

## Structure of Magnesium Hydroxide Sulfate [2MgSO<sub>4</sub>.Mg(OH)<sub>2</sub>] and Solid Solution in Magnesium Hydroxide Sulfate Hydrate and Caminite

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### Abstract

Magnesium hydroxide sulfate [2MgSO<sub>4</sub>.Mg(OH)<sub>2</sub>; MHS] is tetragonal with  $a = 7.454$  (1),  $c = 12.885$  (2) Å,  $V = 716.0$  Å<sup>3</sup>, space group  $P4_32_12$ ,  $Z = 4$  and  $D_x = 2.774$  g cm<sup>-3</sup>. The structure (single-crystal X-ray,  $R = 0.025$ ,  $wR = 0.023$ ) comprises spiral (4<sub>3</sub>) single chains of corner-shared Mg(2) octahedra cross-linked by SO<sub>4</sub> tetrahedra and face-shared Mg(1) octahedra. A linear ternary group of face-shared Mg octahedra [Mg(2)—Mg(1)—Mg(2)] alternates with an unoccupied octahedral position in rows along  $[\bar{1}10]$ . A crystal of MHS was grown hydrothermally (0.15 GPa, 673 K) from gold-bearing Mg—S—O—H fluid. The MHS structure, with Mg(1) octahedra sharing two octahedral faces with Mg(2) octahedra, revises the structure assumed for the complex solid solution magnesium hydroxide sulfate hydrate and the related ocean-floor mineral caminite [2MgSO<sub>4</sub>. $x$ Mg(OH)<sub>2</sub>. $(2 - 2x)$ H<sub>2</sub>O;  $0.5 \leq x < 1.0$ ]. The substitution reaction appears to be  $\text{Mg}(1)^{2+} \rightleftharpoons 2\text{H}^+$ . The H-substituted MHS structure is distinguished from that of kieserite (MgSO<sub>4</sub>.H<sub>2</sub>O), which has straight single chains of corner-shared Mg octahedra.

### 1. Introduction

Magnesium hydroxide sulfate hydrate [2MgSO<sub>4</sub>. $x$ Mg(OH)<sub>2</sub>. $(2 - 2x)$ H<sub>2</sub>O,  $x = 0.5-1.0$ ; 'MHSH'] was discovered by Bischoff & Seyfried (1978) in their studies on the hydrothermal chemistry of sea water at elevated temperatures and pressures. MHSH exhibits retrograde solubility on cooling and occurs naturally as the mineral caminite in black-smoker hydrothermal vents of the submarine hydrothermal deposits at East Pacific Rise (Haymon & Kastner, 1986). Caminite is, therefore, an important phase for defining solution conditions during mass and heat transfer in the oceanic crust and the hydrosphere. The structure of synthetic MHSH, with an assumed formula of [MgSO<sub>4</sub>.1/3Mg(OH)<sub>2</sub>.1/3H<sub>2</sub>O], space group  $I4_1/amd$ ,  $Z = 4$ ,  $a = 5.242$  and  $c = 12.995$  Å, was determined by Keefer, Hochella & de Jong (1981) to contain straight chains of face-shared Mg(O,OH,H<sub>2</sub>O)<sub>6</sub> octahedra, cross-linked by SO<sub>4</sub> tetrahedra. Caminite has the assumed formula [MgSO<sub>4</sub>.0.4Mg(OH)<sub>2</sub>.0.2H<sub>2</sub>O] and is isostructural with MHSH; space group  $I4_1/amd$ ,  $Z = 4$ ,

$a = 5.239$  and  $c = 12.988$  Å (Haymon & Kastner, 1986).

The MHSH structure of Keefer *et al.* (1981) was disordered. The refined occupancy of the Mg position (equi-point 8*d*) was 0.666 (5) and assumed to be an ideal value of 2/3, the assumed occupancy of the H position (equi-point 16*h*) was 1/3,  $B_{\text{eq}}$  were high for all atoms and  $R = 0.041$ . Keefer *et al.* (1981) proposed that in the ordered structure the occupied Mg(O,OH,H<sub>2</sub>O)<sub>6</sub> octahedra were associated in pairs which alternated with unoccupied octahedra along individual octahedral chains. Avoidance of two shared octahedral faces accounted for the unusual stoichiometry of MgSO<sub>4</sub>.1/3Mg(OH)<sub>2</sub>.1/3H<sub>2</sub>O. Also, O(2) atoms, comprising 1/5 of the O atoms in the structure, were statistically distributed between OH<sup>-</sup> radicals and H<sub>2</sub>O molecules in the ratio of H<sub>2</sub>O to OH<sup>-</sup> 1:2.

