

ISIS Experimental Report

Rutherford Appleton Laboratory

Title of Experiment: The structure of ammonia dihydrate phase II.

Principal Proposer: AD Fortes

Affiliation: Dept. Earth Sciences, University College London

Experimental Team: IG Wood, M Alfredsson

RB Number: 14885

Date of Report: 10/06/2004

Local Contact: KS Knight

Instrument: HRPD

Date of Experiment: March '04

Introduction. Ammonia is likely to be an abundant species inside the icy moons of the outer solar system; at the water-rich end of the $\text{NH}_3\text{-H}_2\text{O}$ system, we can expect ammonia dihydrate (ADH) to be a significant rock-forming mineral.¹ The ambient-pressure phase, below the melting point at 176 K (ADH I), is cubic (space-group $P2_13$) and stable up to ~ 0.4 GPa.² Previous neutron diffraction studies had identified the existence of a high pressure polymorph (ADH II);³ we have also observed a mixture of high-pressure dihydrate, monohydrate, and ice phases after melting ADH I at 0.45 GPa.^{1,4} In another study on PEARL, we identified several new high-pressure polymorphs, at least two of which (phases III and IV) exist under similar P-T conditions to phase II.^{1,5}

Our aim in this study was to observe the high-pressure phase II with a view to attempting a structure solution.

Experimental method. Liquid $\text{ND}_3 - \text{D}_2\text{O}$ solution was loaded into a TiZr gas pressure vessel along with a small quantity of silica wool to act as a nucleator. The cell was attached to a cryostat centre stick and loaded into an orange cryostat, which was then positioned in the neutron beam line on HRPD. Data were collected in the 90° detectors with the sample compressed under helium gas.

Results. We initially tried to make phase II by freezing the liquid at 0.55 GPa. However, cooling to 170 K at this pressure produced no Bragg peaks and the sample presumably formed a glass. The sample was therefore warmed and decompressed to atmospheric pressure whereupon cubic ADH phase I was made in the manner reported previously.^{1,2} Upon compression to 0.55 GPa at 175 K, the Bragg peaks of phase I were replaced by peaks from a new phase (Fig. 1). This new diffraction pattern is similar to the pattern of ADH II given by Loveday & Nelmes;³ however, there are some significant differences, and we are not prepared to say with certainty that this is the same polymorph. Attempts to index this pattern have not met with success.

The high-pressure phase was warmed from 175 to 190 K, at which point there was a further change in the diffraction pattern (Fig. 2). This pattern does not resemble any phase of ADH that we have seen previously,^{1,5} so we tentatively identify it as ADH phase VII. Phase VII did not back transform to the pre-existing phase (II ?) upon cooling to 150 K. Attempts to index this pattern have not met with success either. The diffraction patterns of phases II (?) and VII are quite complex, and indicate that they have large unit cells. Correct indexing therefore requires

access to larger d-spacing reflections which cannot be seen on HRPD due to the drop in flux at longer neutron wavelengths.

Figure 1. Diffraction pattern of high-pressure ADH (phase II ?), 0.55 GPa, 175 K.

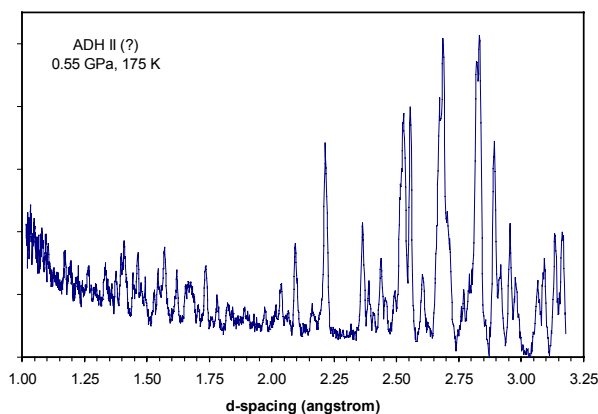
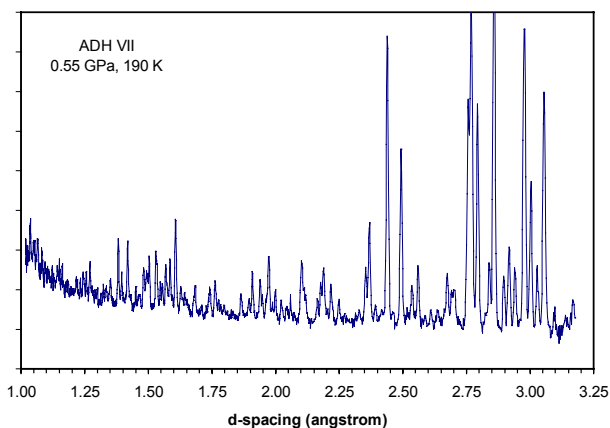


Figure 2. Diffraction pattern of the new phase VII of ADH, at 0.55 GPa, 190 K. Some residual peaks from the lower-temperature phase appear still to be present.



References

- ¹Fortes (2004) PhD Thesis, University of London.
- ²Fortes et al. (2003) *J. Chem. Phys.* 119, 10806.
- ³Loveday and Nelmes (1999) ISIS Experimental Report RB9859 (POLARIS)
- ⁴Fortes et al. (2003) ISIS Experimental Report RB13234 (HRPD).
- ⁵Fortes et al. (2003) ISIS Experimental Report RB13233 (PEARL).