

## The Structure of the Magnesium Hydroxide Sulfate Hydrate $\text{MgSO}_4 \cdot \frac{1}{3}\text{Mg}(\text{OH})_2 \cdot \frac{1}{3}\text{H}_2\text{O}$

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### Abstract

The magnesium hydroxide sulfate hydrate  $\text{MgSO}_4 \cdot \frac{1}{3}\text{Mg}(\text{OH})_2 \cdot \frac{1}{3}\text{H}_2\text{O}$  crystallizes in the tetragonal space group  $I4_1/amd$  with cell dimensions  $a_1 = a_2 = 5.242$  (1),  $c = 12.995$  (3) Å,  $Z = 4$ . The structure was solved by Patterson methods and refined to  $R = 0.041$  using 160 single-crystal X-ray diffraction intensities measured with a four-circle diffractometer.  $\text{Mg}^{2+}$  is octahedrally coordinated by the O atoms of four different  $\text{SO}_4^{2-}$  and two  $\text{OH}^-$  or  $\text{H}_2\text{O}$ . The structure consists of straight chains of face-sharing oxygen octahedra, two-thirds of which have  $\text{Mg}^{2+}$  at their centers. This phase is considered to be stoichiometric; a partially ordered atomic arrangement is proposed to account for the integral coefficients in the formula. The structure is related to those of the sulfate monohydrates of divalent Mg, Mn, Fe, Co, Ni and Zn.

### Introduction

Hydrated magnesium sulfates belong to a rather large group of hydrated metal sulfates which exhibit retrograde solubility upon cooling. Recently a new member in this series of compounds, a magnesium hydroxide sulfate hydrate, has been discovered by Bischoff & Seyfried (1978) in their studies of the hydrothermal chemistry of sea water at elevated temperatures and pressures. The precipitation of this phase causes a dramatic decline in the pH of sea water. Because of this, Bischoff & Seyfried (1978) concluded that sea water could aggressively leach and transport transition metals from basalts extruded on the ocean floor. From analysis of the sea water during the reaction, they determined that the  $\text{MgSO}_4:\text{Mg}(\text{OH})_2$  ratio in this phase was between 2.8:1 and 3.7:1, but because of the small amount of material (<50 µg) recoverable from the synthesis technique and the difficulty of analyzing hydrous phases, they were unable to determine the exact composition of the phase. In this paper we report the crystal structure, stoichiometry and crystal chemistry of this magnesium hydroxide sulfate hydrate, hereafter referred to as MSHH.

### Experimental

The crystals were precipitated on gold-foil strips placed in a Dickson-type hydrothermal pressure vessel (Dickson, Blount & Tunell, 1963) filled with natural sea water and heated at 623 K at a pressure of 50 mPa for 8 h. The vessel was drained of all fluid before quenching to prevent redissolution of the precipitates, anhydrite ( $\text{CaSO}_4$ ) and MSHH. The crystals of the latter phase exhibited perfect tetragonal dipyrmaid forms and were transparent except for faintly discolored areas of slight Fe contamination from the reaction vessel. The Gandolfi powder diffraction pattern of a crystal exactly matched that reported by Bischoff & Seyfried (1978) for magnesium oxide sulfate. Electron-beam microprobe analysis yielded Mg, S and O as the only major constituents with trace amounts of Fe. Quantitative results could not be obtained. Although this technique does not detect Li, Be, B, N or F, the concentration of these elements in sea water is so low as to preclude their being present in significant amounts in MSHH. The average density determined by flotation of two crystals from the same synthesis run was  $2.71 (\pm 0.01) \text{ Mg m}^{-3}$ .

A nearly transparent, colorless, euhedral crystal  $0.135 \times 0.135 \times 0.105$  mm was selected for the X-ray diffraction intensity measurements. Precession photographs proved the crystals to be tetragonal. Twenty reflections in the range  $12\text{--}45^\circ 2\theta$  were centered automatically on a Picker FACS-I four-circle diffractometer using  $\text{Mo } K\alpha$  radiation ( $\lambda = 0.71069$  Å) and a graphite monochromator. Least-squares regression analysis of these 20 observations yielded cell dimensions of:  $a_1 = a_2 = 5.242$  (1),  $c = 12.995$  (3) Å (at 296 K). The intensities at all 661 primitive reciprocal-lattice points  $<60^\circ 2\theta$  in one octant were measured with a  $0.5^\circ \text{ min}^{-1} \theta\text{--}2\theta$  scan  $2.5^\circ$  wide (expanded as a function of  $2\theta$  to account for  $K\alpha_1, K\alpha_2$  dispersion); 100 s background counts were made at each end of the scan. Two standard reflections measured periodically showed no instrument drift or crystal decomposition. The diffractometer intensity measurements showed the systematic conditions for reflections to be  $hkl: h + k + l = 2n$ ,  $hhl: 2h + l = 4n$ , and  $hk0: h = 2n$ , which are unique to space group  $I4_1/amd$ .

