Experimental Report

Proposal:	**5-11-360**	**Council:**	10/2008	

Title: Structural systematics of MgSO4•nD2O (n = 1¼, 2, 2½, 3, 4, 5) using neutron single-crystal diffraction.

This proposal is a new proposal

Researh Area: Other

Main proposer: **FORTES Andrew Dominic**

Experimental Team: FORTES Andrew Dominic

Local Contact: LEMEE-CAILLEAU Marie-Helene

Samples:
MgSO4.(1.25)D2O
MgSO4.(2)D2O
MgSO4.(2.5)D2O
MgSO4.(3)D2O
MgSO4.(4)D2O
MgSO4.(5)D2O

Instrument	Req. Days	All. Days	From	To
VIVALDI	6	6	24/08/2009	31/08/2009

Abstract:

The aim of this proposal is to collect neutron diffraction data from single crystals of four MgSO4-hydrates (n = 1¼, 2, 2½, 3), in order to solve their structures. In addition, it is proposed to measure single-crystal data from MgSO4•4D2O and MgSO4•5D2O, since the only such refinements of these compounds were done more than thirty years ago, and good low-temperature anisotropic structural analyses are wanting. Determining the structures of the lower hydrates will fill a significant gap in our understanding of the MgSO4-hydrate series. Moreover, these compounds provide an exciting opportunity to understand better an entire set of related metal-sulfate hydrate minerals (comprising Ni, Zn, Mg, Co, Mn, Fe, and Cu), where only a single other trihydrate is known, the monoclinic mineral bonattite (CuSO4•3H2O), and only the Mg-sulfates are known to form 1¼-, 2-, and 2½-hydrates (and indeed the 11-hydrate). The work may also form the basis for better computational modelling of inter- and intra-molecular interactions in all complex salt hydrates and aid in calculating the effect of metastable hydrate crystallisation in building material.

Structural systematics of MgSO$_4 \cdot n$D$_2$O (n = 1¼, 2, 2½, 3, 4, 5) using neutron single-crystal diffraction

Introduction

Magnesium sulfate is known to form a large number of crystalline hydrates, MgSO$_4 \cdot n$H$_2$O with n = 1, 1¼, 2, 2½, 3, 4, 5, 6, 7, and 11. Whilst many of these occur naturally as minerals on Earth, there is good evidence for abundant MgSO$_4$ hydrates in the martian regolith [1], and in the bulk of some outer solar system moons [2]. These hydrates also occur in building materials where changes in hydration state can result in volume changes which stress the surrounding matrix and cause structural damage [3,4]. Of these hydrates, only kieserite (n = 1), hexahydrite (n = 6), epsomite (n = 7), and meridianiite (n = 11) are known to be stable in contact with aqueous MgSO$_4$ solution; the other phases generally occur under conditions of reduced water activity, either very low humidity, or in methanolic or acidified solutions [e.g., 5,6].

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 [7-12]; the heavy-atom structures of MgSO$_4 \cdot$2H$_2$O (sanderite) and MgSO$_4 \cdot$2½H$_2$O have been determined recently by X-ray powder diffraction methods [13,14]. At the time of the proposal submission (prior to the publication of the MgSO$_4 \cdot$2H$_2$O and MgSO$_4 \cdot$2½H$_2$O structures), the objective was to collect neutron diffraction data from single crystals of MgSO$_4 \cdot n$D$_2$O with n = 1¼, 2, 2½, and 3 for the purposes of determining their crystal structure, and with n = 4 and 5 for the purpose of obtaining improved precision over the previously published structural data.

All attempts to grow single crystals of MgSO$_4 \cdot n$D$_2$O with n = 1¼, 2, 2½ and 3 using the methods described by Hodenberg and Kuhn [5] and Emons *et al*. [6] failed. However, the technique described by Wallis Bennet [15] in United States Patent 3,297,413 *was* successful in producing single crystals of MgSO$_4 \cdot$3D$_2$O. This simple technique involves nothing more than the gentle evaporation of a 25 wt. % MgSO$_4$ solution at 105°C for ~ 48-72 hours without stirring. The crystals grown in this manner are clusters of well-formed water-clear plates, 1—2 mm in length and 0.1—0.5mm in thickness (Figure 1). After extraction from the mother liquor the crystals of MgSO$_4 \cdot$3D$_2$O become somewhat dull. However, batches of crystals, far from being unstable as reported by Hodenburg & Kühn [5], were preserved in a small glass bottle for a period of ~ 10 days, and withstood repeated exposure to warm air (~30°C) and examination under a microscope.
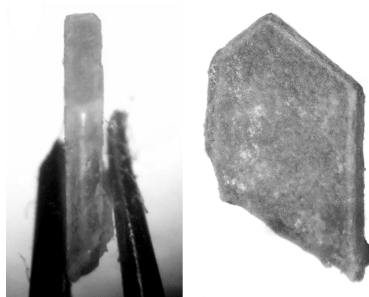

Figure 1.
A cluster of platy MgSO$_4 \cdot$3D$_2$O crystals; the field of view is approximately 6 mm wide.

