ISIS Experimental Report

Rutherford Appleton Laboratory

Title of Experiment:	Thermoelastic properties of ammonium sulfate, $(ND_4)_2SO_4$, and the P-T dependence of the para- to ferro-electric phase transition.
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Introduction: Ammonium sulfate is well known for the first-order phase transition which occurs upon cooling through 224 K (at room pressure) from a para-electric crystal (space group Pnam, Z=4) to a ferro-electric crystal (space-group P$na2_1$, Z=4) [1-5]. The pressure dependence of the transition temperature, dT_c/dP, up to 600 MPa has been found to have a value ≈ -41 K GPa^{-1} in protonated ammonium sulfate [6-9].

It has been suggested that interactions between aqueous ammonia and sulfates leached out of primitive planetary cores will result in (for example) Saturn's moon Titan containing a significant quantity of ammonium sulfate in its crust and mantle [9,10]. Therefore the thermoelastic and phase transition properties of ammonium sulfate must be known in order to model accurately the interiors of large icy moons.

Experimental method: Ammonium sulfate-d8 powder (Sigma Aldrich 175684, 98 at. % D) was loaded into TiZr encapsulated gaskets under a dry helium atmosphere, along with a Pb pressure marker and a 4:1 MeOD/EtOD solution as a pressure transmission medium. The Paris-Edinburgh cell was sealed under a load of 6 tons and mounted on the PEARL/HiPr beamline. Data were collected under loads of 6, 12, 17, and 22 tons at 293 K, counting for 320 μAhr at each datum. The specimen was then cooled (using the V-T insert) to 150 K under a load of 22 tons, a series of observations being made in order to bracket closely the phase transition temperature. The sample was then warmed to 293 K and data were collected at loads of 27 and 32 tons. A second cooling curve was made at a load of 32 tons, down to 110 K, before resuming room-temperature compression. Measurements were collected subsequently in 5 ton increments along the 293 K isotherm up to a maximum load of 72 tons. Longer integrations of 1921 and 1601 μAhr were made at 47 and 72 tons, respectively. At 72 tons, additional measurements on warming to 343 and 393 K showed *no evidence of any new high-pressure phase of ammonium sulfate.*

Results: The refined unit-cell parameters along the 293 K isotherm were fitted with a Murnaghan integrated linear equation of state (MILEOS) (Figure 1), with parameters reported in Table 1. These results agree very well with the axial and volumetric incompressibilities calculated from the elastic constants (bottom row, table 1). The two high-pressure phase transition points, determined from the 22 and 32 ton cooling curves, are plotted on Figure 2, along with the transition points found at room pressure and in the range 0-550 MPa during our related study of ammonium sulfate on HRPD (RB910009).

These data, covering a range (0−2.34 GPa) four times larger than previously studied, fall on a straight line of slope -29.7(4) K GPa^{-1}, comparable to the previously obtained values of -41 K GPa^{-1}. Application of the Clausius-Clapeyron relation, with the volume change of the transition evaluated at 222.5 K being 3.55(1)x10^{-7} m^3 mol^{-1}, yields a latent heat of 2.66(4) kJ mol^{-1} and an entropy change of 12.0(2) J mol^{-1} K^{-1}. The latter is close to the value 2Rln2 predicted by the model of Hasebe [4], but

substantially smaller than the value of ~3Rln2 obtained from specific heat capacity measurements [e.g., Ref. 2].

Figure 1: Unit-cell volume of ammonium sulfate along the 293 K isotherm. The solid red line is the fitted EoS.
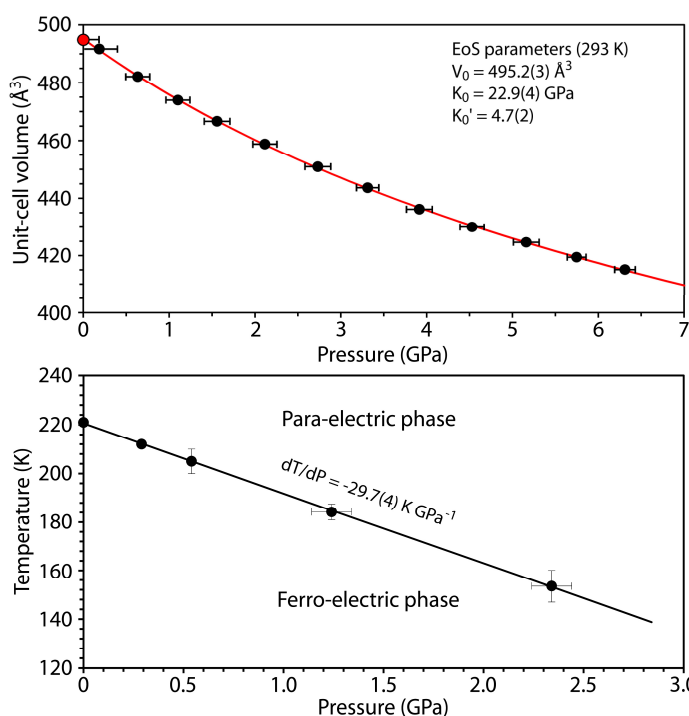

EoS parameters (293 K)
V_0 = 495.2(3) Å^3
K_0 = 22.9(4) GPa
K_0' = 4.7(2)

Figure 2: Observed pressure dependence of the para- to ferro-electric phase transition in deuterated ammonium sulfate.

dT/dP = -29.7(4) K GPa^{-1}

Table 1: MILEOS parameters of $(ND_4)_2SO_4$ at 293 K in the range 0 – 6.3 GPa.

	a-axis	b-axis	c-axis	Volume
V_0	7.781(1) Å	10.624(3) Å	5.991(1) Å	495.2(3) Å^3
K_0 (GPa)	70(2)	56(1)	78(1)	22.9(4)
K_0'	33(1)	9.2(4)	10.4(5)	4.7(2)
HRPD[1]	7.77958(4)	10.62157(5)	5.98852(3)	494.839(3)
SXTL[2]	67.8	51.2	81.1	21.5

[1]Unit-cell parameters $(ND_4)_2SO_4$ at 290 K, atmospheric pressure, measured on HRPD (see report RB910009).
[2]Single crystal axial and volume incompressibilities (GPa) computed from the elastic constants (protonated species) [11].

References:

[1] Matthias & Remeiker (1956): *Phys. Rev.* **103**, 262. [2] Hoshino *et al*. (1958): *Phys. Rev*. **112**, 405. [3] Schlemper & Hamilton (1966): *J. Chem. Phys*. **44**, 4498. [4] Hasebe (1981): *J. Phys. Soc. Japan*. **50**(8), 2660. [5] Hasebe (1981): *J. Phys. Soc. Japan*. **50**(4), 1266. [6] Tsunekawa *et al*. (1972): *J. Phys. Soc. Japan* **33**, 862. [7] Polandov *et al*. (1972): *Russ. J. Phys. Chem*. **46**(2), 281. [8] Jerzak (2002): *Ferroelectrics* **275**, 19. [9] Fortes *et al*. (2007): *Icarus* **188**(1), 139. [10] Grindrod *et al*. (2008): *Icarus* **197**(1), 137. [11] Haussühl (1965): *Acta Cryst*. **18**, 841.