# ISIS Experimental Report

## Rutherford Appleton Laboratory

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| | | **RB Number:** | 1010078 |
| | | **Date of Report:** | 24/05/2010 |
| **Title of Experiment:** | Thermal expansion and phase transition in magnesium sulfate trihydrate | **Local Contact:** | K. S. Knight |
| **Principal Proposer:** | A.D. Fortes | **Instrument:** | HRPD |
| **Affiliation:** | University College London | | |
| **Experimental Team:** | A.D. Fortes, K.S. Knight | **Date of Experiment:** | 4-7/03/2010 |

**Introduction:**

The complete crystal structures of $MgSO_4$-hydrates with $n$ = 1, 4, 5, 6, 7, and 11 have each been refined from single-crystal data; the the heavy-atom structures of $MgSO_4 \cdot 2H_2O$ (sanderite) and $MgSO_4 \cdot 2½H_2O$ have been determined recently by X-ray powder diffraction methods [1,2]. In August 2009 I carried out a single-crystal neutron diffraction study of $MgSO_4 \cdot 3D_2O$ at the ILL; the data was used to solve the crystal structure at room temperature, and to obtain information concerning its behaviour as a function of temperature [3]. It was found that a first-order phase transition occurred upon cooling through 245 K; attempts to derive the low-T unit-cell were unsuccessful. However, the identification of disordered and bifurcated hydrogen bonds in the structure at high temperature suggests that the phase transition is due to ordering of these hydrogen bonds on cooling.

*The objective of this proposed work is (i) to make precise measurements of the unit-cell parameters of $MgSO_4 \cdot 3D_2O$ as a function of temperature, and (ii) to characterise the change in symmetry that occurs on passing through the first-order phase transition at 245 K.*

**Experimental method**

Crystals of $MgSO_4 \cdot 3D_2O$ were prepared by gentle evaporation of a 25 wt. % $MgSO_4$ solution at 110°C for ~ 24 hours without stirring. After extraction from the mother liquor the crystals were ground to a powder under a helium atmosphere. Both the pestle and mortar, and the aluminium sample can were chilled on a bed of dry ice snow inside the helium-filled glove bag. The sample was then mounted in a CCR at 250 K and data were collected in the 100-200ms time-of-flight window. Initial inspection of the data revealed a mixture of phases to be present, $MgSO_4 \cdot 3D_2O$, $MgSO_4 \cdot 6D_2O$ and $MgSO_4 \cdot 7D_2O$, in the approximate proportions 50:30:20. The specimen was then cooled to 230 K, where the splitting of certain $MgSO_4 \cdot 3D_2O$ reflections became evident (e.g., (221), Fig. 1), before being cooled down to 8 K for a long data collection in the 30-130 ms t-o-f window (400 μAhr). A series of shorter (40 μAhr) integrations were made upon warming to 120 K, 273 K, and 295 K in the 100-200 ms t-o-f window, followed by another series of measurements upon cooling from 245K down to 160 K.

**Results**

The unit-cell parameters of all three components in the specimen were refined using the Rietveld method in GSAS. We established that the orthorhombic unit cell of $MgSO_4 \cdot 3D_2O$ above 245 K experiences a modest distortion; in the P*bca* setting of the high-T cell, the angle γ jumps discontinuously from 90.0° to 90.2° and this angle increases to ~ 91.1° as the temperature is reduced to limiting low temperature. Permutation of the cell axes in order to locate the 2-fold axis of the low-T structure along the monoclinic *b*-axis results in a space-group assignment of $P2_1/c$. The data for the low temperature phase were fitted to simple saturation functions of the form $x = x_0 + y \cdot T_S \cdot \coth(T_S/T)$ in order to quantify the strain due to the phase transition, where $T_S$ is a 'saturation' temperature.

**Table 1.** Parameters obtained by fitting the saturation function to the low-T $P2_1/c$ unit-cell axes and volume.

| | *b*-axis (*a*-axis high-T) | *c*-axis (*b*-axis high-T) | *a*-axis (*c*-axis high-T) | Unit-cell volume |
|---|---|---|---|---|
| $x_0$ | 8.119(2) Å | 10.729(8) Å | 12.31(3) Å | 1073(1) Å$^3$ |
| y | 2.12(6)x10$^{-4}$ | 6.2(2)x10$^{-4}$ | 2.2(7)x10$^{-4}$ | 1.08(3)x10$^{-1}$ |
| $T_S$ | 105(6) K | 169(8) K | 243(57) K | 154(6) K |

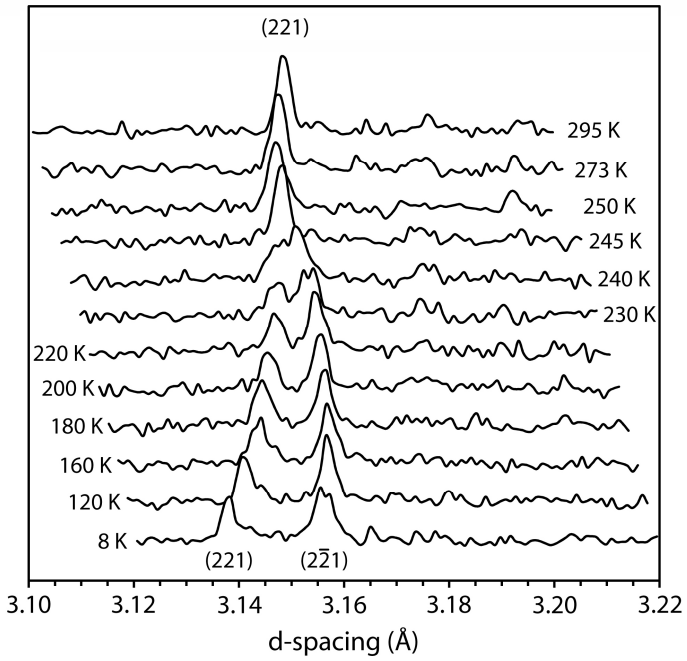


**Figure 1**. Splitting of the (221) reflection as the high-T P*bca* phase of $MgSO_4 \cdot 3D_2O$ is cooled below 245 K.

**References**


[1] Ma et al. (2009): Am. Min. 94, 622-625.

[2] Ma et al. (2009): Am. Min. 94, 1071-1074.

[3] Fortes & Lemée-Cailleau, ILL Experimental report number 5-11-360.