. We report in Fig. 4 the distribution of the instantaneous value of ϵ as function of the temperature, across the superionic transition. We observe that the system is isotropic before and after the transition, and that fluctuations are of the order of 5% , *i.e.* much larger than the experimental relative variation in the c axis. This result fully justifies our choice to perform our ab initio simulations in the NVT ensemble.

A molecular system is considered plastic when the molecules freely rotate around their center of mass, which itself only vibrates close to the lattice site. To determine whether the system is plastic, we consider the time auto-correlation function of the unit vector u_i pointing along the direction of the C_3 symmetry axis of molecule i , and averaged over all molecules: $1/N \sum_i \mathbf{u}_i(t) \cdot \mathbf{u}_i(0)$. This function is close to unity in crystalline, non-plastic systems, while it drops to zero in a fully plastic system.

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- [1] F. Datchi, R. LeToullec, and P. Loubeyre, J. Appl. Phys. **81**, 3333 (1997).
 - [2] F. Datchi, A. Dewaele, Y. L. Godec, and P. Loubeyre, Phys. Rev. B **75**, 214104 (2007).
 - [3] S. Ninet and F. Datchi, J Chem Phys **128**, 154508 (2008).
 - [4] J. Rodriguez-Carvajal, Physica B **192**, 55, see [<http://www.ill.eu/sites/fullprof/>] (1993).
 - [5] P. Giannozzi and al., J. Phys. Condens. Matter **21**, 395502 (2009).