

# ISIS Experimental Report

## Rutherford Appleton Laboratory

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Title of Experiment: High-pressure study of triclinic  $\text{MgSO}_4 \cdot 11\text{D}_2\text{O}$

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Instrument: HRPD

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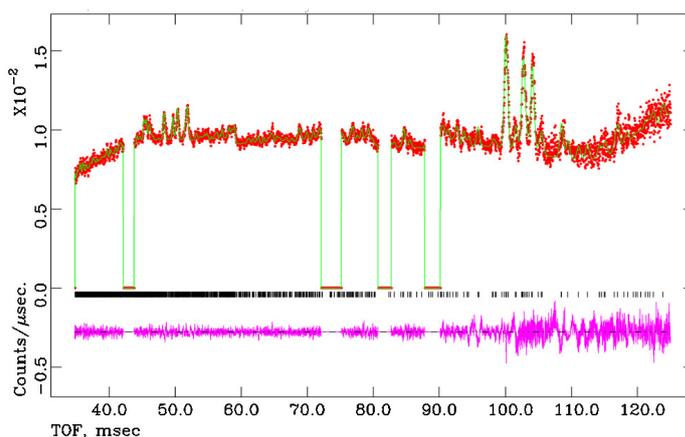
**Introduction:** The title substance is a relatively poorly characterised material. However, it has been the subject of greater scrutiny in the past few years since it has been suggested that it may be an important mineral on Mars [1], and also that it may be a major rock-forming mineral in the outer solar system [2]. It was recently identified in terrestrial frozen brine ponds [3], and named meridianiite (for Meridiani Planum on Mars). Peterson and Wang [4] solved the structure from single-crystal X-ray diffraction data. We have carried out a range of experimental and computational studies of meridianiite, including a neutron powder diffraction study over the temperature range 4.2 – 250 K on HRPD [5], a single-crystal study of the protonated phase on SXD (see RB820008), and a high-pressure study using the Paris-Edinburgh cell on PEARL/HiPr (see RB820064). The objective of this work was to complement the studies using the P-E cell, and to characterise precisely the evolution of the unit-cell parameters as a function of pressure and temperature in the range  $0 < P < 550$  MPa and  $50 < T < 250$  K. These measurements are expected to provide a similar definition of the P-V-T surface to that we obtained for epsomite,  $\text{MgSO}_4 \cdot 7\text{D}_2\text{O}$  [6], as well as ‘ground truth’ for our *ab initio* simulations of meridianiite (unpublished).

**Sample preparation:** Meridianiite was formed by rapid quenching with liquid- $\text{N}_2$  of a stoichiometric (supersaturated) solution of  $\text{MgSO}_4$  in  $\text{D}_2\text{O}$ . Slugs of fine polycrystalline material formed in this way were broken up and ground to a powder in the UCL Earth Sciences cold rooms. Approximately  $1.5 \text{ cm}^3$  of this powder was loaded into a TiZr gas cell, the body of which was packed in dry ice.

**Data collection:** Despite the best possible manual optimisation of the gas cell in the beam line, it was found that the signal from the specimen was very weak indeed, far weaker than expected. The resulting diffraction data were therefore rather poor (figure 1). In contrast, the results from the P-E cell on PEARL/HiPr were significantly better than expected (RB820064).

Data were collected, counting for two hours per point, at eleven points between 513 – 5453 bar (in  $\sim 500$  bar increments) along the 250 K isotherm, followed by a further eight points between 250 – 90 K (in 20 K increments) at  $5425 \pm 25$  bar: finally, the specimen was decompressed at 90 K from 5400 – 436 bar (in  $\sim 700$  bar increments).

Figure 1. Diffraction pattern acquired in the HRPD  $90^\circ$  detectors at 513 bar, 250 K.



**Results:** The refined unit-cell volumes collected along the 250 K isotherm were fitted with a 3<sup>rd</sup> order Birch-Murnaghan equation of state (BMEOS3). The fit parameters obtained are the zero-pressure volume,  $V_0 = 703.3(1) \text{ \AA}^3$ , zero-pressure bulk modulus,  $K_0 = 22.0(7)$  GPa, and the first pressure derivative of the bulk modulus,  $K' = 8(2)$ . These results compare well with those found from our earlier neutron powder diffraction study ( $V_0 = 706.469(7) \text{ \AA}^3$  at 250 K [5]), and our *ab initio* calculations;  $K_0 = 23.1(1)$  GPa,  $K' = 2.9(3)$ , in the athermal limit. Indeed fixing  $K' \equiv 2.9$  in the fit to the experimental data yielded  $V_0 = 703.124(8) \text{ \AA}^3$  and  $K_0 = 23.5(2)$  GPa, with only a very small reduction in  $R^2$  (0.99958 for the free fit, to 0.99940 for the fit with  $K'$  fixed).

A parabolic fit to the data collected upon cooling at high pressure gives the volume thermal expansion at 5425 bar, 250 K,  $\alpha_V = 64 \times 10^{-6} \text{ K}^{-1}$ . We can use the value found at room pressure, 250 K [5],  $72 \times 10^{-6} \text{ K}^{-1}$ , to determine the Anderson-Grüneisen parameter,  $\delta_T$ , and hence obtain the temperature dependence of the bulk modulus,  $\partial K/\partial T \approx -9$  MPa  $\text{K}^{-1}$ . This value is very similar to that found for other ice and hydrate phases [e.g., 7].

#### References:

- [1] Chou & Seal (2007): *J. Geophys. Res. Planets.* **112**, article E11004.
- [2] Kargel (1991): *Icarus* **94**(2), 369-390.
- [3] Peterson *et al.*, (2007): *American Min.* **92**(10), 1756-1759.
- [4] Peterson & Wang (2006): *Geology* **34**(11), 957-960.
- [5] Fortes *et al.*, (2008): *Phys. Chem. Min.* **35**(4), 207-221.
- [6] Fortes *et al.*, (2006): *Eur. J. Min.* **18**(4) 449-462.
- [7] Fortes *et al.*, (2008): *J. Chem. Phys.* **128**(5), article 054506.