ISIS Experimental Report

Rutherford Appleton Laboratory

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Title of Experiment:	Single crystal analysis of triclinic $MgSO_4 \cdot 11H_2O$ (meridianiite)	**Local Contact:**	M. J. Gutmann
Principal Proposer:	A. D. Fortes	**Instrument:**	SXD
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Experimental Team:	A. D. Fortes, I. G. Wood, M. J. Gutmann	**Date of Experiment:**	11-16/09/2008

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]. These data yielded improved precision on the hydrogen (deuterium) atom positions - compared to Peterson and Wang [4] - and the lengths of the hydrogen bonds in the structure, as well as allowing us to determine the coefficients of the thermal expansion tensor and relate these to the temperature dependent behaviour of, primarily, the weak bifurcated hydrogen bond. There was some indication in the powder data of a proton transfer from a water molecule to a sulfate oxygen, although the refinements were necessarily done with heavy restraints.

In addition to probing the speciation of the sulfate tetrahedron (SO_4^{2-} vs. HSO_4^-) at low- and high-temperature, we also wish to refine anisotropic temperature factors so as to clarify the role of specific hydrogen bonds (most critically the bifurcated bond) in controlling the thermal expansion along different directions through the crystal. Given the low symmetry ($P\bar{1}$), and the size of the unit cell (~ 700 Å^3), a single-crystal analysis was essential.

Sample preparation: All attempts to grow deuterated single crystals failed. Experiments at a range of temperatures indicate to us that the stability field of the deuterated phase must be much small than the protonated species (itself only 6 K wide), and possibly the 11-hydrate is entirely metastable in the deuterated system. Comparison with other sulfate salts in D_2O (for example, $CuSO_4$ [6]) suggest upward shifts of several Kelvin in eutectic points. However, protonated single crystals are extremely easy to produce, and whilst this increases integration times several-fold, it does not pose as severe a problem as in a powder experiment. Cm-sized crystals were carved into irregular blocks ~ 3mm on a side in the UCL Earth Sciences cold rooms (-15°C) and stored in liquid nitrogen. In the absence of a suitable ISIS cold room, crystals were mounted into a rolled aluminium foil pouch (thickness 60 μm) in a Pyrex dish of liquid nitrogen. This is rather unsatisfactory since atmospheric water readily accumulates as ice crystals in the nitrogen, which tend to float into the open end of the pouch. Two crystals were mounted in order to ensure good reciprocal-space coverage since the cryostat limits crystal orientation to ω-rotation only. The aluminium bag was tied to the end of a standard SXD mounting pin with a length of wire passed through a hole drilled in the pin. The pin was attached to a cryostat centre stick and then inserted into a pre-cooled CCR and the temperature was reduced to 5 K.

Data collection:

	5.2 K	**60 K**	**125 K**	**250 K**
a (Å)	6.7283(13)	6.7293(13)	6.7331(13)	6.7493(15)
b (Å)	6.7859(14)	6.7846(13)	6.7906(13)	6.8161(14)
c (Å)	17.332(4)	17.3310(35)	17.3170(35)	17.303(4)
α (°)	88.181(13)	88.199(13)	88.176(13)	88.117(15)
β (°)	89.349(14)	89.397(13	89.414(13)	89.449(15)
γ (°)	62.515(12)	62.540(11)	62.566(11)	62.620(13)
V (Å^3)	701.46(26)	701.76(25)	702.36(25)	706.44(28)
ρ_{calc} (kg m^{-3})	1508.1(6)	1507.4(5)	1506.2(6)	1497.5(6)
Integrated current (μ A hr)	4234.9	3300.6	4200.6	5800.5
Obs reflections	14940	10894	9065	7121
d-spacing$_{min}$ (Å)	0.364	0.362	0.448	0.403
d-spacing$_{max}$ (Å)	8.662	8.661	8.654	8.647
h =	16 → -17	15 → -18	13 → -13	14 → -12
k =	16 → -18	16 → -16	14 → -15	11 → -12
l =	25 → -37	22 → -37	20 → -31	21 → -29
Intensity extraction	3D gaussian peak profiling in *SXD2001[7]*			
Extinction coefficient	7.9(1)x10^{-5}	8.0(2)x10^{-5}	7.9(2)x10^{-5}	1.03(3)x10^{-4}
Refinement				
Refinement method	Full matrix least squares on F_o^2, using *GSAS / EXPGUI*			
Restraints / parameters	0 / 367	0 / 367	0 / 367	0 / 367
R*w* (F_o^2) %	17.2	17.7	18.1	19.2
R (F_o^2) %	13.2	13.9	14.3	15.6
R*w* (F_o) %	9.3	9.8	9.9	10.7
R (F_o) %	7.1	7.4	7.6	8.1

Results: Refinements yield approximately an order of magnitude improved precision on atomic coordinates, bond lengths and angles, compared with the powder refinement, without the need for any restraints. Anisotropic thermal ellipsoids are consistent in shape and orientation as a function of temperature (proving particularly useful in understanding the bifurcated bond), and the temperature dependence for each atom has been fitted with a Debye model. Consistent changes in bond lengths and angles, and polyhedral volumes have been obtained. Interesting differences in the temperature dependence of the unit-cell shape compared to the deuterated phase have also been observed, most notable being the apparent lack of any negative volume thermal expansion at low temperature.

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] Miles & Menzies (1937): *J. Am. Chem. Soc*. **59**, 2392-2395.
[7] Gutmann (2005): *SXD2001 - a program for treating data from TOF neutron single-crystal diffraction*. ISIS-RAL, UK.