Data Collection

Measurements were made upon two separate crystals of MgSO$_4 \cdot$3D$_2$O, each approximately 2 mm x 1 mm x 0.25 mm (~ 1 mg) sealed into a glass capillary with silica wool (Figures 2 & 3). Although each of these appeared morphologically to be single crystals, the diffraction data revealed that both were in fact twinned, probably at the microscopic level.

Data were collected from crystal 1 at 295 K, and it was possible to confirm the unit-cell and space-group for MgSO$_4 \cdot$3D$_2$O previously published by Hodenberg and Kuhn [5]. Moreover, it was determined that


Figure 2. Crystal 1 seen perpendicular to the (010) face (right), and in profile. The crystal is 1.25 mm across and 0.30 mm thick.

Figure 3. Crystal 2, mounted in its glass capillary. The broad upper face is (010) and the edge parallel to the bottom of the image is (102).

the two twin domains within the crystal shared a common b-axis orientation, also in agreement with the observation of a ubiquitous (102) twin planes in macroscopically twinned crystals [5]. Upon cooling to 20 K,

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however, it was evident that a phase transition had occurred, many of the Laue spots becoming split in two, with streaks of diffuse scattering from the domain walls linking them. Note in the illustration below that the (020) spot, common to both twins at high-temperature, has split into four, these representing the split reflections for each twin domain. Subsequent warming revealed that the split spots moved closer together (as measured directly from the Laue image (Figure 4), but at 245 K the spots of the high-temperature phase re-appeared, co-existing with the spots of the low-temperature form: at 253 K only the high-T spots remain.
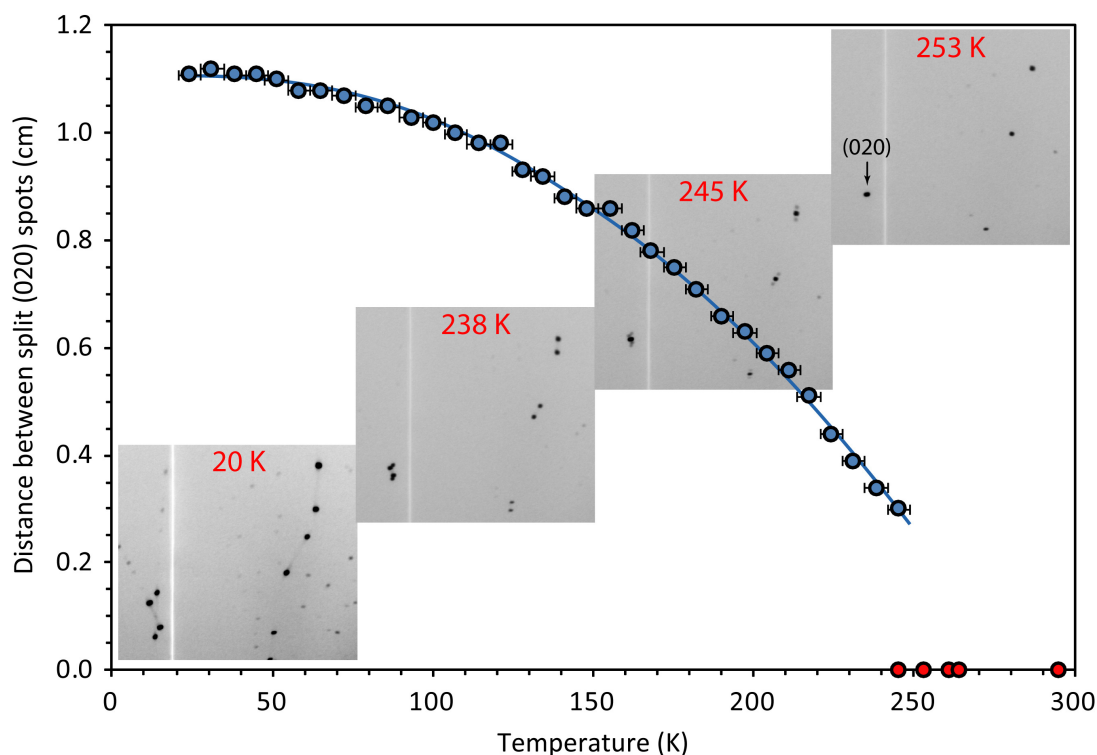
Figure 4.
Temperature dependence of the splitting between spots due to the reduction in symmetry in the low-temperature phase of MgSO$_4$·3D$_2$O. Streaks of intensity between the spots represent scattering from domain walls.

Crystal 2 was examined at 273 K, and found to exhibit both the same diffraction pattern, and the same twinning, as crystal 1 at 295 K.