Hochella, Keefer & de Jong (1983) reasoned that the substitution  $\text{Mg}^{2+} \rightleftharpoons 2\text{H}^+$  would result in a variable Mg content and H<sub>2</sub>O/OH<sup>-</sup> ratio for MHSH. They proposed that MgSO<sub>4</sub>.1/3Mg(OH)<sub>2</sub>.1/3H<sub>2</sub>O was a special composition in the solid solution series MgSO<sub>4</sub>. $x$ Mg(OH)<sub>2</sub>. $(1 - 2x)$ H<sub>2</sub>O, and that MHSH-type structures were limited to  $0 \leq x \leq 0.5$ .

We presently revise the formula of MHSH to 2MgSO<sub>4</sub>. $x$ Mg(OH)<sub>2</sub>. $(2 - 2x)$ H<sub>2</sub>O, with  $0.5 \leq x \leq 1.0$ . In Hochella *et al.* (1983) MHSH of the formula 2MgSO<sub>4</sub>.2/3Mg(OH)<sub>2</sub>.2/3H<sub>2</sub>O was labelled MHSH(2/3) and the limiting composition with no molecular water [2MgSO<sub>4</sub>.Mg(OH)<sub>2</sub>] was labelled MHSH(3/4), where the number in parentheses is the proportion of octahedral sites occupied within individual octahedral chains and is calculated from  $(2+x)/4$ . Chemical mass balance calculations and mineral stability data indicated that at least two MHSH stoichiometries must exist, 2MgSO<sub>4</sub>.1/2Mg(OH)<sub>2</sub>.H<sub>2</sub>O [*i.e.* MHSH(5/8)] and MHSH(3/4); the latter coexisting with brucite (Janecky & Seyfried, 1983). MHSH(5/8) and MHSH(3/4) are the compositions corresponding to the minimum and maximum Mg site occupancies, respectively, deduced by Keefer *et al.* (1981) for their structure of MHSH.

### 2. Experimental

Single crystals of magnesium hydroxide sulfate [2MgSO<sub>4</sub>.Mg(OH)<sub>2</sub>], hereinafter referred to as MHS,

Table 1. *Experimental details*

Crystal data	
Chemical formula	2MgSO <sub>4</sub> ·Mg(OH) <sub>2</sub>
Chemical formula weight	299.07
Cell setting	Tetragonal
Space group	<i>P</i> 4 <sub>3</sub> 2 <sub>1</sub> 2
<i>a</i> (Å)	7.454 (1)
<i>c</i> (Å)	12.885 (2)
<i>V</i> (Å <sup>3</sup> )	716.0
<i>Z</i>	4
<i>D<sub>c</sub></i> (Mg m <sup>-3</sup> )	2.774
Radiation type	Mo <i>K</i> α
Wavelength (Å)	0.70926
No. of reflections for cell parameters	20
$\theta$ range (°)	14.2–17.0
$\mu$ (mm <sup>-1</sup> )	1.04
Temperature (K)	293 (2)
Crystal form	Tablet
Crystal size (mm)	0.17 × 0.16 × 0.08
Crystal colour	Colourless
Data collection	
Diffractometer	Enraf-Nonius CAD-4
Data collection method	$\omega$ scans
Absorption correction	Analytical, Gaussian grid
<i>T<sub>min</sub></i>	0.864
<i>T<sub>max</sub></i>	0.909
No. of measured reflections	2540
No. of independent reflections	1367
No. of observed reflections	801
Criterion for observed reflections	<i>I</i> > 3σ( <i>I</i> )
<i>R<sub>int</sub></i>	0.0184
$\theta_{\max}$ (°)	40.0
Range of <i>h, k, l</i>	0 → <i>h</i> → 13 0 → <i>k</i> → 13 0 → <i>l</i> → 23
No. of standard reflections	3
Frequency of standard reflections	Every 500 reflections
Intensity decay (%)	None
Refinement	
Refinement on	<i>F</i>
<i>R</i>	0.0245
<i>wR</i>	0.0227
<i>S</i>	1.1604
No. of reflections used in refinement	1367
No. of parameters used	71
H-atom treatment	H atoms: unconstrained
Weighting scheme	$w = 1/\sigma^2(F)$ , $\sigma$ based on agreement between equivalent reflections, unobserved reflections given low weight
( $\Delta/\sigma$ ) <sub>max</sub>	0.00052
$\Delta\rho_{\max}$ (e Å <sup>-3</sup> )	0.630
$\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	-0.720
Extinction method	Coppens & Hamilton (1970)
Extinction coefficient	$g = 1.23(2) \times 10^{-4}$
Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Tables 2.2A and 2.3.1)
Computer programs	
Data collection	CAD-4 Express (Delft Instruments, 1992)
Cell refinement	CAD-4 Express (Delft Instruments, 1992)
Data reduction	DATA777 (Coppens, 1977a)
Molecular graphics	ATOMS (Dowty, 1989, 1995)
X-ray powder patterns	POWDR2 (Smith, 1967)
Structure refinement	LINEX77 (Coppens, 1977b)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)*

