

# ISIS Experimental Report

## Rutherford Appleton Laboratory

RB Number: 920238

Date of Report: 30/09/2009

**Title of Experiment:** High pressure behaviour of sulfuric acid tetrahydrate.

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**Instrument:** PEARL/HiPr

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**Date of Experiment:** 28/07 - 01/08/2009

**Introduction:** The sulfuric acid-water system provides rich territory for exploring the hydrogen bonding between neutral and ionised water molecules. As a function of composition, there are numerous hydrates observed at atmospheric pressure,  $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$  with  $n = 1, 2, 3, 4, 6\frac{1}{2}$ , and 8, containing various combinations of  $\text{H}_2\text{O}$ ,  $\text{H}_3\text{O}^+$ , and  $\text{H}_5\text{O}_2^+$  with  $\text{SO}_4^{2-}$  [1]. To date, only the structure of the trihydrate remains unknown. Some exploration of the behaviour of these hydrates as a function of temperature and of pressure has been undertaken: of particular interest are the studies of sulfuric acid monohydrate (SAM), and sulfuric acid tetrahydrate (SAT), which have revealed the existence of new high-pressure polymorphs [2-4]. Investigation of these high-pressure structures is important since there are likely to be changes in both the hydrogen bond topology as well as possible changes in ion speciation. It is also plausible that pressure-induced dehydration may occur; this phenomenon is seen in many systems explored by us, including ammonia dihydrate [5] and the 7- and 11-hydrates of  $\text{MgSO}_4$  [6].

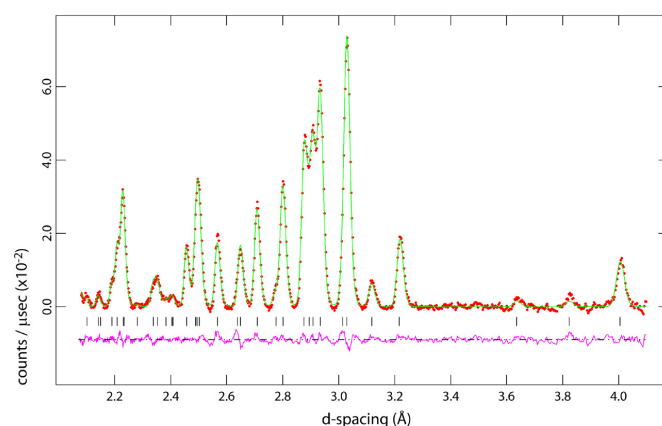
In an earlier gas-cell experiment on GEM, we discovered a new phase of SAT (SAT-II) that is formed when the low-pressure phase is warmed above 230 K at 535 MPa [4]; although we have indexed the diffraction pattern of SAT-II (Figure 1) the crystal structure has not yet been determined. SAT-II was indexed with a monoclinic unit-cell (probable space-group  $\text{P}2_1/a$ ,  $Z = 4$ ,  $a = 6.1902(3)$  Å,  $b = 11.1234(5)$  Å,  $c = 5.6446(3)$  Å, and  $\beta = 110.280(4)^\circ$  at 235 K, 535 MPa). The objective of this work was to carry out a survey of the high-pressure behaviour of deuterated sulfuric acid tetrahydrate in order to extend our earlier work beyond 0.5 GPa and up to higher temperatures.

**Experimental:** Aldrich sulfuric acid-d2 (96-98 wt. %  $\text{D}_2\text{SO}_4$  in  $\text{D}_2\text{O}$ ) was diluted with Aldrich  $\text{D}_2\text{O}$  to form an aqueous solution with the stoichiometry  $\text{D}_2\text{SO}_4 : \text{D}_2\text{O} = 1:4.0 \pm 0.1$ . This liquid was loaded into the encapsulated gaskets of the Paris-Edinburgh cell along with a small pellet of Pb to act as the pressure calibrant, and a small quantity of silica wool to act as a nucleating agent. The cell, equipped with a variable-temperature insert was sealed under a load of 7 tons at room temperature and was then craned into the beamline. Crystallisation of the liquid at high pressure proved to be more difficult and time-consuming than expected. The liquid specimen was initially cooled to 250 K under a load of 11 tons, and was then compressed step-wise up to a load of 23 tons ( $\sim 1.6$  GPa) at 250 K. Warming to 280 K and further compression to 26 tons failed to induce crystallisation. Only when the temperature was rapidly reduced to 200 K at a load of 26 tons did crystallisation occur.

