

# ISIS Experimental Report

## Rutherford Appleton Laboratory

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Title of Experiment:	Thermoelastic properties of ammonium sulfate, $(\text{ND}_4)_2\text{SO}_4$ , and the P-T dependence of the para- to ferro-electric phase transition.	Local Contact:	K. S. Knight
Principal Proposer:	A.D. Fortes	Instrument:	HRPD
Affiliation:	University College London	Date of Experiment:	21-23/02/2009 17-19/06/2009
Experimental Team:	A.D. Fortes, P.M. Grindrod, K. S. Knight		

**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  $\text{Pn}am$ ,  $Z=4$ ) to a ferro-electric crystal (space-group  $\text{Pna}2_1$ ,  $Z=4$ ) [1-5]. The pressure dependence of the transition temperature,  $dT_c/dP$ , up to 600 MPa has been found to have a value  $\approx -41$  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.

The objective of this study was to make the most precise measurements possible of the unit-cell parameters of ammonium sulfate, both at atmospheric pressure in the range 4-290 K, but also as a function of T up to 550 MPa. A companion study on PEARL (RB910010) reports similar measurements up to 6.3 GPa.

**Experimental method:** Ammonium sulfate-d8 powder (Sigma Aldrich 175684, 98 at. % D) was loaded into an aluminium framed slab can for the room-pressure experiment, and into a TiZr gas cell for the high-pressure study. In both cases, this was done under a dry helium atmosphere.

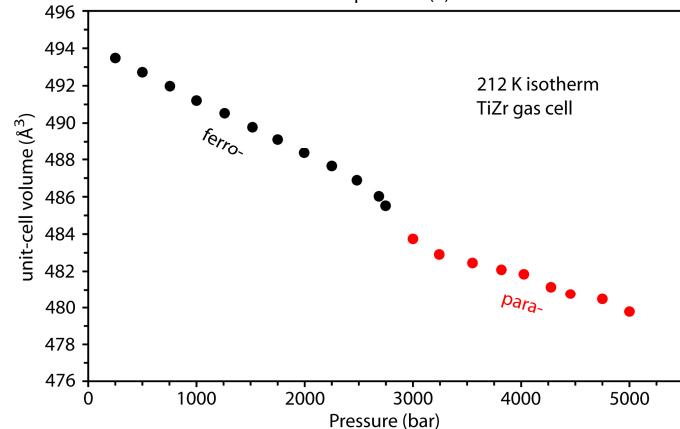
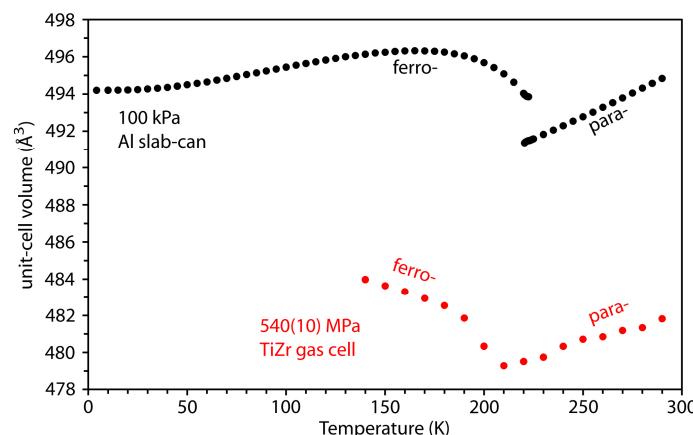
For the ambient pressure study, data were collected initially at 4.2 K, and then in 5 K increments from 10-220 K, 0.5 K increments from 220-225 K, returning to 5 K increments from 225-290 K. A second set of data were then acquired upon cooling in 0.5 K increments over the range 225-214.5 K in order to investigate any hysteresis in the phase transition.

For the high-pressure study, we chose to compress the specimen along the 212 K isotherm, calculating that we would observe the pressure-induced transition from the low-T ferro-electric phase to the high-T para-electric phase approximately in the middle of our 550 MPa pressure range. Data were collected in  $\sim$ 250 bar increments along this isotherm. Upon reaching 550 MPa, the temperature was increased to 290 K and data were collected subsequently upon cooling to 140 K in 10 K steps.

**Results:** Figures 1 and 2 depict the behaviour of the unit-cell volume of  $(\text{ND}_4)_2\text{SO}_4$  over the whole P-T range investigated; Figure 1 reports the isobaric data collected at room pressure and at 540 MPa, and Figure 2 shows the isothermal compression data. The phase transition is clear in all of the data-sets, occurring at 290(10) MPa at 212 K, and at 205(10) K at 540 MPa; in combination with a companion data-set collected on PEARL (RB910010), these results yield the pressure dependence of the phase transition,  $dT_c/dP = -29.7(4)$  K GPa $^{-1}$ . The volume change at the phase transition (at 222.5 K, room pressure) is  $2.359(9)$  Å $^3$  [ $3.55(1) \times 10^{-7}$  m $^3$  mol $^{-1}$ ], in agreement with earlier dilatometric measurements.

A thorough analysis of the temperature dependence of the elastic properties is in progress, along with a detailed examination of the vibrational contributions to the room-pressure thermal expansion tensor.

**Figure 1:** Temperature dependence of the unit-cell volume at room pressure (black circles) and at 540 MPa (red circles).



**Figure 2:** Temperature dependence of the unit-cell volume along the 212 K isotherm.

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