Structure solution

MgSO$_4$-trihydrate exists in space-group Pbca above 245 K, with unit-cell dimensions of a = 8.20 Å, b = 10.93 Å, and c = 12.39 Å. The integrated intensities extracted from one of the twin domains of crystal 1 were used to determine the structure at 295 K with SHELX. Figure 5 depicts a view of the crystal structure along the a-axis, with atoms labelled as in Table 1. MgSO$_4$·3D$_2$O consists of sheets of corner-linked MgO$_6$ and SO$_4$ tetrahedra in the (010) plane, linked along the b-axis by hydrogen bonds, which accounts for the macroscopic crystal habit. Each SO$_4$ tetrahedron shares its three basal oxygens with neighbouring Mg atoms, whilst the apical oxygen (O4) accepts three D···O bonds from water molecules in the adjacent sheet. Water molecule Ow1's deuterons *both* appear to be involved in three-centred interactions (bifurcated hydrogen bonds) to adjacent MgO$_6$ octahedral corners. In the case of Ow3, it appears that instead of a bifurcated H-bond, there are two distinct partially occupied deuteron sites.

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Table 1.

Atomic coordinates in MgSO$_4\cdot$3D$_2$O at 295 K determined from the single-crystal data. Pbca, a = 8.20 Å, b = 10.93 Å, and c = 12.39 Å

Atom	x	y	z	Occ.
Mg	0.1280(4)	0.2603(3)	0.1199(2)	1.00
S	0.2322(6)	0.1548(6)	0.3707(4)	1.00
O1	0.1233(3)	0.1754(3)	0.4635(2)	1.00
O2	0.3821(4)	0.2237(5)	0.3858(3)	1.00
O3	0.1471(4)	0.1982(4)	0.2745(3)	1.00
O4	0.2641(5)	0.0244(5)	0.3586(4)	1.00
Ow1	0.3665(4)	0.3222(4)	0.1282(3)	1.00
Ow2	0.0605(5)	0.4300(4)	0.1841(3)	1.00
Ow3	0.1905(6)	0.0920(5)	0.0614(4)	1.00
Dw1a	0.4364(6)	0.2852(6)	0.0778(5)	1.00
Dw1b	0.4255(6)	0.3123(7)	0.1901(5)	1.00
Dw2a	0.1123(5)	0.4681(4)	0.2443(3)	1.00
Dw2b	-0.0432(5)	0.4645(4)	0.1686(4)	1.00
Dw3a	0.2075(6)	0.0646(4)	-0.0108(4)	1.00
Dw3b	0.156(2)	0.0146(9)	0.0942(8)	0.57(3)
Dw3c	0.279(2)	0.039(1)	-0.1007(8)	0.43(3)

Figure 5.

View of the MgSO$_4\cdot$3D$_2$O crystal structure along the a-axis (with the b-axis vertical and the c-axis horizontal). Atom labels correspond to those used in Table 1 on the left.
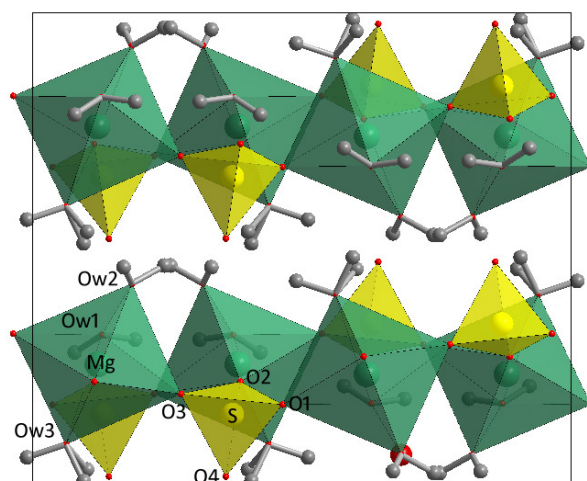
The linkage of SO$_4$ to M^{2+}O$_6$ octahedra in MgSO$_4\cdot$3D$_2$O is the same as that found in CuSO$_4\cdot$3H$_2$O (bonattite [16]); i.e., three shared basal oxygens and one H-bond accepting apical oxygen. However, in bonattite, the neighbouring chains of polyhedra are canted with respect to one another, forming a three-dimensional network; in MgSO$_4\cdot$3D$_2$O the chains are not canted and so form 2D sheets which are linked by hydrogen bonds. The occurrence of three-centred interactions and partially occupied hydrogen sites is not unusual; bifurcated H-bonds occur in both the tetra- and undecahydrates of MgSO$_4$ (stakeyite and meridianiite, respectively) and, and partially occupied H-bonds occur in sodium sulfate decahydrate (mirabilite).

The discovery of disordered and bifurcated hydrogen bonds in the structure at high temperature suggests that the phase transition upon cooling through 245 K is due to ordering of the hydrogen bonds on cooling. So far, attempts to determine the symmetry of the low-T phase have not been successful. However, future neutron powder diffraction experiments will allow us to establish with high precision the change in unit-cell shape with temperature and potentially index the low-T diffraction pattern.

References

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