ISIS Experimental Report

Rutherford Appleton Laboratory

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Introduction. Ammonia hydrates are examples of simple molecular solid in which we can study, by experimental and computational methods, hydrogen bonding of the kind found in more complex biological systems. Moreover, they are of interest to planetary scientists since ammonia-water mixtures are expected to be found in the interiors of many of the solar system's icy moons. Ammonia hemihydrate ($2NH_3.H_2O$, referred to as AHH) is the least studied of the solids in the ammonia-water system. Heat capacity measurements [1] have shown that there are one or more phase transitions in the region of 55 K (in the protonated form). Both X-ray [2] and neutron diffraction studies [3-6] have indicated that this is the result of orientational disorder in one of the NH_3 molecules becoming frozen out. We have recently used *ab initio* calculations to determine the equation of state of AHH [7].

Our aims were to study the ordering transition in more detail and to solve the low temperature crystal structure, both at ambient and high pressure. We also wished to know whether the crystal would become ordered by compression at high temperatures. Finally, the measurements we proposed to make would also provide data for the determination of thermal expansion and incompressibility for comparison with our earlier calculations.

Experimental. Deuterated ammonia gas (Aldrich 99 at. % D) was condensed into an evacuated glass bulb at -60°C (using a dry-ice cooled acetone bath), weighed and diluted to the correct stoichiometry (66.633 wt. % ND_3) with D_2O (Adlrich 99 at. % D). The solution was stored as a solid at 77 K until use. For the ambient pressure experiment, an aluminium framed slab can containing a wad of silica wool was cooled in liquid nitrogen and the melted sample was poured in directly. The solution began to boil as it passed along the neck of the glass vial, resulting in loss of ammonia and subsequent crystallisation of minor ammonia monohydrate (AMH). We suspect that highly oriented crystals of AHH formed on the back window of the slab can, whereas much of the sample formed a satisfactory powder in the silica wool; this resulted in our observation of a very textured specimen in backscattering, but a good powder in the 90° detectors. The slab can sample was cooled to 4.2 K in the beam line and diffraction data were collected in the 75-175ms t-o-f window at 5 K intervals upon warming to 170 K, counting for 35 minutes (18μAhr) at each point. In order to collect high quality powder data in backscattering, the specimen in the slab can (AHH + silica wool + minor AMH) was recovered under liquid nitrogen and ground to a powder in a nitrogen-cooled steel mortar. This powder was loaded into a standard 12mm vanadium can and placed back in the beam line at 4.2 K to collect a low-noise pattern in the 30-130ms and 130-230ms t-o-f windows. For the high pressure experiment, a TiZr gas pressure cell, loaded with silica wool and with the Bridgeman seal made at room temperature, was cooled to 200 K in a jug of dry ice. The stored sample, freshly warmed from 77 K was loaded in the ISIS cold room (at -5°C) into the cell using a plastic syringe cooled to -60°C in an acetone bath. This resulted in no discernible boiling of the sample, and the diffraction patterns do not exhibit peaks due to AMH; however, the specimen did prove to be strongly textured. The pressure cell was attached to a centre stick, fitted with heating elements and collimator, and transported to the beam line at dry-ice temperatures. At 170 K, diffraction data were collected in 500 bar intervals upon compression (under helium) from 100 bar to 5500 bar, counting for 1 hour (~33μAhr) at each point in the 40-140ms t-o-f window. The sample was then cooled from 170 K to 50 K at 5500 bar, and data were collected in 10 K intervals, again counting for 1 hour at each point. At 50 K, the pressure was released in 500 bar increments from 5500 bar down to 100 bar; data were collected for 1 hour at each point. Minor blockages of the pressure line resulted in some data at high pressure being discarded, but these cleared themselves.

Results. During the ambient pressure warming run, we observed the low-temperature form of AHH transform to the high-T form between 60 and 65 K as expected. The data have allowed us to determine the volumetric and axial thermal expansion of both phases of AHH. Similarly, we observed the transformation upon cooling at 5500 bar; the transformation temperatures (within the limits imposed by our relatively coarse sampling) are the same at 5500 bar and room pressure. We did not observe any difference in the relative intensities of the superlattice peaks, in contradiction to Nelmes et al. ( ). At both high and low pressures, the temperature evolution of *c*-axis is strikingly similar; that of the *a*- and *b*-axes differ considerably. Under compression, the *a*- and *b*-axes contract at different rates, the crystal passing through a point of being metrically tetragonal at ~ 2kbar; this coincides with a marked discontinuity in the *c*-axis and a smaller discontinuity in the unit cell volume. The similar pattern is observed at 500 bar upon decompression at 50 K, the principal difference being that the *a*- and *b*-axes do not reverse. The measurements made yield the bulk modulus of AHH at 170 K and 50 K, and the thermal expansivity at 1 bar and 5500 bar.

References.

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