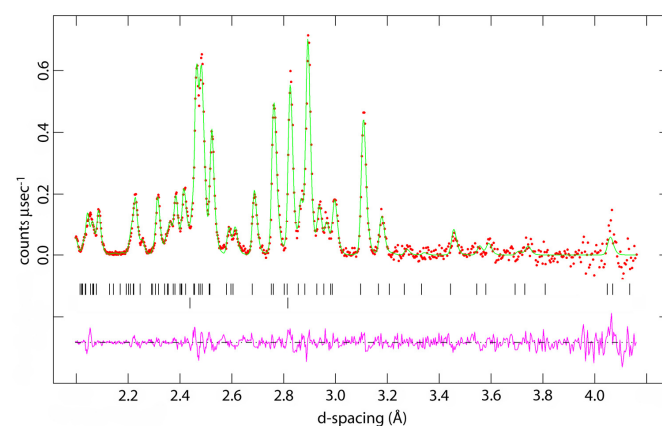
**Results:** The newly crystallised phase obtained at 200 K, 26 tons (1.56 GPa), could not be identified as either of the previously known phases of sulfuric acid tetrahydrate, SAT-I or SAT-II. The diffraction pattern (Figure 2) of this new phase, SAT-III, was successfully indexed with a monoclinic unit cell with refined dimensions,  $a = 7.6612(5)$  Å,  $b = 9.6428(7)$  Å,  $c = 8.1327(6)$  Å, and  $\beta = 94.241(5)^\circ$ ,  $V = 599.16(4)$  Å<sup>3</sup>,  $Z = 8$ . This corresponds to a volume roughly 10 % smaller than that of SAT-II extrapolated to the same P,T conditions. The unit-cell is primitive, and systematic absences indicate an  $n$ -glide parallel to (010). Powder diffraction data were integrated for 6 hours at 200 K, 26 tons, after which the load was increased in 2 ton increments along the 200 K isotherm up to 41 tons, where a second long count (8 hr) was made. The specimen was then warmed in 10 K increments up to 300 K, counting for one hour at each datum. Above 300 K, counting times were reduced to 15 minutes, simply to identify the onset of melting. Melting of SAT-III was observed to occur at 380 K, 41 tons ( $\sim 3.9$

GPa). Rapid cooling back down to 200 K failed to induce re-crystallisation; this only occurred when warmed up to 295 K at 41 tons load, whereupon the diffraction pattern of SAT-III re-appeared. Crystalline SAT-III formed both before and after melting *in situ* was observed to be very strongly textured, and as a consequence our attempts to solve the crystal structure from the powder data have so far not been successful. However, SAT-III is clearly an important high-pressure polymorph in this system, being stable from approximately 1.5 to 4 GPa, and up to 380 K at the higher pressure.

**Figure 1.** The diffraction pattern of SAT-II observed previously on GEM (0.535 GPa, 235 K).



**Figure 2.** The diffraction pattern of SAT-III observed on PEARL/HiPr during this experiment (1.56 GPa, 200 K). Tick marks represent the Bragg reflections of Pb (lower set) and SAT-III (upper set).



### References

- [1] Beyer *et al.*, (2003): J. Phys. Chem. A **107**, 2025.
- [2] Allan *et al.*, (2002): J. Chem. Soc. Dalton Trans. **2002**, 1867.
- [3] Fabbiani *et al.*, (2008): Inorg. Chim. Acta **361**, 487.
- [4] Fortes *et al.*, (2008): J. Chem. Phys. **128**, article 054506
- [5] Fortes *et al.*, (2007): High Press. Res. **27**, 201.
- [6] See ISIS Experimental reports 520039, 620224, 820064 and 910226.