

ISIS Experimental Report

Rutherford Appleton Laboratory

Title of Experiment: The structure and compressibility of ammonia dihydrate phases I and II.

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The pressure and temperature dependencies of the molar volume of the ambient pressure phase of ammonia dihydrate (ADH I) have never been measured previously, but are of importance to Planetary Science. Icy moons in the outer Solar System may contain up to 15 wt% NH_3 . An ammonia-water solution of this stoichiometry will crystallise a mixture of ice Ih + ADH I [1,2]. In order to model the internal structure and thermal history of these icy moons, accurate values for the thermal expansivity and incompressibility of ADH I are required, and these are the properties we proposed to measure in this experiment. We recently published the results of *ab initio* calculations on ADH, reporting the equation of state in the athermal limit [3].

ADH I is known to be cubic (space group $P2_13$) and disordered at 150 K [4]. We wished to establish whether this disordered state became frozen in at low temperatures, or whether the structure was kinetically able to transform to an ordered crystal as recently proposed [3].

Furthermore, ADH I is known to transform to a denser solid (ADH II) at pressures of ~ 3 –4 kbar [5,6]. Although diffraction patterns have been collected from this phase, the structure is unknown [6]. Our final objective was to observe this phase on the high resolution diffractometer.

Experimental method

A liquid solution of the correct stoichiometry ($33\frac{1}{3}$ mol% ND_3) was prepared by mixing an appropriate volume of condensed ammonia with heavy water.

An aluminium slab-can was employed for the ambient pressure experimental runs and a cylindrical aluminium gas-pressure cell was used for the high-pressure runs. In both cases the sample cavity was loosely padded with silica wool to ensure nucleation of a good powder from the liquid, and ND_3 $2\text{D}_2\text{O}$ solution was dripped onto the wool until the space was filled. The cans were sealed, attached to centre sticks, and quenched to 77 K in a nitrogen dewar. Each assembly was then placed in a cryostat pre-cooled to 50 K and allowed to thermally equilibrate before being warmed to 174 K. In order to produce crystalline ADH the temperature was cycled across the melting point a number of times according to the recipe of Bertie and Shehata [7].

In both sample environments this process resulted in the formation of an highly crystalline powder of ADH phase I.

Diffraction data were collected at temperature intervals of 2 K whilst cooling the sample from 174 K to 4.2 K; a cooling rate of 8 K hr^{-1} , allowing for five minutes of thermal equilibration at each temperature point. No obvious signs of the expected ordering transition were observed during this period; the sample was taken offline and held at 120 K for ~ 36 hours in an effort to promote the ordering transformation. This sample was then returned to the beamline and cooled to 40 K. Finally, diffraction patterns suitable for high quality structure refinement ($\sim 60 \mu\text{Ahr}$ per spectrum) were collected at 20 K intervals upon warming from 40 K to 160 K.

Diffraction patterns were collected at 174 K from the pressurized sample at intervals of ~ 500 bar, from the nominal loading pressure of 410 bar, up to the maximum rated pressure of the sample can: ~ 4.6 kbar. The phase transition to ADH II had not occurred at 4.6 kbar, so the sample was warmed to 179 K whereupon it melted to a slurry of ice II crystals in ammonia-water liquid. Once cooled back to 174 K, high pressure phases of ammonia monohydrate (AMH II) and ammonia dihydrate (ADH II) crystallised in coexistence with ice II over a period of ~ 4 hours. This polyphase sample was then cooled to 110 K

and subsequently decompressed to ~ 500 bar, but no further phase changes were observed.

Figure 1: the variation of unit cell volume with temperature at ambient pressure.

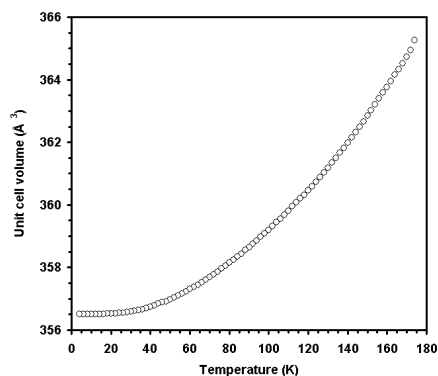
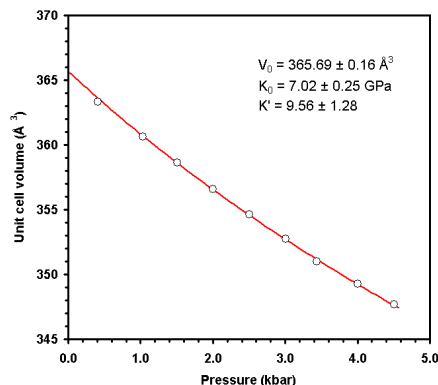


Figure 2: the variation of unit cell volume with pressure at 174 K.



References

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