

# ISIS Experimental Report

## Rutherford Appleton Laboratory

RB Number: 510035

Date of Report: 12 August 2005

**Title of Experiment:** The thermal expansion and phase transitions of anhydrous  $\text{MgSO}_4$

**Local Contact:** K. S. Knight

**Principal Proposer:** A. D. Fortes

**Instrument:** HRPD

**Affiliation:**

**Experimental Team:** I. G. Wood, L. Vočadlo, H. E. Brand

**Date of Experiment:** 26-28/08/05

**Introduction.**  $\text{MgSO}_4$  is the most important leachate from chondritic materials which probably form the rocky cores of the solar system's large icy moons [1]. We expect it to be strongly hydrated, crystallising salts such as  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ , which will comprise the mantles of these icy moons (see ISIS 2004 Science Highlight 'Epsom salt in the moons of Jupiter'). Our goal is to understand the structure and history of large icy moons from the physical properties of the constituent salts; we have carried out a detailed neutron diffraction study of the 7- and 12-hydrates (RB14491 & 15133). This experimental work is complemented by computational simulation. However, due to the computational expense of high-level quantum mechanical (QM) calculations, it is necessary to employ interatomic potential (IP) calculations as well. We have therefore made detailed measurements of the physical properties of two polymorphs of anhydrous  $\text{MgSO}_4$  ( $\alpha$ - and  $\beta$ - $\text{MgSO}_4$ ) thereby allowing us to fit Mg - O and S - O potentials, without the added complication of bound water. Such potentials will greatly extend our ability to understand the more complex  $\text{MgSO}_4$  hydrates that are so important in the outer solar system.

**Experimental method.** Anhydrous  $\beta$ - $\text{MgSO}_4$  was supplied by Sigma and dried at  $400^\circ\text{C}$  for 24 hours. Anhydrous  $\alpha$ - $\text{MgSO}_4$  was made by reacting MgO with  $\text{H}_2\text{SO}_4$  in excess followed by drying at  $200^\circ\text{C}$  for 24 hours. Both phases were characterised by X-ray diffraction prior to the experiment. The dry powders (4.4095g of  $\alpha$ - $\text{MgSO}_4$ , 5.006g of  $\beta$ - $\text{MgSO}_4$ ) were loaded into aluminium framed slab cans, attached to centre sticks and equilibrated in an OC50 cryostat at 4.2 K on the HRPD beamline. For both phases, data were collected at 4.2 K for  $\sim 3$  hours (100 $\mu\text{Ahr}$ ); subsequently, data were collected in 10 K intervals upon warming to 300 K, counting for 10 $\mu\text{Ahr}$ . At 300 K, another low-noise data set was collected for each phase (100 $\mu\text{Ahr}$  for  $\alpha$ - and 80 $\mu\text{Ahr}$  for  $\beta$ - $\text{MgSO}_4$ ). All diffraction data were treated using the GSAS package, structure refinement being started from the known structures of  $\alpha$ - and  $\beta$ - $\text{MgSO}_4$  [2,3]

**Results.**  $\alpha$ - $\text{MgSO}_4$  crystallises in space group Cmc $m$  ( $Z=4$ ); the unit cell dimensions at 4.2 K are  $a = 5.168630(33)$  Å,  $b = 7.867805(54)$  Å,  $c = 6.466745(54)$  Å, and at 300 K,  $a = 5.174713(29)$  Å,  $b = 7.875632(48)$  Å,  $c = 6.495166(46)$  Å. The linear and volume thermal expansion coefficients are positive at all temperatures and exhibit no unusual behaviour. Structures were refined at 4.2 and 300 K to  $R_p < 3\%$  (See Fig. 1), more poorly determined structural parameters being extracted from the shorter counts during warming from 4.2 - 300 K.

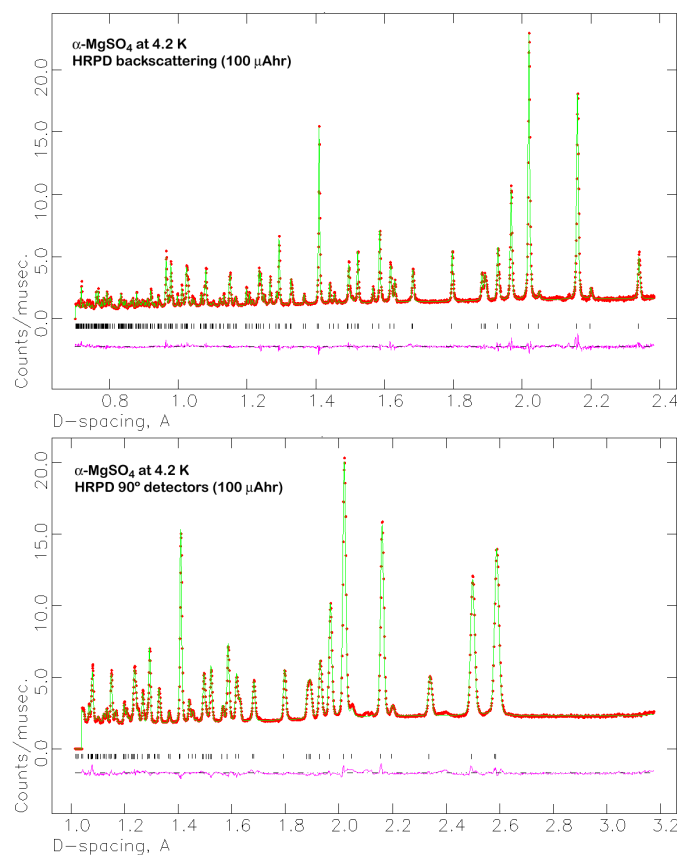
$\beta$ - $\text{MgSO}_4$  has a more complex structure, crystallising in space group Pbn $m$  ( $Z=4$ ); the unit cell dimensions at 4.2 K are  $a = 4.734527(93)$  Å,  $b = 8.581639(141)$  Å,  $c = 6.672507(115)$  Å, and at 300 K,  $a = 4.746156(187)$  Å,  $b = 8.582944(124)$  Å,  $c = 6.709208(109)$  Å. As shown in Fig 2, the linear expansion of the  $a$ - and  $c$ -axes, and the volume thermal expansion coefficient are positive at all temperatures and normally behaved. However, the thermal expansion of the  $b$ -axis is both very small and negative below  $\sim 150$  K. Similar behaviour is seen in the  $a$ -axis of epsomite (RB14491) and is attributable to rigid body motion of the  $\text{SO}_4$ -tetrahedra. We suspect that the greater structural degrees of freedom in the  $\beta$ -phase, compared to the  $\alpha$ -phase, allow for similar rigid body motion.

Work on fitting interatomic potentials to the wealth of structural data acquired during this experiment is in progress.

### References

- [1] Kargel, J. S. (1991): *Icarus* **94**(2), 368-390; Kargel *et al.*, (1994): *Icarus* **112**(1), 219-252.
- [2] Rentzperis, P.J., and C. T. Soldatos (1958): *Acta Cryst.* **11**, 686-688.
- [3] Coing-Boyat, J. (1962): *C. R. Acad. Sci. Paris* **255**, 1962-196

**Figure 1.** Diffraction patterns of  $\alpha$ - $\text{MgSO}_4$  at 4.2 K.



**Figure 2.** Variation of the unit cell dimensions of  $\beta$ - $\text{MgSO}_4$  as a function of temperature.