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The 373 allowed reflections were corrected for Lp effects assuming 0.5 monochromator crystal perfection. Estimated standard deviations were calculated with the formula  $\sigma_{F^2} = [\sigma_s^2 + (0.03I_{\text{net}})^2]^{1/2}/Lp$  where  $\sigma_s$  is derived from counting statistics. After the composition of the crystal had been established from the preliminary refinement, an absorption correction was made for all allowed reflections using an analytical method\* ( $\mu = 0.977 \text{ mm}^{-1}$ ,  $T_{\text{max}} = 0.946$ ,  $T_{\text{min}} = 0.912$ ). Equivalent observations were then averaged to yield 160 unique reflections, of which 133 (83%) were more intense than  $3\sigma$ . The  $R$  factor of averaging  $F^2$  was 0.040. Eight observations yielded net negative intensities which were reset to negligible but positive values for computational purposes.

### Solution and refinement of the structure

The coordinates of all non-hydrogen atoms were determined from the Patterson function. Least-squares refinement of the positional and isotropic thermal parameters of all atoms with all sites at full occupancy converged to a conventional  $R = 0.155$  [the neutral-atom scattering factors and anomalous-dispersion corrections of Cromer & Waber (1974) were used]. At this point a large thermal parameter [ $B = 5.23$  (5)  $\text{\AA}^2$ ] of the Mg atom indicated that the site was not fully occupied. Additional cycles of refinement, varying positional and anisotropic thermal parameters of all atoms and the Mg site occupancy, converged with the Mg site occupancy of 0.666 (5) and  $R = 0.044$ . The correlation coefficients of the Mg site occupancy with the Mg anisotropic thermal parameters  $\beta_{11}$ ,  $\beta_{22}$ , and  $\beta_{33}$  were 0.41, 0.33, and 0.49, respectively. These values are low enough to permit a reliable determination of the Mg site occupancy. Since this site occupancy is within experimental error of  $\frac{2}{3}$  we conclude that this phase is stoichiometric.

The H atom was approximately located in a difference Fourier synthesis but, due to its low site occupancy ( $\frac{1}{3}$ ), its position could not be refined. The H atom, however, was retained in the model fixed at a chemically reasonable position consistent with the difference synthesis. This reduced the values of  $|\Delta F|/\sigma$  for the three most aberrant observations from 6–10 to 3–5 and reduced the overall  $R$  to 0.041.

All 160 observations were included in the final cycles of refinement in which 16 parameters were varied to minimize the quantity  $\sum (|\Delta F|^2/\sigma_{F^2})$ . The final conventional  $R$  was 0.041,  $R_w = \{[\sum \sigma^{-2}(\Delta F)^2/\sum \sigma^{-2} F_o^2]^{1/2}\}$  was 0.042 and the standard deviation of a unit-weight observation was 1.84. A final difference

\* The formula of de Meulenaer & Tompa (1965) in the program *AGNOST* was used. Programs used for other calculations were Finger & Prince's (1975) *RFINE* and programs written locally by K. Keefer for reducing and correcting the data.

synthesis was featureless. The final positional and thermal parameters are given in Table 1 and interatomic distances and angles in Table 2. The calculated density,  $2.71 \text{ Mg m}^{-3}$ , exactly agrees with the observed value.\*

The Mg site occupancy of  $\frac{2}{3}$  leads to the unusual stoichiometry  $\text{MgSO}_4 \cdot \frac{1}{3}\text{Mg}(\text{OH})_2 \cdot \frac{1}{3}\text{H}_2\text{O}$ ,  $Z = 4$ . A crystal structure refinement yielding a non-integral stoichiometry may occur if the chosen cell is actually a subcell of a larger lattice or if the true symmetry of the cell is lower than the apparent symmetry. Tetragonal symmetry was confirmed by careful diffractometer measurements of both the  $2\theta$  positions and intensities of  $hkl$ ,  $khl$  pairs of reflections which were identical within normal experimental error. Precession photographs revealed no superlattice reflections. Diffractometer scans, made of reciprocal-lattice points of hypothetical tetragonal supercells with dimensions  $a_1$ ,  $a_2$ ,  $3c$  and  $3a_1$ ,  $3a_2$ ,  $c$ , yielded no statistically significant intensities. Thus, all experimental evidence

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35656 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters

Fractional coordinates are with respect to the  $2/m$  origin of  $I4_1/amd$ . The H atom parameters were not refined.  $B_{\text{eq}}$  is defined as:  $\frac{1}{3}(\beta_{11} a_1^2 + \beta_{22} a_2^2 + \beta_{33} c^2)$ . Estimated standard deviations of the last digits are in parentheses.

