

ISIS Experimental Report

Rutherford Appleton Laboratory

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Title of Experiment: Characterisation of the rotor phase of solid ND₃-ammonia II

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Instrument: GEM

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Introduction: The aim of this experiment was to study the dynamics of the molecular rotation in the high-pressure phase II of solid ammonia. Unfortunately, the gas cell suffered from a persistent unmanageable leak; after three attempts to reload and reseal the cell over two days, all of our sample was exhausted. With the agreement of our local contact, it was decided to carry out a very similar experiment to that originally envisaged but using a sample of sulfuric acid tetrahydrate (SAT) that we were investigating on POLARIS at the same time (see RB500086).

Experimental method: A TiZr gas pressure vessel was loaded with 2 cc of D₂SO₄.4D₂O solution and approximately 0.1 g of silica wool. The cell was mounted to a centre stick and sealed under 150 bar of helium gas before being loaded into an Orange cryostat on the GEM beamline. Initial inspection of the diffraction pattern at 160 K showed that the specimen was an amorphous solid. Warming to 220 K, caused the specimen to crystallise SAT; the pressure and temperature were stabilised at 115 bar, 200 K and a low-noise data set (170 μ Ahr) was collected in all six detector banks. Diffraction data were then collected upon compression under helium gas at 200 K (500 bar increments, 23 μ Ahr each) up to 5450 bar. A further low-noise data set was collected (190 μ Ahr) before the temperature was reduced to 50 K. From 50 K, the sample was warmed in 5 K intervals, counting for 8 minutes (20 μ Ahr) with 5 minutes of equilibration at each point. Pressure was maintained at 5475 \pm 15 bar during warming from 50 - 235 K. Upon reaching 230 K (at 5470 bar) the diffraction pattern changed, indicating the formation of a new high-pressure polymorph of SAT. Data were collected at 235 K (5455 bar) for one hour (170 μ Ahr), and then the specimen was cooled to 50 K; having failed to revert to the original SAT diffraction pattern, a four hour dataset (673 μ Ahr) was collected at 50 K, 5435 bar. The specimen was rapidly warmed to 200 K and the gas pressure was reduced to 2750 bar: a series of short counts (20 μ Ahr per datum) were then made at 5 K intervals upon warming from 200 K to 245 K at 2750 \pm 10 bar. Regrowth of familiar SAT crystals became evident at 230 K, with significant back-transformation being observed at 240 K: the sample was seen to be molten in diffraction data acquired at 245 K, 2760 bar. Immediate cooling of the sample to 230 K failed to induce crystallisation, so the gas pressure was reduced to \sim 400 bar, and the temperature was reduced to 100 K; warming to 200 K at 400 bar subsequently resulted in the formation of SAT crystals. Finally, the newly crystallised SAT was compressed to 5500 bar at 200 K and then warmed to 240 K, where the new diffraction pattern was observed once more. This new high-pressure sample was cooled to 100 K, whereupon the gas pressure was reduced to 100 bar. A low-noise dataset (\sim 350 μ Ahr) from the high-pressure specimen was collected at 70 K, 125 bar.

Results: thermoelastic properties of SAT. The unit cell dimensions of SAT (P $\bar{4}$ 2₁c) were refined using GSAS (with the structural model obtained in our earlier HRPD study,

RB20047). Along the 200 K isotherm, these results were fitted with a third-order Birch Murnaghan equation of state to obtain the bulk modulus ($K_{T,0}$) and axial incompressibilities (K_a , K_c), and their first pressure derivatives (K' , K'_a , K'_c), which are given in the table below.

V_0 (\AA^3)	358.43(8)	K_a (GPa)	18.3(10)
$K_{T,0}$ (GPa)	9.15(19)	K'_a	6(4)
K'	7.9(8)	K_c (GPa)	4.54(1)
		K'_c	5.6(5)

A blockage in the high-pressure capillary meant that data from 50 – 160 K at 5.5 kbar had to be discarded. But the data from 165 – 230 K allowed us to establish the high-pressure thermal expansivity. In combination with ambient pressure expansivity data (RB500086), we were able to estimate the pressure dependence of the volume thermal expansion, and thus the temperature dependence of the bulk modulus. Using two different methods, we found a value of -0.01 GPa K⁻¹, which is almost identical to the value for deuterated ice Ih.

Results: SAT II. A new high-pressure polymorph of sulfuric acid tetrahydrate was discovered (SAT II), formed by warming SAT above 235 K at 5.5 kbar. The diffraction pattern of SAT II has been indexed with a monoclinic unit cell of dimensions $a = 6.16196(32)$ \AA , $b = 11.09054(56)$ \AA , $c = 5.61734(36)$ \AA , $\beta = 110.207(4)^\circ$, and $V = 360.258(22)$ \AA^3 at 5.435 kbar, 50 K. The density is consistent with an asymmetric unit containing four molecules, and the most likely space-group is P2₁/a. Attempts at structure solution have not yet met with success, but the low-pressure specimen of SAT was found to be strongly textured, so it is likely that a method for forming a good SAT II powder will need to be found before the structure can be determined.

Fig 1. Le Bail fit to the SAT-II data collected in bank 4 with the monoclinic cell indexing given above.