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
Mg(1)	0.1239 (4)	0.1239 (4)	1/2	0.0079 (2)
Mg(2)	0.1007 (2)	0.3555 (2)	0.25618 (6)	0.0082 (2)
S	0.2506 (1)	0.99719 (9)	0.12740 (5)	0.00598 (8)
O(1)	0.1416 (6)	0.1099 (6)	0.1943 (1)	0.0141 (5)
O(2)	0.3696 (6)	0.8796 (6)	0.1897 (1)	0.0110 (4)
O(3)	0.2417 (3)	0.4884 (3)	0.1378 (1)	0.0081 (3)
O(4)	0.1351 (6)	0.8737 (6)	0.0669 (1)	0.0118 (4)
O(5)	0.3555 (6)	0.1109 (7)	0.0586 (1)	0.0140 (5)

Table 3. *Selected geometric parameters (Å, °)*

Mg(1)—O(2 <sup>i</sup> )	2.059 (5)	Mg(2)—O(3 <sup>iii</sup> )	2.025 (1)
Mg(1)—O(3 <sup>i</sup> )	2.028 (2)	Mg(2)—O(4 <sup>iii</sup> )	2.181 (5)
Mg(1)—O(4 <sup>i</sup> )	2.115 (3)	Mg(2)—O(5 <sup>iii</sup> )	2.025 (2)
Mg(1)—O(2 <sup>iii</sup> )	2.059 (5)	S—O(1 <sup>vii</sup> )	1.453 (3)
Mg(1)—O(3 <sup>iii</sup> )	2.028 (2)	S—O(2)	1.482 (3)
Mg(1)—O(4 <sup>iii</sup> )	2.115 (3)	S—O(4)	1.482 (3)
Mg(2)—O(1)	2.020 (5)	S—O(5 <sup>vii</sup> )	1.454 (3)
Mg(2)—O(2 <sup>i</sup> )	2.170 (1)	H—O(3)	0.80 (3)
Mg(2)—O(3)	2.101 (1)		
O(1 <sup>vii</sup> )—S—O(2)	110.8 (1)	O(2)—S—O(4)	105.4 (4)
O(1 <sup>vii</sup> )—S—O(4)	110.2 (4)	O(2)—S—O(5 <sup>vii</sup> )	110.7 (4)
O(1 <sup>vii</sup> )—S—O(5 <sup>vii</sup> )	109.0 (4)	O(4)—S—O(5 <sup>vii</sup> )	110.8 (1)

Symmetry codes: (i)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{4} - z$ ; (ii)  $-x, 1 - y, \frac{1}{2} + z$ ; (iii)  $y - \frac{1}{2}, \frac{1}{2} - x, \frac{1}{4} + z$ ; (iv)  $1 - y, -x, \frac{1}{2} - z$ ; (v)  $1 - y, 1 - x, \frac{1}{2} - z$ ; (vi)  $x - \frac{1}{2}, \frac{1}{2} - y, \frac{3}{4} - z$ ; (vii)  $x, 1 + y, z$ .