	Occupancy factor	Wyckoff notation	x	y	z	$B_{\text{eq}}$ ( $\text{\AA}^2$ )
S	1	4(a)	0	$\frac{1}{2}$	$\frac{1}{2}$	0.95 (3)
Mg	0.666 (5)	8(d)	0	0	$\frac{1}{2}$	1.84 (6)
O(1)	1	16(h)	0	0.5195 (4)	0.1895 (1)	1.69 (4)
O(2)	1	4(b)	0	$\frac{1}{2}$	$\frac{1}{2}$	1.73 (7)
H	$\frac{1}{3}$	16(h)	0	0.4200	0.4100	4.00

Table 2. Bond distances ( $\text{\AA}$ ), polyhedral edge lengths ( $\text{\AA}$ ) and interatomic angles ( $^\circ$ )

S—O(1)	(4 $\times$ )	1.471 (2)	O(1)—S—O(1 <sup>vi</sup> )	110.5 (2)
Mg—O(1 <sup>iv</sup> )	(4 $\times$ )	2.081 (2)	O(1)—S—O(1 <sup>ii</sup> )	109.0 (1)
Mg—O(2)	(2 $\times$ )	2.087 (1)	O(1 <sup>iv</sup> )—Mg—O(1 <sup>v</sup> )	85.5 (1)
O(1)—O(1 <sup>vii</sup> )	(2 $\times$ )	2.417 (4) <sup>a</sup>	O(1 <sup>v</sup> )—Mg—O(2)	84.2 (1)
O(1)—O(1 <sup>ii</sup> )	(4 $\times$ )	2.394 (3) <sup>a</sup>	O(1 <sup>v</sup> )—Mg—O(1 <sup>vi</sup> )	94.5 (1)
O(1)—O(1 <sup>i</sup> )	(2 $\times$ )	2.825 (4) <sup>b</sup>	O(1 <sup>v</sup> )—Mg—O(2)	95.8 (1)
O(1)—O(2)	(4 $\times$ )	2.794 (2) <sup>b</sup>	S—O(1)—Mg <sup>viii</sup>	140.6 (1)
O(1)—O(1 <sup>iii</sup> )	(2 $\times$ )	3.056 (2) <sup>c</sup>	Mg <sup>viii</sup> —O(2)—Mg <sup>x</sup>	77.8 (1)
O(1)—O(2 <sup>ix</sup> )	(4 $\times$ )	3.093 (1) <sup>c</sup>	Mg <sup>viii</sup> —O(2)—Mg	127.3 (1)

#### Symmetry code

(i)	$0, \frac{1}{2} - x, z$	(vi)	$-\frac{1}{2} + x, -\frac{1}{2}, \frac{1}{2} + z$
(ii)	$\frac{3}{4} - x, \frac{3}{4}, \frac{1}{4} - z$	(vii)	$0, \frac{1}{2} - x, z$
(iii)	$\frac{1}{2}, x, \frac{1}{2} - z$	(viii)	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
(iv)	$\frac{1}{4} - x, \frac{1}{4}, \frac{3}{4} - z$	(ix)	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
(v)	$-\frac{1}{4} + x, \frac{1}{4}, \frac{3}{4} - z$	(x)	$-\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$

(a) Tetrahedral edge. (b) Octahedral edge, shared. (c) Octahedral edge, unshared.

indicates that the reported unit cell, space group and stoichiometry are correct.

### Discussion

The most interesting and unusual feature of this structure is that the six O atoms that octahedrally coordinate the Mg site form infinite straight chains in which octahedral faces are shared. As can be seen in Fig. 1, these chains are arrayed in layers which are stacked in the direction [001]. The chains are parallel to [100] and [010] in alternate layers. In each octahedron, four equivalent O atoms [O(1)] are shared with four  $\text{SO}_4^{2-}$  tetrahedra. The tetrahedra link together not only the chains within a layer, but also the layers themselves (Fig. 1). The other two O atoms of the octahedra [O(2)] are part of either an  $\text{OH}^-$  radical or an  $\text{H}_2\text{O}$  molecule and lie at the vertices shared by four octahedra in two different layers (Fig. 2).  $\text{Mg}^{2+}$  occupies the centers of two-thirds of the octahedra; the other third are occupied (but not at the center) by two H atoms from two different  $\text{OH}^-$  or  $\text{H}_2\text{O}$  groups. The circumstances which govern whether O(2) is part of an  $\text{OH}^-$  radical or an  $\text{H}_2\text{O}$  molecule are discussed below.

