

NEW HIGH-PRESSURE PHASES OF AMMONIA DIHYDRATE. A. D. Fortes,¹ I. G. Wood,¹ K. S. Knight,² W. G. Marshall,² J. P. Brodholt,¹ M. Alfredsson,¹ and L. Vočadlo¹. ¹Department of Earth Sciences, University College London, Gower Street, London, WC1E 6BT, United Kingdom (*andrew.fortes@ucl.ac.uk*), ²ISIS facility, Rutherford Appleton Laboratory, Chilton, Oxfordshire, OX11 0QX, United Kingdom.

Introduction: Ammonia dihydrate (ADH) is very likely to be the most significant mineral after water ice in the mantles of ice rich moons orbiting Saturn, Uranus and Neptune [1]. It allows for low temperature melting, and is invoked to explain a wide variety of geological processes observed on these bodies. The physical properties and phase relations of ADH are poorly constrained [2]. There were two previously known phases (I and II) at low pressures [3-5]. ADH I (stable at ambient pressure) has a cubic unit cell but the structure of ADH II (stable above ~4.5 kbar) is unknown. The wider context of this study in our programme of using neutron diffraction to study planetary ices is given in a companion abstract [6].

Experimental: We carried out experiments on deuterated ADH using two instruments at the ISIS neutron spallation source, Rutherford Appleton Laboratory, U. K. To determine the thermoelastic properties of the low pressure phase (ADH I); and to establish the structure of ADH II, we used the High Resolution Powder Diffractometer (HRPD), and to study the phase behaviour of ADH up to ~ 10 GPa we used the PEARL-HiPr diffractometer. In both experiments, deuterated ADH was loaded into sample containers in the liquid state with blobs of silica wool to promote the nucleation of a random powder. The PEARL experiment also called for the use of a pressure calibrant, and a chip of polycrystalline lead was used.

The HRPD study: At atmospheric pressure we collected time-of-flight neutron diffraction patterns from ADH powder at 2 K intervals during cooling from 174 K down to 4.2 K. We also collected patterns upon warming (at 20 K intervals) from 40 K - 160 K, following a 36 hour period of annealing offline at 120 K.

The high-pressure experiment was conducted using an aluminium gas pressure cell with He as a pressure transmitting medium. Neutron diffraction patterns were collected from a powder of ~90 % ADH I + ~10% ice Ih in ~500 bar increments from 400 - 4600 bar at 174 K. At the maximum rated pressure of the gas cell (4.6 kbar) the phase change to ADH II had not occurred, so we increased the temperature from 174 K to 179 K and saw the sample melt to a slurry of ice IX crystals and ammonia-water liquid. After cooling back to 174 K, the sample recrystallised over several hours. The new diffraction pattern seems to be a complex polyphase mixture of dihydrate phase II, monohydrate phase II, ice IX, and possibly ice II as well. As a re-

sult, we have not been able to index the ADH II pattern.

The HRPD experiment resulted in the first measurement of the thermal expansivity and bulk modulus of ADH I. This work was published in 2003 [7], but the following results of the high-pressure study are presented here for the first time.

The PEARL study: Using the Paris-Edinburgh large-volume press, we were able to compress about 50mm³ of ADH to 8.7 GPa at temperatures between 170 - 200 K. In so doing, we observed at least four, and possibly six, new high-pressure structures. At no time did we observe a diffraction pattern similar to that of ADH II. Up to 2 GPa, we observed two new phases - ADH III and IV. Above ~ 5 GPa we also observed two new phases - ADH V and VI. ADH VI appears to be a substitutionally and orientationally disordered body centred cubic crystal similar to phase VI of ammonia monohydrate [8], and possibly part of a solid solution series between AMH VI and ice VII. In the intervening pressure range, 2 - 5 GPa, two poorly characterised phases were seen which require additional study; we call these Intermediate Phases A and B. It seems likely that with longer annealing, these phases would yield better powders and sharper diffraction patterns.

Our observation belie those of Boone [2], who concluded, on the basis of optical studies with a diamond anvil cell, firstly that there were no phase changes from 0 - 2.5 GPa, and secondly that ADH 'decomposed' to AMH + ice at pressures in excess of 2.5 GPa (depending on temperature). Our observations also do not agree with the recent work of Mousis *et al.* [9]. Their melting experiments have been interpreted as meaning that a step jump occurs in the peritectic at ~ 0.5 GPa, possibly requiring the existence of two new high-pressure phases. Instead, our observations of the melting line agree better with Hogenboom *et al.* [4]. The steep peritectic of Mousis *et al.* [9] at 0.5 GPa implies that a deep subsurface ocean inside Titan could be flooded by high-pressure phases of ADH. Our work suggests otherwise.

Implications: In the pressure range appropriate to large icy moons (0 - 2 GPa, at 100 - 300 K), we have discovered at least two new phases of ADH (phases III and IV) about which we know very little, except that they exist. We have also accurately measured key thermoelastic properties of ADH I. With this work,

and in future studies using HRPD and PEARL in 2004 we will progressively improve our ability to model the interiors of ammonia-bearing icy moons, and understand how thermal expansion and phase changes could have shaped their geological evolution. There is clearly a conflict in measurements of the melting point of ADH in the 0.4 – 0.8 GPa region, which potentially has a bearing on the internal structure of Titan.

Figure captions: Diffraction patterns of the high-pressure phases:

a) ADH III at 0.56 GPa, 170 K. Red stars mark the strongest peaks from the Pb pressure calibrant, and the green dagger indicates the strongest peak due to the tungsten carbide anvils of the Paris-Edinburgh Cell.

b) ADH IV at 0.66 GPa, 200 K formed by pressure freezing the liquid. Peaks from the Pb pressure calibrant are marked with red stars.

c) ADH V at 8.1 GPa, 200 K. This structure has a very simple pattern. The three strongest peaks from the sample are marked with blue stars. The peak at a

d-spacing of $\sim 2.38 \text{ \AA}$ is superposed on the Pb [002] peak and actually has an intensity the same as the peak at 2.25 \AA .

d) ADH VI at 8.6 GPa, 170 K. This diffraction pattern bears a striking similarity to the pattern of monohydrate phase VI [8]. The ADH VI pattern can be fitted with a model structure similar to AMH VI which is body-centered-cubic and both substitutionally and orientationally disordered. Peaks from the ADH are marked with blue stars.

References: [1] Schubert *et al.* In, *Satellites*. University of Arizona Press, pp224-292. [2] Boone. S (1989) PhD Thesis UCLA. [3] Loveday. J., and R. J. Nelmes (2000) Proc. AIRAPT 17, pp133-136. [4] Hogenboom *et al.* (1997) *Icarus* 128, 171. [5] Loveday *et al.* (1999) ISIS Report RB 9859 (POLARIS). [6] Fortes. A. D. *et al.* (2004) *LPSC XXXV*. [7] Fortes. A. D. *et al.* (2003) *J. Chem. Phys.* 119, 10806. [8] Loveday. J., and R. J. Nelmes (1999) *Phys. Rev. Lett.* 83, 4329. [9] Mousis *et al.* (2002) *Geophys. Res. Lett.* 29, 2192.

