

ISIS Experimental Report

Rutherford Appleton Laboratory

RB Number: 610128

Date of Report: 06/10/2006

Title of Experiment: The thermal expansivity of mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{D}_2\text{O}$)

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Instrument: HRPD

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Date of Experiment: 10-13/07/06

Introduction: The presence of salts such as Na_2SO_4 in chondritic meteorites has led to the suggestion that the water-rich icy moons of the Gas Giant planets should have ice mantles dominated by multiply hydrated salts such as mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ [1], with implications for the geophysics and astrobiology of these objects [2]. This suggestion has been supported by observational evidence from the Near Infrared Mapping Spectrometer (NIMS) instrument aboard the Galileo space-craft, which orbited Jupiter from 1995 to 2003. NIMS collected multispectral images of the surfaces of Jupiter's icy moons, Europa, Ganymede, and Callisto and these spectra have been interpreted as showing deposits of hydrated alkali salts [3]. In addition, mirabilite forms abundant thick deposits on the Earth in association with salt domes and hydrocarbon reservoirs. When constructing geophysical models of these icy moons to interpret the observed surface geomorphologies, it is important to know the phase behaviour of the constituent materials under the appropriate pressure and temperature conditions; for the large icy moons we are concerned with pressure up to ~ 5 GPa, and temperatures from 100 – 300 K. We therefore proposed to make measurements of the bulk thermoelastic properties of mirabilite under these conditions. Within the beam-time awarded, we were able to make measurements only at ambient pressure, and we will submit a continuation to carry out high-pressure studies.

Experimental method: Crystals of fully deuterated mirabilite were grown from a supersaturated solution of Na_2SO_4 (Sigma Ultra) in D_2O (Aldrich) in a sealed flask. Large crystalline lumps of mirabilite were extracted from the mother liquor and characterised by powder X-ray diffraction prior to the ISIS experiment. On the day of the experiment, solid lumps were dried and powdered in the ISIS cold room (to prevent dehydration, which occurs at 32°C). The powder was loaded into an aluminium-framed slab can, attached to a centre stick, placed in an OC50 cryostat on the HRPD beamline. The sample temperature was reduced rapidly to 4.2 K, and data were collected for ~ 3 hours. Data were then collected upon warming from 10K to 300 K in 10K steps, counting for 7 μAhr at each datum, and allowing 10 minutes equilibration time. At 300 K, another long count was undertaken so as to obtain another structural data set. The sample was cooled back down to 4K in 10K steps (interleaved between the warming points), counting for 7 μAhr at each temperature. The diffraction patterns obtained were refined using GSAS (Figure 1). It was found that a small amount of highly oriented ice was contributing parasitic Bragg peaks to the diffraction pattern, possibly as frost on the windows of the slab-can.

Results: $\text{Na}_2\text{SO}_4 \cdot 10\text{D}_2\text{O}$, crystallizes in space group $\text{P2}_1/\text{c}$ $Z = 4$; at 4K $a = 11.44226(8)$ Å, $b = 10.34252(6)$ Å, $c = 12.75472(8)$ Å and $\beta = 107.849(1)^\circ$; at 300K; $a = 11.51490(15)$ Å, $b = 10.36499(12)$ Å and $c = 12.84661(15)$ Å and $\beta = 107.757(1)^\circ$. As shown in Figure 2, the volume thermal expansion is positive and normally behaved; the axial expansivities are largely positive, although the b -axis displays a small degree of negative thermal expansion at low temperatures (below $\sim 50\text{K}$). The beta angle decreases upon warming, but appears to be increasing again as the dehydration temperature is approached. This behaviour is common to a number of sulfates, including $\text{CuSO}_4 \cdot 5\text{D}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{D}_2\text{O}$, and $\text{MgSO}_4 \cdot 11\text{D}_2\text{O}$. Subtle differences in the beta angle on warming and cooling appear to be related to changes in behaviour of the orientational ordering of the sulphate tetrahedra at limiting low temperature (see Levy and Lisensky [4]).

Figure 1. Backscattering diffraction pattern of mirabilite at 4.2K

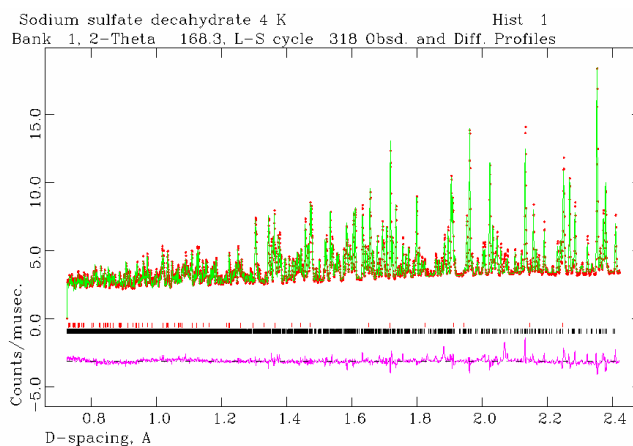
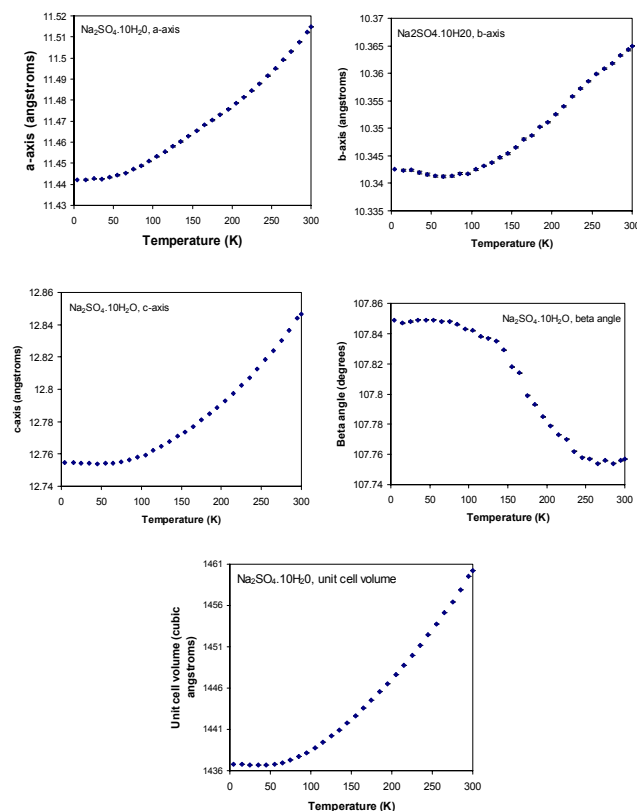


Figure 2. Variation of the unit cell parameters.



References

- [1] Kargel (1991) *Icarus* **94**, 368-390
- [2] Hogenboom *et al.* (1997) *Lunar Planet. Sci. Conf.* **28**, p 579.
- [3] Dalton *et al.* (2005) *Icarus* **177**, 472 – 490.
- [4] Levy and Lisensky (1978) *Acta Cryst.*, **B34**, 3502–3510.