ISIS Experimental Report

Rutherford Appleton Laboratory

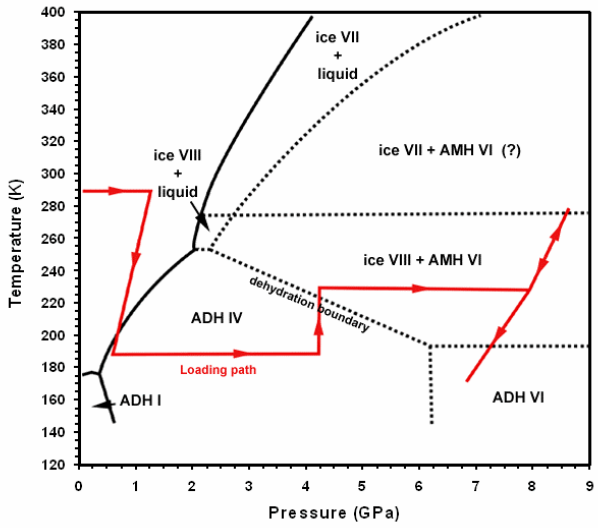
RB Number:	15134		
Date of Report:	Dec 2004		
Title of Experiment:	Characterization of the high-pressure phases of ammonia dihydrate.	**Local Contact:**	W. G. Marshall
Principal Proposer:	A. D. Fortes.	**Instrument:**	PEARL
Affiliation:	Department of Earth Sciences, University College London		
Experimental Team:	I. G. Wood, L. Vocadlo, M. Alfredsson	**Date of Experiment:**	12-16/11/04

Introduction. The purpose of this experiment was to build on our previous study of the high-pressure phase diagram of ammonia dihydrate [1-3]. The specific aims were to reproduce the previously observed phases and collect higher quality diffraction data (12 hour integration times vs. 1-2 hours previously). The system is of relevance to understanding the interior structure and evolution of large icy moons in the outer solar system [3].

Experimental. A fresh sample of stoichiometric liquid was made by condensing a predetermined volume of ND_3 gas onto an appropriate mass of D_2O ice. The mixture was warmed and stored in a refrigereator for one week prior to use. The sample was loaded into the gasket space by using a syringe to soak a small ball of silica wool. The system was sealed under a load of 10 tons. In our previous study, pressures were determined by use of an in-situ lead calibrant [3]. The pressure-load relationship was found to be well-described by a linear function, P = 0.1228 x load - 1.2831 (r^2 = 0.9926), and we were confidant of being able to use this to determine sample pressure from the applied load to ± 0.25 GPa. The formation of ice VIII during the experiment also allowed us to calculate the pressure from its known equation of state [3], and this agreed with the linear pressure-load calibration to 0.05 GPa, reassuring us of the validity of the method. Initial crystallisation of the sample proved more difficult than before, taking ~24 hours to form the first crystalline solid; it is possible that the lead pressure calibrant acted as a superior nucleator to the silica wool alone.

Results. In the earlier study we observed diffraction patterns from four distinct crystalline phases, which we called ADH III, IV, V, and VI. In addition, diffraction patterns from two highly strained phases were dubbed Intermediate A and B. In this study we failed to reproduce either ADH III or ADH VI but successfully reproduced ADH IV and collected 12 hour datasets (~2200μA) at 0.8 and 1.9 GPa (at 190K). Moreover, our observations of this substance at higher pressures lead us to conclude that Intermediate phase B and ADH IV are probably the same crystalline phase. ADH IV was observed up to 4.4 GPa, proving itself to be a robust structure, in comparison with other icy materials.

Warming of ADH IV at 4.4 GPa caused it to transform, at 225 K, into the phase previously identified as ADH V. Collection of a 12 hour dataset at 4.5 GPa, 230 K, and further observation at higher P,T conditions has allowed us to determine that this is not a single ADH phase but a mixture of ice VIII and ammonia monohydrate phase VI (a disordered bcc phase [4]). This confirms the work of Boone [5], whose optical work in a diamond anvil cell revealed the breakdown of ADH to AMH + ice at a high-pressure instability boundary. Warming of this mixture to 283 K failed to cause the transformation of ice VIII to ice VII. Subsequent cooling and unloading back through the instability boundary also did not lead to the formation of ADH, although this diffusion-limited reaction is probably very slow indeed at 170 K.



Summary. The in-situ studies using PEARL-HiPr continue to improve dramatically our understanding of the ammonia dihydrate system at high pressure. We now know that ADH IV is a robust phase existing over a relatively large pressure range (for an icy substance), and that ADH does indeed experience a pressure-induced dehydration reaction as suggested by Boone [5]. It is important to characterise this dehydration boundary at a range of P,T conditions, and in particular to explore the behaviour of ADH VI upon heating through this boundary.

References

[1] Fortes et al., (2003) ISIS Experimental report RB13233.
[2] Fortes et al., (2004) Lunar Planet. Sci. Conf. 35, 1254.
[3] Fortes (2004) PhD Thesis. University of London.
[4] Loveday & Nelmes (1996) Phys. Rev. Lett.
[5] Boone (1988) PhD Thesis. UCLA