ISIS Experimental Report

Rutherford Appleton Laboratory

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Title of Experiment: Thermal expansivity of sulfuric acid tetrahydrate
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Instrument: POLARIS
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Date of Experiment: Oct. 2005

Introduction: The sulfuric acid - water system is of great interest, not least from a crystal chemical point of view, but because it plays a role in the formation of aerosols in the terrestrial stratosphere (e.g., Zhang *et al*., 1993: Bertram *et al*., 1996). Sulfuric acid tetrahydrate (SAT) is thought to be particularly important because of its role in promoting the nucleation of stratospheric ice clouds (Fortin *et al*., 2003: Girard *et al*., 2005), themselves responsible for controlling the heat balance in the upper atmosphere. We serendipitously crystallised a sample of SAT from a 1:3 D_2SO_4:D_2O mixture during a recent experiment on HRPD (see experimental report RB20047); this provided an opportunity to collect high resolution neutron diffraction data suitable for structure refinement. The data we collected allowed us to refine the structure ($P\bar{4}2_1c$) at 4.2 K and 217 K based on existing X-ray data for deuterated SAT (Kjällman & Olovsson 1972. Moreover, we were able to estimate crudely the volume and axial thermal expansivities. Whilst the volume thermal expansion and the expansion of the *c*-axis appeared normal; the thermal expansion of the *a*-axis showed indications of becoming small, or even negative, near the melting point. Since it is very important to be able to model surface interactions between SAT condensates and water molecules, and appreciation of the behaviour of the crystal at stratospheric temperatures (150 - 250 K) is critical. Calculations depend on robust interatomic potentials that are able to reproduce the anomalous expansivity displayed by the *a*-axis of SAT, and accurate crystallographic measurements underpin the fitting of such potentials.

We have therefored investigated the thermal expansion of a phase-pure SAT specimen on the POLARIS diffractometer.

Experimental method: An aluminium-framed slab can with vanadium windows (sealed with indium wire) was loaded with 6.34 g of SAT solution and ~ 0.1 g of silica wool to aid the crystallisation of a randomly oriented polycrystalline mass. Gadolinium oxide foil shielding was screwed over the front face of the aluminium body of the can, which was then dropped into a dewar of liquid nitrogen and subsequently transferred into a dewar of dry ice (at 195 K) for ~12 hours. The sample can was screwed to a cryostat centre stick and wired with heater and thermocouple whilst the bottom of the can was sat in a pyrex dish of liquid nitrogen. The centre-stick assembly was loaded into an Orange cryostat pre-cooled to 100 K and left for a further 20 hours before being mounted on the POLARIS beamline. Preliminary inspection of the diffraction pattern from the solid specimen at 100 K showed that SAT had crystallised, so the temperature was reduced to 1.7 K and a low-noise diffraction pattern (150 μAhr) was collected in the backscattering (2θ = 154°) and 90° banks of POLARIS. Diffraction patterns were then acquired upon warming, in 4 K intervals from 6 - 232 K, counting for ~10 minutes (30 μAhr) with 5 minutes of warming and thermal equilibration at each datum. The absence of Bragg peaks in the diffraction pattern collected at 232 K indicated that the sample had melted (indeed the 230 K diffraction pattern showed evidence of the onset of melting), which is in agreement with the approximate melting temperature of the deuterated isotopomer, 234 K, found by Kjällman & Olovsson (1972): the hydrogenous isotopomer melts at 244.9 K. The sample temperature was immediately reduced to 220 K, which caused the specimen to recrystallise promptly; diffraction data were collected at 220 K for 42 μAhr. Finally, low-noise data sets were collected from the recrystallised sample at 225 K (165 μAhr), 150 K (150 μAhr), and 75 K (365 μAhr).

Results: With the exception of an anomalous region from 164-192 K (likely due to minor glass devitrification), the volume and axial thermal expansivities are entirely regular (Figs. 1-3), indicating that our 1:3 specimen on HRPD had been subjected to strain from residual glass in the sample can. Nonetheless, the thermal expansion of the *a*-axis is clearly very much smaller than that of the *c*-axis. The data collected here are particular useful in combination with high-pressure results obtained on GEM. The latter experiment was only possible because of the unavoidable loss of the sample we were meant to be investigating (see RB520271).

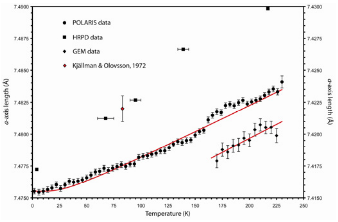

Fig. 1. *a*-axis of SAT.
N.B. GEM data is at 5.5 kbar.

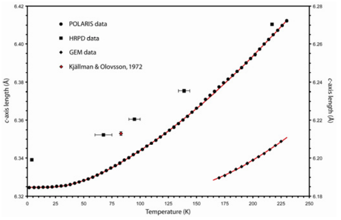

Fig. 2. *c*-axis of SAT.
N.B. GEM data is at 5.5 kbar.

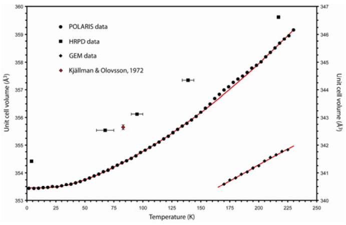

Fig. 3. Unit cell volume of SAT.
N.B. GEM data is at 5.5 kbar.

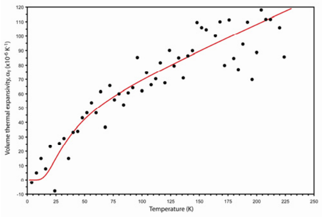

Fig. 4. Volume thermal expansivity of SAT.

References

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