

# ISIS Experimental Report

## Rutherford Appleton Laboratory

**Title of Experiment:** Characterization of the high-pressure phases of ammonia dihydrate.

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**Instrument:** OSIRIS

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### Introduction

The purpose of this experiment was to verify an earlier high-pressure study of ammonia dihydrate (ADH) polymorphs carried out on HRPD (RB 14885), in which we observed diffraction patterns of two high-pressure phases of ADH (now called phases II and III), and to collect data extending to longer d-spacings. Both of these crystals had previously produced diffraction patterns of some complexity, which we were unable to index, but which were indicative of large unit cells. Since the long wavelength flux on HRPD is quite low, we selected OSIRIS, which receives a much more intense long wavelength flux, to characterise the larger d-spacing Bragg reflections from ADH II and III.

### Experimental

2 cm<sup>3</sup> of 33.3 mol % ND<sub>3</sub> in D<sub>2</sub>O (prepared by condensing an appropriate volume of ND<sub>3</sub> gas onto a pre-weighed sample of deuterated ice in a sealed system at ~220 K) was loaded into a TiZr pressure vessel together with a wad of silica wool. The cell was sealed under a nominal pressure of 100 bar of helium gas, attached to a centre stick and loaded into an OC100 cryostat. The sample was initially cooled to 173 K and then temperature-cycled close to the melting point to promote crystallisation.

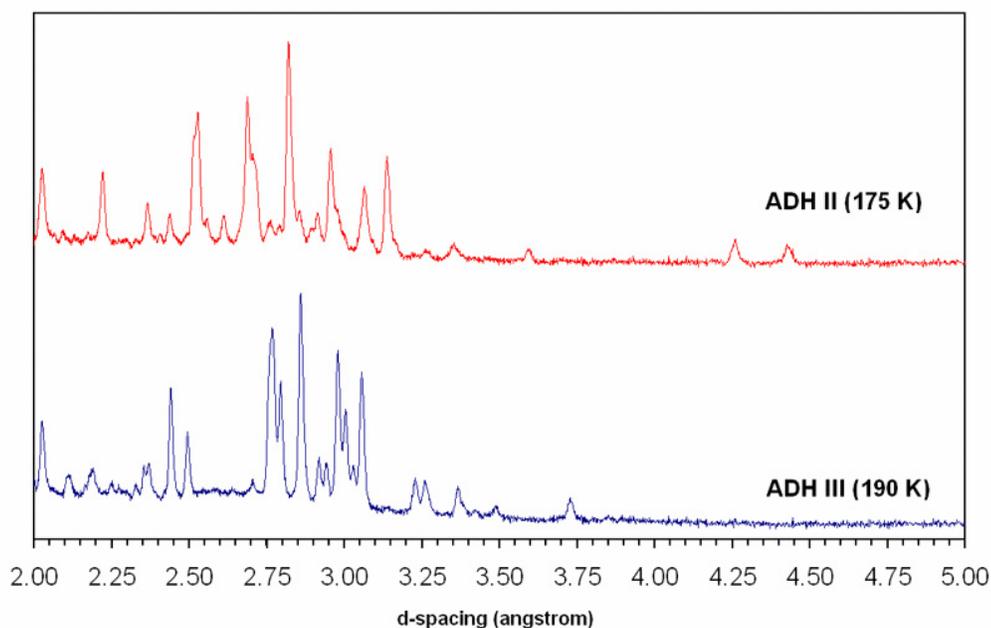
We had the opportunity to observe the crystallisation process in the beam line on two occasions. This is the first time that the devitrification of ADH glass has been directly observed; the data show that the temperature cycling is very effective, indicates and the number of temperature cycles required.

At the end of the annealing process, the sample consisted of polycrystalline ADH phase I (see Fortes *et al.* 2004). At a temperature of 175 K, the helium gas pressure was then increased initially to 4 kbar. From 4 kbar to 5.5 kbar, diffraction data were collected in d-range 2 (1.70 - 4.50 Å, counting for ~15 minutes, or ~40 μAhr) to observe the phase change from ADH I to ADH II, the transition being observed between 4.50 and 4.75 kbar. After the formation of ADH II, diffraction data were collected in d-ranges 2 - 7 (1.70 - 11.00 Å). It is apparent that the phase II diffraction pattern does not appear to exhibit any Bragg reflections at d-spacings larger than ~4.5 Å.

Warming of ADH II led to the formation of ADH III at 190 K, 5.5 kbar - as observed previously on HRPD. Time constraints prevented us from collecting diffraction data on this phase beyond d-range 4 (i.e., beyond 6 Å), but no Bragg reflections at d-spacings larger than 3.75 Å were observed.

Subsequent warming of ADH III caused it to melt congruently at 196 K, 5.40 kbar. A data set in d-ranges 2 - 4 was collected from the liquid phase at high pressure; cooling, temperature cycling, decompression and recompression failed to recrystallize the sample. At the end of the run, a dataset was collected in d-ranges 2 - 4 from the empty TiZr can, in order to characterize the strong background from the pressure vessel and Bragg scattering from the other sample environment equipment.

Indexing of the observed patterns is in progress.



Left: diffraction patterns of ADH phases II and III collected at 5.5 kbar. The slight residual background, after subtraction of the sample environment contribution, is probably due to scattering from the silica wool.

### References

Fortes *et al.* (2004) *J. Chem. Phys.* 119(20), 10806-10813.