

ISIS Experimental Report		RB Number:	910178
Rutherford Appleton Laboratory		Date of Report:	12/08/2010
Title of Experiment:	Single-crystal analysis of disorder in deuterated and protonated mirabilite	Local Contact:	M. Gutmann
Principal Proposer:	Dr Ian Wood	Instrument:	SXD
Affiliation:	Dept. Earth Sciences, UCL	Date of Experiment:	6/6/2009
Experimental Team:	H Brand, A D Fortes, L Vočadlo		

The properties of sodium sulfate decahydrate are of relevance to many areas of geology, planetary science, chemical physics and even the construction industry. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ occurs naturally as the mineral mirabilite in evaporite deposits the world over, and even as microscopic inclusions in the polar ice sheets; moreover, it is thought to be a major rock-forming mineral on the solar system's icy moons. It has been used as an energy storage material, due to the large latent heat of hydration, and its formation during weathering of building stone causes structural damage to buildings, due to the large volume change upon hydration.

A previous single-crystal neutron diffraction study of the structure of protonated mirabilite at 298 K [1] had revealed orientational disorder in some of the Na-coordinated water molecules, and also orientational disorder of the SO_4 tetrahedra and of the hydrogen-bonds donated to the apices of these tetrahedra. In contrast, our refinement of the sulfate site occupancies from a recent neutron powder diffraction study of deuterated mirabilite (HRPD), in which we investigated the temperature dependencies of the partial occupancies, was consistent only with ordered sulfate tetrahedra and ordered hydrogen bonds donated to the tetrahedra's apices [2]. However, these powder refinements required minor corrections for texture and for extinction. It was also impossible to obtain meaningful site occupancies and isotropic temperature factors without the use of stiff bond-distance and bond-angle restraints on the sulfate tetrahedron and on all of the water molecules. This is due to the low symmetry ($P2_1/c$) and large size ($\sim 1435 \text{ \AA}^3$) of the unit-cell, leading to a very large number of parameters to be refined (~ 200).

The purpose of this experiment on SXD was, therefore, to determine whether the apparent difference in behaviour shown in the two experiments [1] and [2] was due to some aspect of the sample preparation or crystal growth (e.g., deuteration), the thermal history of the sample during the experiment, or possibly alteration of the specimen during the long period required for data collection in the earlier study [1].

Data were collected on SXD from crystals of protonated mirabilite at 4 K and 270 K and from deuterated mirabilite at 4 K, 70 K, 140 K, 210 K and 270 K. Our preliminary analysis of these data indicates that:

- a/. the protonated and deuterated samples show very similar behaviour
- b/. The orientational disorder in the Na-coordinated water molecules is as reported in earlier studies [1, 2]
- c/. As previously suggested [1], there is thermally-activated disorder in the SO_4 tetrahedra which was not revealed in our previous powder diffraction study [2]. This can be seen in the two Fourier maps, calculated from the SXD data from deuterated mirabilite, that are shown in Fig. 1; in these maps, the SO_4 tetrahedron is viewed normal to its basal (O7-O6-O4) plane. The left hand (4 K) map shows no disorder. In the right-hand (270 K) map the "tails" in the scattering density of the oxygen atoms correspond to a clockwise rotation of the tetrahedron around the line of the S-O5 bond, similar to the multi-site disorder reported in [1].

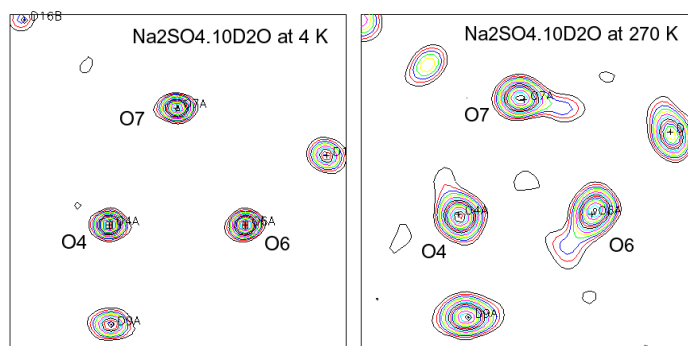


Fig 1: Scattering density in $\text{Na}_2\text{SO}_4 \cdot 10\text{D}_2\text{O}$ at 4K and 270 K

Detailed analysis of the disorder in the mirabilite structure is ongoing; it will clearly necessitate the use of higher-order, anharmonic, approximations to describe the atomic displacements.

References: [1] Levy & Lisensky (1978) Acta Cryst B, **34**, 3501-3510. [2] Brand et al. (2009) Phys. Chem Minerals, **36**, 29-36.