Table 4. *Bond valences for MHS (after Brown, 1981)*

	Mg(1)	Mg(2)	S	H	$\Sigma$
O(1)		0.40	1.56	0.09	2.05
O(2)	0.37	0.28	1.44		2.09
	(×2)				
O(3)	0.39	0.33, 0.40		0.80*	1.92
	(×2)				
O(4)	0.32	0.27	1.44		2.03
	(×2)				
O(5)		0.40	1.56	0.11	2.07
$\Sigma$	2.16	2.08	6.00	1.00	

\* By difference from 1.00.

capsules and the experiments were conducted in standard cold-seal hydrothermal vessels. MHS was present as rare crystals, 300 μm maximum dimension, attached to the wall of the gold capsule. The single crystal used for collection of X-ray reflection intensities was synthesized in an experiment at 0.15 GPa, 673 K, 8 d run time (#Mg32). The charge consisted of 0.02 g of MgS, prepared from analytical grade Mg metal and pure S, 0.01 g pure SiO<sub>2</sub> and 0.03 cm<sup>3</sup> of deionized water. The products consisted of hydrous magnesium silicate [Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>, serpentine], Mg(OH)<sub>2</sub> (brucite), MHS and Au-bearing Mg—S—H—O fluid. Other experimental details are described elsewhere (Fleet & Knipe, 1997).

MHS was characterized by petrographic microscopy, analytical scanning electron microscopy (SEM), electron microprobe analysis (EPMA), and powder and

were encountered as products in experiments on the solubility of gold in Mg—S—O—H fluids. Starting compositions were contained in sealed fine gold

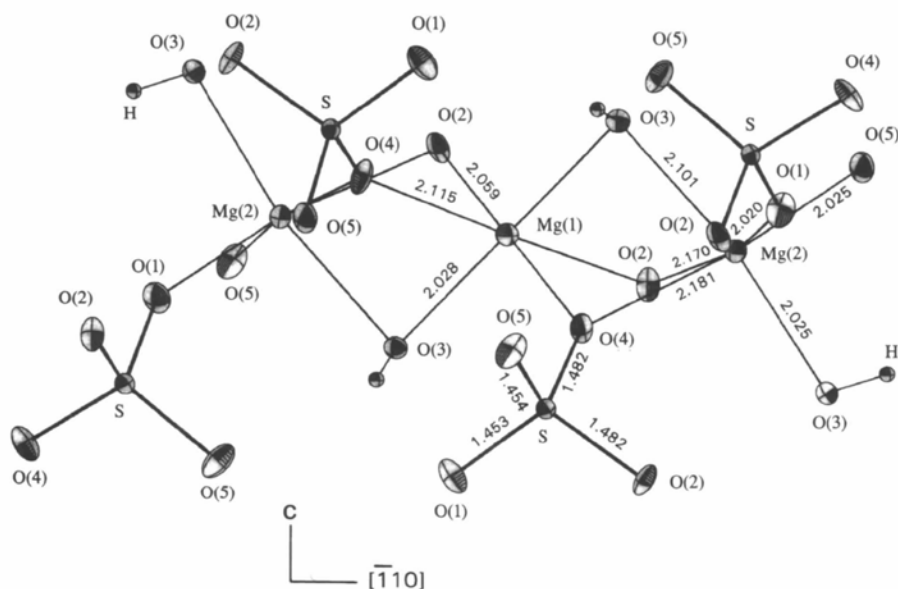
STRUCTURE OF  $2\text{MgSO}_4 \cdot \text{Mg}(\text{OH})_2$ 

Fig. 1. Structure of magnesium hydroxide sulfate (MHS), showing a linear ternary group of Mg octahedra and cross-linking  $\text{SO}_4$  tetrahedra; Mg(1) is at 0.88, 0.88, 0.0 (cf. Fig. 2a) and bond distances are in Å. Thermal ellipsoids are scaled to enclose 50% probability.

