

ISIS Experimental Report

Rutherford Appleton Laboratory

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Title of Experiment: Thermal expansion and phase transition in magnesium sulfate trihydrate

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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 heavy-atom structures of $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ (sanderite) and $\text{MgSO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ 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 $\text{MgSO}_4 \cdot 3\text{D}_2\text{O}$ 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 $\text{MgSO}_4 \cdot 3\text{D}_2\text{O}$ 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 $\text{MgSO}_4 \cdot 3\text{D}_2\text{O}$ 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, $\text{MgSO}_4 \cdot 3\text{D}_2\text{O}$, $\text{MgSO}_4 \cdot 6\text{D}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{D}_2\text{O}$, in the approximate proportions 50:30:20. The specimen was then cooled to 230 K, where the splitting of certain $\text{MgSO}_4 \cdot 3\text{D}_2\text{O}$ 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 $\text{MgSO}_4 \cdot 3\text{D}_2\text{O}$ above 245 K experiences a modest distortion; in the $Pbca$ setting of the high-T cell, the angle γ jumps

discontinuously from 90.0° to 90.2° and this angle increases to $\sim 91.1^\circ$ 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	$2.12(6) \times 10^{-4}$	$6.2(2) \times 10^{-4}$	$2.2(7) \times 10^{-4}$	$1.08(3) \times 10^{-1}$
T_S	105(6) K	169(8) K	243(57) K	154(6) K

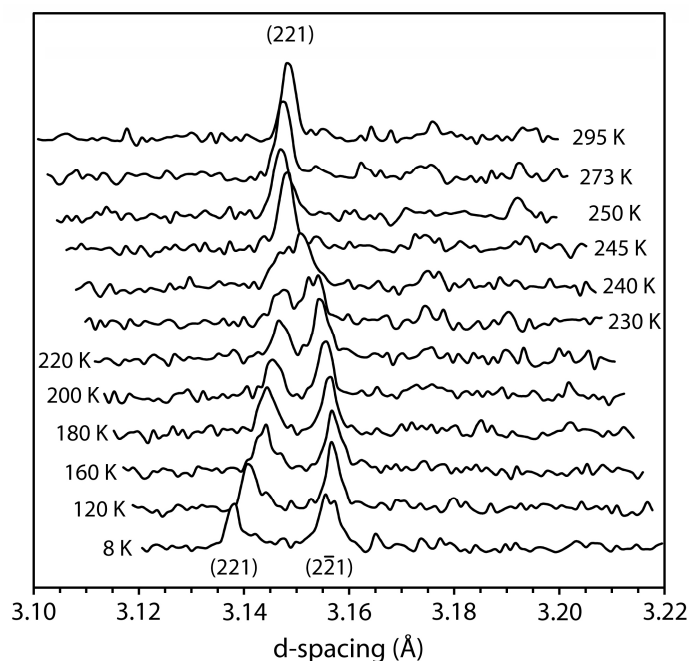


Figure 1. Splitting of the (221) reflection as the high-T $Pbca$ phase of $\text{MgSO}_4 \cdot 3\text{D}_2\text{O}$ is cooled below 245 K.

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.