

# ISIS Experimental Report

## Rutherford Appleton Laboratory

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Title of Experiment: The phase transitions in epsomite ( $\text{MgSO}_4 \cdot 7\text{D}_2\text{O}$ ).

Local Contact: M. G. Tucker

Principal Proposer: A. D. Fortes, University College London  
Affiliation:

Instrument: PEARL/HiPr

Experimental Team: A. D. Fortes, I. G. Wood, M. G. Tucker

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**Introduction:** We have previously carried out a powder neutron diffraction study of epsomite on PEARL/HiPr using the Paris-Edinburgh cell.  $\text{MgSO}_4 \cdot 7\text{D}_2\text{O}$  was compressed to 5 GPa (in 300 MPa steps) both at room temperature and at 200 K [1]. We observed a sequence of sluggish phase transitions at room temperature. Although we attempted to recover one of the high-pressure phases to room pressure under liquid nitrogen, we were unsuccessful [2]. In collaboration with colleagues at the Institute for High Pressure Physics (Troitsk, Russia) we have just completed a study of protonated and deuterated epsomite in the range  $0 < P < 2.8$  GPa,  $77 < T < 295$  K using a piston-cylinder device [3]. These studies show that our earlier 300 MPa pressure resolution was not suited to a proper study of epsomite's high-pressure behaviour, since two of the phase transitions observed in the piston-cylinder cell appear to be separated by only  $\sim 200$  MPa. Most remarkable of all are the large differences observed between data collected in the piston-cylinder cell at 295 K and 285 K.

**Experimental:** Fully deuterated epsomite crystals, grown from aqueous solution, were powdered in air at room temperature. This powder was loaded into encapsulated gaskets along with a single Pb pellet to act as the pressure calibrant, and fluorinert to act as the pressure transmitting medium. In this experiment, any liquid evolved during incongruent melting of epsomite is immiscible in the pressure medium, whereas previously, such liquid would have mixed with the MeOD/EtOD pressure medium. The P-E cell was sealed under a load of 7 tons and mounted in the beamline. Diffraction data (Figure 1) were acquired in one ton increments on increasing load at room temperature from 7–23 tons, and in 2 ton increments thereafter. Neutron counts were integrated for one hour at the majority of these points at and below 21 tons, and for two hours at higher load (all indicated in red on Figure 1). At 7, 20, 23, and 31 tons, however, neutron counts were integrated for 12-13 hours (indicated in black on Figure 1).

**Results:** From 7-19 tons (0 to 1.2 GPa) the powder diffraction pattern is due to the familiar low-pressure  $\text{P}2_12_12_1$  phase of epsomite. On increasing the load from 19 to 20 tons, however, the diffraction pattern changed over a period of  $\sim 90$  minutes, indicating that a phase transition had occurred. This diffraction pattern was present at only two pressure points (i.e., it was stable over a pressure interval of roughly 200 MPa, as expected from the piston-cylinder data). We have not been able to index this diffraction pattern; the presence of what may be a weak hump of diffuse scattering around  $d = 2.6$  Å (which is not apparent at the scale used in Figure 1) suggests that epsomite has undergone incongruent melting to a lower hydrate of as-yet unknown hydration number. At 22 tons, the diffraction pattern altered once more, over a period of around 30 minutes; the scattering from this phase (or phase mixture, proved to be much weaker than at lower loads, and consequently the integration times were doubled. The diffraction pattern observed at 23-27 tons is the same as that observed in our previous high-pressure studies of epsomite, from which we had collected a high-quality 20-hour integration. We have not indexed this diffraction pattern, and now believe it to be a mixture of some unidentified lower hydrate of  $\text{MgSO}_4$  and high-pressure ice. At 29 and 31 tons we observed changes in the diffraction pattern which may indicate a change in the  $\text{MgSO}_4 \cdot n\text{D}_2\text{O}$  phase, and certainly mark the growth of ice VII in the specimen.

The load was subsequently completely released and the specimen was recovered from the encapsulated gaskets at room P,T. The extracted pellet was loaded into a vanadium tube approximately 30 minutes after

the release of the load and diffraction data were collected. We found that the specimen had reverted to the low-pressure  $\text{P}2_12_12_1$  phase of epsomite. We believe that the mixture of fine-grained  $\text{MgSO}_4 \cdot n\text{D}_2\text{O}$  + brine was able to rehydrate very quickly once the pressure was completely removed, since the brine had not itself been able to mix with the pressure medium.

The available time was not sufficient to explore the significant temperature dependence of the phase transition behaviour observed by our Russian colleagues; we had originally intended to make a second run of observations at 285 K as well as 295 K.

### References

- [1] ISIS Experimental Report RB520039.
- [2] ISIS Experimental Report RB620224.
- [3] Gromnitskaya *et al.* (2009): Ultrasonic study of epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) under pressure. 47<sup>th</sup> EHPRG.

Figure 1: Changes in the diffraction pattern of  $\text{MgSO}_4 \cdot 7\text{D}_2\text{O}$  on increasing load at room temperature. Data in red represent 'short' integrations (1-2 hr) whereas data in black represent 'long' integrations (12 hr +).