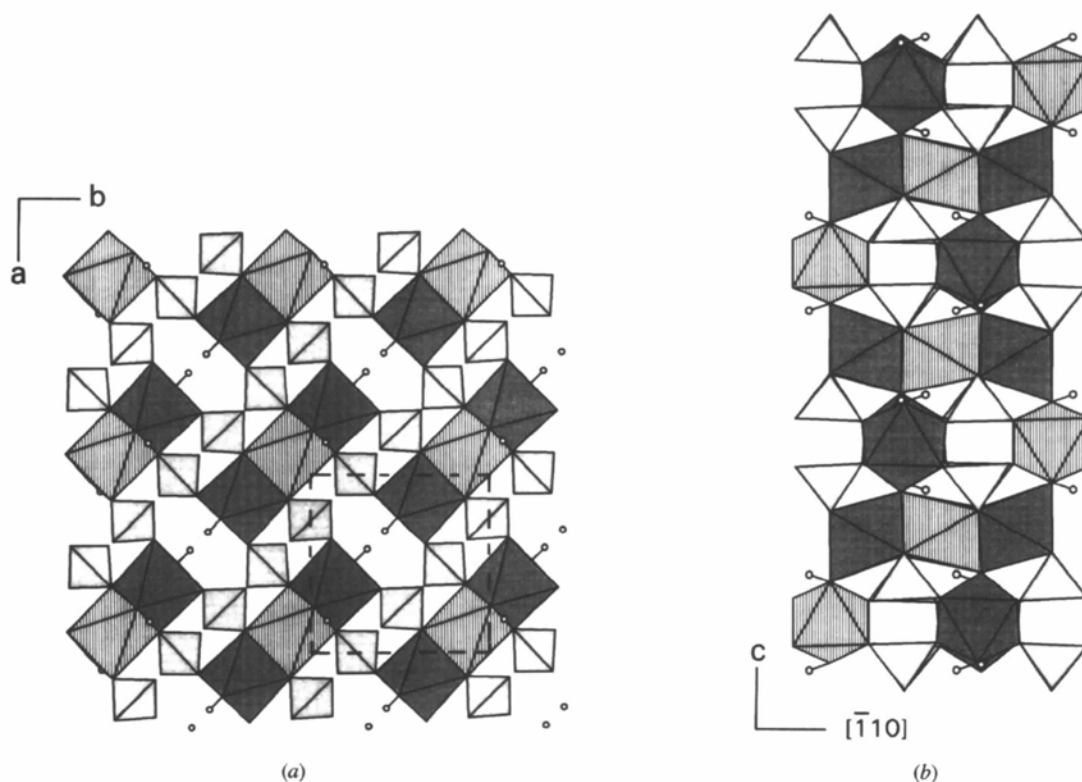
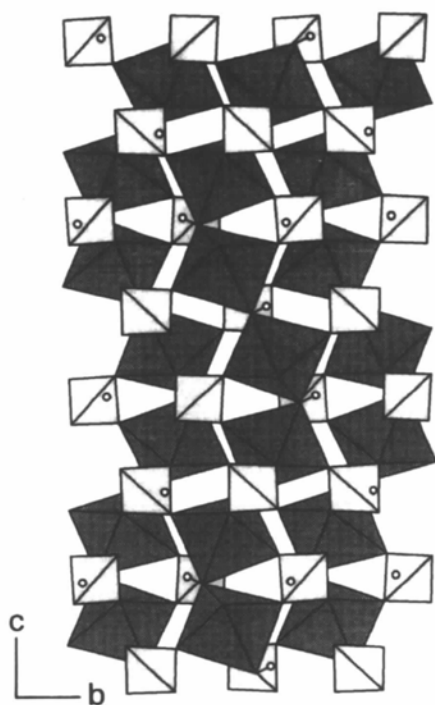
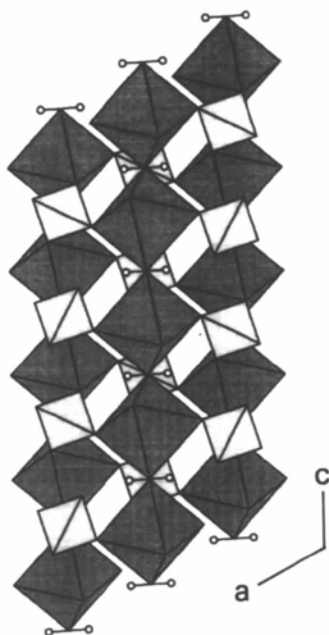


