ISIS Experimental Report

Rutherford Appleton Laboratory

Title of Experiment:	Probing the high pressure stability of ammonia dihydrate phase IV	**RB Number:**	520044
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		Date of Experiment:	16-18/11/2005 11-12/02/2006

Introduction: Ammonia dihydrate (ADH) is a likely constituent of the icy moons of the gas giant planets. The properties of this molecular solid under high pressures (0 – 10 GPa) and low temperatures (50 – 300 K) are of great importance in modelling the geodynamics of these large icy satellites. We have carried out a programme of computational and experimental study on ADH, which has included several high-pressure studies using the PEARL/HiPr beamline. At pressures > 0.6 GPa the liquidus phase is an orthorhombic crystal we have named ADH IV. This phase has been observed to pressures of 50 - 60 kbar, indicating that it has a relatively robust crystal structure – for an icy substance; however, we have observed (RB15134) that ADH IV decomposes upon warming to 220 K at 4.4 GPa into a mixture of ice VIII and ammonia monohydrate phase VI (AMH VI). This agrees with an earlier diamond anvil cell study. In our most recent experiment (RB510034), we observed another new liquidus phase, at ~ 2 GPa, 240 K.

The purpose of this experiment is to explore the behaviour of ADH IV upon warming at pressures from 1.5 – 5.0 GPa. This will allow us to test our hypothesis that ADH IV transforms to a new phase prior to melting at 1.5 – 2.5 GPa, and to map the decomposition boundary (ADH → AMH + ice) at 2.5 – 5.0 GPa.

Sample preparation: Deuterated aqueous ammonia samples of the requisite stoichiometry were prepared by condensing ND_3 gas into an evacuated glass bulb immersed in a bath of solid-CO_2-cooled acetone (at ~ 220 - 230 K), weighing, and then adding the appropriate quantity of D_2O. Liquid specimens were loaded into the gaskets of the Paris-Edinburgh cell by soaking a small wad of silica wool. Lead powder was added as a pressure calibrant (we had previously used Pb foils). The gaskets were sealed under a load of ~ 15 tons and the cell was craned into the beam-line.

Data collection: Diffraction data were collected during cooling from room temperature to 190 K under 15 tons load. Our initial observation was that the scattering from the lead powder was very weak indeed. Upon reaching 190 K, the load was stepped up in 3 tons increments until crystallisation of a mixture ADH IV + ice VI occurred at 22 tons. The load was increased to 25 tons, and data were collected upon warming. Partial melting of the specimen to ice VI + liquid occurred between 235 K and 240 K (Fig. 1).

This partially molten specimen was unloaded to 15 tons, cooled to 190 K, subsequently reloaded to 25 tons and warmed to 220 K. The quality of the sample (peak sharpness) was such that a longer integration (4 hours) was made at this P,T datum prior to continuing with the increase of load to 32 tons. Warming measurements at 32 tons were cut short by a major component failure in the ISIS synchrotron.

The second experimental run (using Pb foils), carried out three months later, aimed to resume the measurements. ADH IV was crystallised under a load of 15 tons at 190 K, and a long integration was made. A second long integration at 25 tons, where we observed the growth of ice VI peaks, presumably from residual glass in the sample. At 230 K, the load was increased in 3 tons increments, evidence of the expected dissociation to AMH + ice being observed at 34 tons. This phase mixture was compressed up to 52 tons and warmed to 280 K without any further change.

Results: We have now clearly identified ADH IV as an orthorhombic crystal, with unit-cell dimensions at 0.75 GPa, a = 12.5187 Å, b = 6.6039 Å, c = 6.3233 Å, V = 522.764 Å^3 (Z = 8), the most likely space-group being Pccn. Our measurements upon this phase in several experiments, including this one, have allowed us to estimate the equation of state over the pressure range 0.6 - 2.0 GPa. In addition, we have observed this phase co-existing both with ice II (near 0.6 GPa) and with ice VI at higher pressures. In this experiment, we observed the eutectic melting (between ice VI and ADH IV) at 235 - 240 K, 1.25 GPa (Fig. 1), in agreement with earlier literature data.

The higher-pressure liquidus phase observed in RB15134, we now believe to be a polymorph of ammonia monohydrate, and we have indexed these diffraction patterns with a monoclinic unit cell (Z = 8).

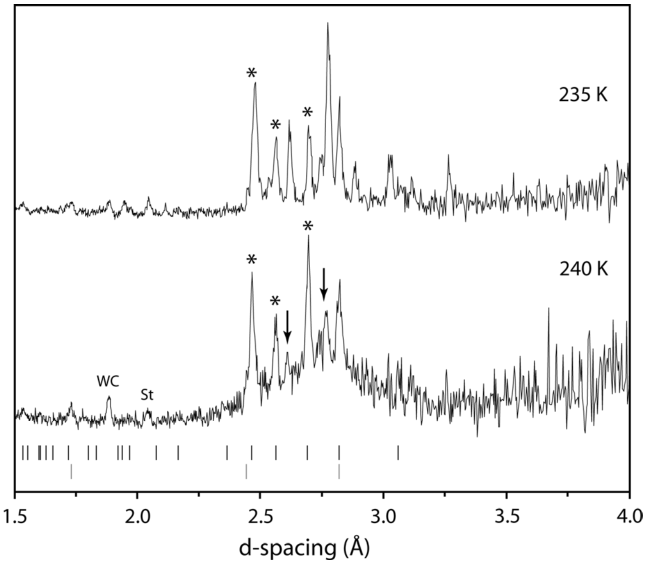

Fig.1. Melting of the ADH IV - ice VI mixture between 235 - 240 K. Tick marks show the Bragg reflections for ice VI (black) and Pb (grey); the three strongest ice VI reflections in both datasets are indicated with asterisks, and residual ADH IV in the melt is indicated by arrows. The strongest sample environment peaks from tungsten carbide (WC) and steel (St) are labelled.