

ISIS Experimental Report

Rutherford Appleton Laboratory

Title of Experiment: The crystal structure of high-pressure ammonia-water solids containing 15, 67, and 80 mol % ND₃

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RB Number: 510034

Date of Report: March 2005

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Instrument: PEARL

Date of Experiment: 21-24/02/05

Introduction

The purpose of this experiment was to explore the hypothesis that a solid solution series might exist at high pressure in the ammonia-water system. Above 6.5 GPa at 285 K, ammonia monohydrate, NH₃·H₂O, is observed to form a substitutionally disordered body-centred-cubic crystal - AMH VI (Loveday and Nelmes 1999), and we have observed a similar phase in our studies of ammonia dihydrate (NH₃·2H₂O) at pressures of > 6.3 GPa at 170 K (RB 13233; Fortes 2004; Fortes *et al.* 2004), which we call ADH VI. We therefore wished to explore the compositional space between ammonia dihydrate and pure ice (i.e., 15 mol% ND₃), and that between ammonia monohydrate and pure ammonia (67 and 80 mol% ND₃), at high pressure to search for possible evidence of solid solution. However, in light of our most recent high-pressure studies on ADH (RB 15134), in which we have failed to reproduce our original observation of ADH VI, we decided that it would be more useful to compress a solution of 33 mol % ND₃ rather than 15 mol % ND₃.

Experimental

All three compositions (33, 67 and 80 mol % ND₃) were loaded into the Paris-Edinburgh cell by soaking a small ball of silica wool with the appropriate solution. For the two concentrated ND₃ solutions, the anvils and gaskets were cooled to ~220 K in a bath of liquid nitrogen using a specially constructed cryo-cradle; the solutions and loading syringe were cooled in dry ice. Once loaded, each sample was placed initially under a load of 30 tons and then cooled. The 33 mol % solution was cooled to 160 K, whilst the set point temperature for the two more concentrated solutions was 200 K. All loads were converted to approximate pressure using a linear relationship established previously (Fortes 2004).

RESULTS

33 mol % ND₃

This sample crystallized promptly at 240 ± 5 K, 19.5 ± 1 kbar, and yielded a diffraction pattern different from the expected pattern of ADH IV (RB 13233 and 15134). This appears to be a novel phase of ADH, that we presume to be the liquidus phase at ~20 kbar: data from this phase were collected for ~600 μAhr after crystallisation. ADH IV may well transform to this new phase upon warming at 20 kbar, but we were nonetheless able to cool the new phase to 160 K, the field in which we have previously seen only phase IV. Upon compression at 160 K, we observed no phase changes up until the failure of the anvils under a load of 75 tons (~80 kbar).

67 mol % ND₃

This sample crystallised at 235 ± 5 K, 19 ± 1 kbar, and exhibited a relatively simple diffraction pattern which we believe to represent a single high-pressure phase of ammonia hemihydrate. Data from this phase, which has never been seen before, were collected for ~600 μAhr after crystallisation. Upon compression at 200 K, we observed no phase transition up to an applied load of 80 tons (~86 kbar); another long count (300 μAhr) was collected at 53 kbar (192 K). Warming to 220 K and decompression to 15.5 tons (~ 6 kbar) also failed to induce any phase change.

80 mol % ND₃

The liquid was cooled to 215 K, by which time the load fell to 19.8 tons; further loading to 28.4 tons (22 kbar) at this temperature caused the sample to crystallise. The diffraction pattern contains Bragg reflections which appear to be from solid ammonia II and some other phase which we presume to be a high-pressure phase of ammonia hemihydrate, which does not match that seen in the 67 mol % ND₃ run. Data were collected for ~750 μAhr after crystallisation. At 200 K, no phase changes were observed up to an applied load of 80 tons and subsequent warming to ~220 K. This is surprising since ammonia II should transform to ammonia IV above ~ 10 kbar.

Summary

The experiment failed to produce any evidence for a high-pressure solid solution series on the ND₃-rich side of the ammonia-water T, X phase diagram. Neither, for the second time, were we able to reproduce our observation of ADH VI. The persistence of the observed phases under compression proved surprising, given the behaviour observed in the ADH and AMH P,T phase diagrams. The results of this work highlight the need to understand the complex polymorphism of ammonia dihydrate, particularly the behaviour of ADH IV upon warming, and of ammonia hemihydrate. It is also apparent that further structural work needs to be carried out on solid ammonia II; this phase may transform from a free rotator (or plastic crystal) to a statically disordered phase under the P,T conditions of our experiment.

References

- Fortes *et al.*, (2004) Lunar Planet. Sci. Conf. 35, 1254.
- Fortes (2004) PhD Thesis. University of London.
- Loveday, J. S., and R. Nelmes (1999): Phys. Rev. Lett. **83**, 4329-4332.