Fig. 2. Polyhedral representation of the structure of MHS; (a) [001] projection of the partial structure from  $z = -0.2$  to  $z = 0.2$ , showing a single layer of ternary groups of face-shared Mg octahedra and underlying and overlying layers of cross-linking  $\text{SO}_4$  tetrahedra; (b) [110] projection. Shading of octahedra is light for Mg(1) and moderate for Mg(2). Open small circles are H, which project toward the unoccupied octahedron. O(3) (Fig. 1) links face-shared Mg(1)—Mg(2) octahedra with an underlying (or overlying) Mg(2) octahedron. In the magnesium hydroxide sulfate hydrate (MHSH) solid solution, an  $\text{Mg}(1)^{2+}$  cation is substituted by  $2\text{H}^+$ , converting the two linking  $\text{O}(3)\text{H}^-$  radicals to  $\text{H}_2\text{O}(3)$  molecules; the additional H project toward the vacant Mg(1) octahedron (b).



(a)



(b)

Fig. 3. (a) [100] projection of MHS structure with Mg(1) octahedra omitted, revealing spiral chains of Mg(2) octahedra; (b) structure of kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ; Hawthorne *et al.*, 1987), which has straight single chains of corner-shared Mg octahedra. Open small circles are H.

single-crystal X-ray diffraction, and confirmed to be analogous to MSHS and caminite (Keefe *et al.*, 1981; Haymon & Kastner, 1986). The EPMA composition of the crystals was determined with a JEOL 8600 superprobe, giving  $\text{MgO} = 40.7(3) \text{ wt\%}$ ,  $\text{SO}_3 = 51.7(4) \text{ wt\%}$ , total =  $92.3(4) \text{ wt\%}$  (average of 21 microprobe spot analyses). Operating conditions included an accelerating voltage of 15 kV, a beam current of 10 nA, a beam diameter of  $10 \mu\text{m}$ , 20 s counts and pure forsterite ( $\text{Mg}_2\text{SiO}_4$ ) and pyrite ( $\text{FeS}_2$ ) as standards. The surface of the areas analysed degraded visually during analysis, presumably reflecting the loss of volatile material. In view of this analytical difficulty, the EPMA composition appears reasonably close to the ideal formula  $2\text{MgSO}_4 \cdot \text{Mg}(\text{OH})_2$  ( $\text{MgO} = 40.44 \text{ wt\%}$ ;  $\text{SO}_3 = 53.54 \text{ wt\%}$ ,  $\text{H}_2\text{O} = 6.02 \text{ wt\%}$ ).

In a second experiment, in which it was confirmed as a product phase [#Mg29 ( $\text{MgS} + \text{H}_2\text{O}$  reacted at 973 K)], magnesium hydroxide sulfate coexisted with brucite [ $\text{Mg}(\text{OH})_2$ ] (*cf.* Janecky & Seyfried, 1983) and had a similar EMPA composition [ $\text{MgO} = 39.9(2) \text{ wt\%}$ ,  $\text{SO}_3 = 52.1(5) \text{ wt\%}$ ,  $n = 8$ ] and Gandolfi powder X-ray diffraction pattern to MHS of experiment #Mg32. Thus, the composition, formula of  $2\text{MgSO}_4 \cdot \text{Mg}(\text{OH})_2$  and unit-cell characteristics of MHS are well established.

### 3. Discussion

#### 3.1. MHS structure

The structure of MHS (Tables 1–4; Fig. 1)\* has a similar topology to the disordered structure of MSHS of Keefe *et al.* (1981), but the ordered structure proposed in the earlier study appears to be incorrect. The Mg octahedra in the structure of MHS do not form face-shared chains along  $[\bar{1}10]$  ( $[100]$  for the unit cell of Keefe *et al.*, 1981; Fig. 2). Rather, they are associated into a linear ternary group that alternates with an unoccupied octahedral position in rows along  $[\bar{1}10]$ . The ternary groups are formed from a Mg(1) octahedron sandwiched between two Mg(2) octahedra and cross-linked by  $\text{SO}_4$  tetrahedra *via* shared O(1), O(2), O(4) and O(5), and linked to underlying and overlying ternary groups *via* O(3). The Mg(2) octahedra actually form spiral ( $4_3$ ) single chains parallel to  $[001]$  (Fig. 3). Thus, alternatively, the MHS structure may be considered to comprise spiral single chains of corner-shared Mg(2) octahedra cross-linked by  $\text{SO}_4$  tetrahedra and face-shared Mg(1) octahedra.