As would be expected, the O—O separations in the shared faces of the octahedra are considerably shorter than those of the unshared faces, although the Mg site is virtually equidistant from all six O atoms (Table 2). This results in O—Mg—O angles which differ from  $90^\circ$  (and  $180^\circ$ ) by approximately  $5^\circ$ . In contrast, the O—S—O angles of the  $\text{SO}_4^{2-}$  tetrahedra are almost ideal and the O—O separations are nearly identical.

The partial occupancy of the Mg site in this type of structure is the result of the bonding requirements of the O(2) anion. Of the several possible arrangements of

$\text{Mg}^{2+}$  and  $\text{H}^+$  in the four octahedra shared by O(2), only two are chemically reasonable. In one of these arrangements, O(2) is part of an  $\text{OH}^-$  radical coordinated by  $\text{Mg}^{2+}$  at the centers of three of the octahedra with the  $\text{H}^+$  lying in the fourth. In the other arrangement, O(2) is part of an  $\text{H}_2\text{O}$  molecule coordinated by two  $\text{Mg}^{2+}$ , each at the center of an octahedron in a different layer. Both of these arrangements are shown in Fig. 2.

The restriction that of the four octahedra linked by O(2) no more than three nor fewer than two may have  $\text{Mg}^{2+}$  at their centers limits the Mg site occupancy of this structure type to a maximum of 0.75, in which case all O(2) are part of  $\text{OH}^-$  radicals, and a minimum of 0.5, in which case all O(2) are part of an  $\text{H}_2\text{O}$  molecule. At the observed Mg site occupancy of  $\frac{2}{3}$ , the ratio of  $\text{H}_2\text{O}$  to  $\text{OH}^-$  is 1:2.

To the best of our knowledge, this is the first reported instance of face-sharing Mg coordination octahedra. This suggests that this is probably a structurally unfavorable arrangement. Accordingly, we propose that at the observed Mg occupancy of  $\frac{2}{3}$ , the occupancy of the chains is ordered such that no more than one face of each Mg coordination octahedron is shared, *i.e.* that the center of every third octahedron in each chain is vacant. Although each chain is completely ordered in this scheme, as shown in Fig. 1, the position of these vacant sites can be completely random with respect to those in adjacent chains, effecting complete crystallographic disorder. This results in the high symmetry observed and accounts for the complete absence of superlattice reflections. This scheme also accounts for the stoichiometric  $\text{MgSO}_4:\text{Mg}(\text{OH})_2$  ratio of 3:1, due to the ordered chains, and for the fractional formula, which arises from the disorder among the different chains in the unit cell.

The largest principal axis of the Mg thermal-motion ellipsoid is directed exactly toward the center of the

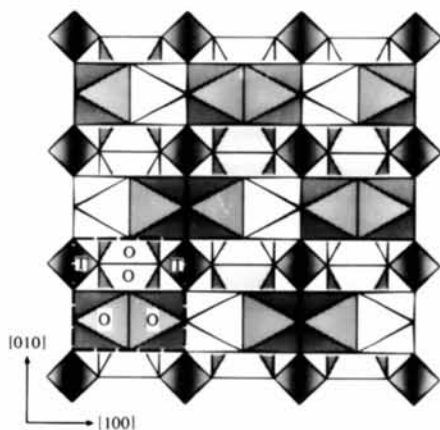


Fig. 1. Projection on (001) of the coordination polyhedra in the magnesium hydroxide sulfate hydrate structure. Several octahedra and tetrahedra are labeled O and T, respectively. Shaded octahedra represent those occupied by  $\text{Mg}^{2+}$  in the proposed ordering scheme. The unshaded octahedra are occupied by  $\text{H}^+$  from the  $\text{OH}^-$  and  $\text{H}_2\text{O}$  groups.