The H atom is bonded to O(3), forming an OH radical in *trans* configuration to both  $\text{Mg}(1)\text{O}_4(\text{OH})_2$  and  $\text{Mg}(2)\text{O}_4(\text{OH})_2$  octahedra (Fig. 1) and projects toward the unoccupied octahedron (Fig. 2a). O(3) is then coordinated to H, Mg(1) and two Mg(2). The refined H—O(3)

\* Lists of anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: BR0053). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bond distance is short (0.80 Å; Table 3; *cf.* 0.86 Å for  $\text{H}_2\text{O}$  in the X-ray structure of kieserite,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ; Hawthorne, Groat, Raudsepp & Ercit, 1987) and the second-shell H—O distances are relatively long [2.42 Å to O(5) and 2.58 Å to O(1)]. However, the residual electron density at the H position was insignificant and the significant positive features in the difference synthesis were limited to the Mg(1) position (possible positional disorder along the axis of the ternary group) and the S—O bonds ( $\sigma$  bond electron density). Bond valences (Table 4) and O—H...O bond angles are also consistent with hydrogen bonds to O(5) and O(1).

The Mg(1) position may have a very weak tendency to disorder along the axis of the ternary group, possibly in response to repulsion related to the shared octahedral faces. However, refinements with the Mg(1) position disordered ( $x \neq y$ ) and constrained ( $x = y = 1/8$ ), and combined with anisotropic displacement parameters, were unsatisfactory because of the small apparent displacement of the Mg(1) atoms.

### 3.2. MHS–MHS<sub>H</sub> solid solution

The present structure for MHS permits a new crystal–chemical understanding of the solid solution  $2\text{MgSO}_4 \cdot x\text{Mg}(\text{OH})_2 \cdot (2-2x)\text{H}_2\text{O}$  and the structure of MHS<sub>H</sub> and caminite. The H atoms introduced by substitution for Mg ( $\text{Mg}^{2+} \rightleftharpoons 2\text{H}^+$ ) react with the  $\text{OH}^-$  radical in *trans* configuration in the Mg octahedra to form water molecules. O(3) is the only oxygen free to accept hydrogen, because hydration of the oxygens bonded to S [O(1), O(2), O(4) and O(5)] would leave them significantly overbonded. The most evident constraint influencing which Mg atoms are substituted is minimization of the number of shared octahedral faces. Mg(1) shares two octahedral faces and Mg(2) one; therefore, the former most probably participates in the substitution reaction.

Because three Mg octahedra are corner shared with O(3) (Fig. 2*b*), the substitution of one  $\text{Mg}(1)^{2+}$  by two  $\text{H}^+$  creates two water molecules and changes the stereochemical environment of four Mg(2) atoms from  $\text{Mg}(2)\text{O}_4(\text{OH})_2$  to  $\text{Mg}(2)\text{O}_4(\text{OH})(\text{H}_2\text{O})$ . In terms of the more strongly bonded interactions, the coordination of the Mg(2) atoms nearest-neighbouring substituted Mg(1) sites is 5 + 1 and effectively square pyramidal. Substitution of both Mg(1) atoms nearest-neighbouring Mg(2) would result in the *trans*  $\text{Mg}(2)\text{O}_4(\text{H}_2\text{O})_2$  (4 + 2) configuration. Thus, the  $\text{Mg}(1)^{2+} \rightleftharpoons 2\text{H}^+$  substitution may be limited to an Mg(1) occupancy of 0.5 ( $x = 0.5$ ). A new ordered structure at  $x = 0.5$ , with all Mg(2) in  $\text{Mg}(2)\text{O}_4(\text{OH})(\text{H}_2\text{O})$  octahedra, and MHS would correspond to, respectively, the two stoichiometries MHS<sub>H</sub>(5/8) and MHS<sub>H</sub>(3/4) defined in the phase equilibrium study of Janecky & Seyfried (1983). Of course, random substitution of Mg(1) by 2H would require  $x$  to be somewhat greater than 0.5.