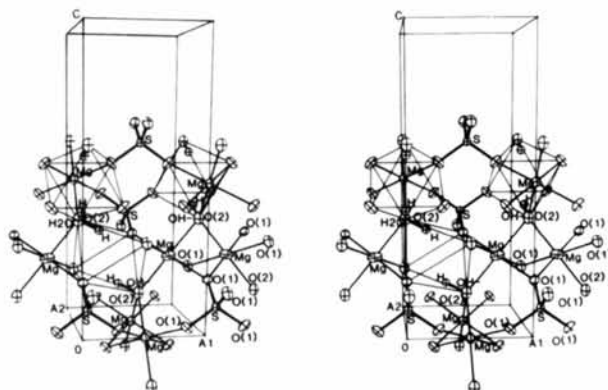


Fig. 2. Stereodiagram (Johnson, 1965) of the magnesium hydroxide sulfate hydrate structure viewed approximately along [010]. Both cases of O(2) coordination, as part of an  $\text{OH}^-$  and as part of an  $\text{H}_2\text{O}$ , are shown. Octahedra drawn as containing  $\text{H}^+$  instead of  $\text{Mg}^{2+}$  are outlined.

shared octahedral face (Fig. 2) and is abnormally large [the r.m.s. amplitude of displacement is 0.202 (4) Å compared to 0.109 (4) and 0.129 (4) Å for the other two axes]. This indicates that  $\text{Mg}^{2+}$  may be slightly displaced from the center of the octahedron. In our proposed arrangement, this displacement would be expected because each  $\text{Mg}^{2+}$  coordination octahedron shares one face with another such octahedron, but the opposite face is shared with an octahedron vacant of  $\text{Mg}^{2+}$ . This lowers the effective symmetry of the Mg site and, as a result, the position of the potential-energy minimum is no longer necessarily at the center of the octahedron.

As stated above, the minimum Mg occupancy in this structure type is  $\frac{1}{2}$ , at which all of the O(2) atoms are part of  $\text{H}_2\text{O}$  molecules. Such a compound, with the appropriate formula  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$  ( $Z = 4$ ), occurs naturally as the mineral kieserite. Its structure is known (Brégeault, Herpin, Manoli & Pannetier, 1970; Brégeault, Herpin & Coing-Boyat, 1972), but the relationship between it and the structure reported here is not immediately obvious. The space group and cell dimensions of kieserite ( $C2/c$ ;  $a = 6.89$ ,  $b = 7.62$ ,  $c = 7.64$  Å,  $\beta = 117.68^\circ$ ) are quite different from those of MSH. However, the positions of all atoms in the kieserite structure are transformed to the approximate positions of their equivalents in the MSH structure by the equation

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} -0.9294 & -1.0279 & 0.4787 \\ 0.9294 & -1.0279 & -0.4787 \\ 0 & 0 & 0.5206 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

where  $x, y, z$  and  $x', y', z'$  are fractional coordinates in the kieserite and MSH unit cell, respectively. Thus, the structures are topologic equivalents. This transformation demonstrates that the Mg site in kieserite [4(b)] and the unoccupied 4(c) site together are the equivalent of the single, partially occupied Mg site [8(d)] in MSH. With one site fully occupied and the other vacant, the  $\text{Mg}^{2+}$  in kieserite is ordered such that only the centers of alternate octahedra in the chains of face-sharing octahedra\* are occupied.  $\text{Mg}^{2+}$  coordination octahedra, therefore, do not share faces and the intervening octahedra, which contain two  $\text{H}^+$ , are

\* The chains referred to by Brégeault *et al.* (1970, 1972) describe the vertex sharing of Mg coordination octahedra in different layers, not the chains of face-sharing octahedra described here.

collapsed and highly distorted. This ordering and distortion produce the much lower symmetry  $C2/c$ .

The compounds in the isostructural series  $\text{MSO}_4 \cdot \text{H}_2\text{O}$  ( $M$  is divalent Mn, Fe, Co, Ni or Zn) (Le Fur, Coing-Boyat & Bassi, 1966) also crystallize in  $C2/c$  and are very similar to kieserite. The principal difference is that in this series the site 4(c) is occupied by the divalent cation and 4(b) is unoccupied (the reverse of kieserite). Since the single divalent-cation site in MSH is essentially equivalent to both of these sites, it is probable that the compounds  $\text{MSO}_4 \cdot \frac{1}{3}\text{M}(\text{OH})_2 \cdot \frac{1}{3}\text{H}_2\text{O}$  (with  $M$  as described above) exist and are isostructural with MSH. Furthermore, it seems quite possible that these cations may form analogues of this structure with an  $M$  occupancy of  $\frac{3}{4}$  [ $2\text{MSO}_4 \cdot \text{M}(\text{OH})_2$ ,  $Z = 2$ ], particularly since fully occupied chains of face-sharing coordination octahedra with these metal cations are known to occur [e.g. the structure of  $\text{Co}_2(\text{AsO}_4)\text{Cl}$  reported by Rea, Anderson & Kostiner (1977)].

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