Table 5. Powder X-ray diffraction data for MHS, MHS<sub>H</sub> and caminite

MHS*			MHS <sub>H</sub> †			Caminite‡	
<i>d</i> (Å)	<i>I</i> / <i>I</i> <sub>0</sub>	<i>hkl</i>	<i>d</i> (Å)	<i>I</i> / <i>I</i> <sub>0</sub>	<i>hkl</i>	<i>d</i> (Å)	<i>I</i> / <i>I</i> <sub>0</sub>
6.452	6.6	101					
5.271	2.3	110					
4.879	6.6	111	4.861	10	101	4.858	10
4.874	3.4	102					
4.080	1.6	112					
3.727	0.0	200					
3.721	1.0	103					
3.580	2.7	210					
3.334	2.2	210					
3.330	100.0	113	3.339	100	103	3.345	100
3.227	3.3	211					
3.226	90.0	202	3.220	91	112	3.220	80
3.221	0.7	004					
2.961	0.3	212					
2.957	0.1	104					
2.815	1.2	203					
2.749	0.7	114					
2.636	20.9	220	2.621	22	200	2.628	15
2.633	2.8	213					
2.582	0.0	221					
2.440	0.8	301					
2.439	0.9	222					
2.437	0.0	204					
2.436	0.1	105					
2.357	0.3	310					
2.319	9.3	311	2.307	9	211	2.309	10
2.318	1.9	302					
2.316	5.6	214					
2.315	0.1	115					
2.246	0.0	223					
2.214	0.6	312					
2.151	0.7	303					
2.120	0.3	205					
2.067	0.0	320					
2.066	15.5	313	2.062	16	213	2.062	20
2.064	0.0	106					
2.041	0.0	321					
2.040	13.0	224	2.040	15	204	2.041	20
2.039	1.1	215					

\* Calculated using POWDR2. † Hochella *et al.* (1983).

‡ Haymon & Kastner (1986).

The formula of  $\text{MgSO}_4 \cdot 1/3\text{Mg}(\text{OH})_2 \cdot 1/3\text{H}_2\text{O}$  assumed by Keefer *et al.* (1981) for their crystal of MHS<sub>H</sub> does not correspond to a special composition. The present structure of MHS provides the crystal chemical basis for the MHS<sub>H</sub> composition series and excludes the possibility of paired face-shared Mg octahedra alternating with unoccupied octahedra along octahedral chains to give an overall Mg occupancy of 2/3. The local structure of MHS<sub>H</sub> is most likely based on that of MHS. The powder X-ray diffraction patterns of MHS,

MHSH and caminite are very similar (Table 5) and reflections characteristic of the larger MHS unit cell would be very weak or absent if crystals of MHSH and caminite were constructed from coherently twinned domains of MHS structure. If this were the case a true order-disorder relationship would not exist between MHS and MHSH/caminite, although a case for cluster ordering in synthetic MHSH could be made.

Substitution of all Mg(1) atoms in MHS and the conversion of all O(3)H<sup>-</sup> radicals to H<sub>2</sub>O(3) molecules results in a single-chain structure for the MgSO<sub>4</sub>.H<sub>2</sub>O composition (Fig. 3a) with nearest-neighbour coordinations analogous to those in the single-chain structure of kieserite (MgSO<sub>4</sub>.H<sub>2</sub>O; cf. Hawthorne *et al.*, 1987). However, the H-substituted MHS (with  $x = 0$ ) and kieserite structures do not have the same topology, as suggested by Keefer *et al.* (1981), because the single chains of MgO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> octahedra are spiral in the former and straight in the latter (Fig. 3). Hence, significant structural differences exist to inhibit the extensive solid solution between MHSH (with  $x = 0.5$ ) and kieserite. Whereas the solid solution 2MgSO<sub>4</sub>. $x$ Mg(OH)<sub>2</sub>.(2 - 2 $x$ )H<sub>2</sub>O could extend beyond 2MgSO<sub>4</sub>.1/2Mg(OH)<sub>2</sub>.H<sub>2</sub>O, to compositions with  $x < 0.5$ , with a matrix of the H-substituted MHS structure, substitution of Mg into kieserite would be limited because the kieserite structure does not readily accommodate additional Mg octahedra.

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