There are two essential differences between the two polymorphs of Sb$_2$O$_4$. Firstly, the Sb^V octahedra are more distorted in the α form, and secondly, alternate chains of Sb^{III} polyhedra along **c** have an opposite tilt about **a**. Andersson & Åstrom (1972) have discussed the packing of oxides containing stereochemically active lone pairs, each lone pair being considered as a packing sphere. The hexagonal close packing apparent in β-Sb$_2$O$_4$ (Andersson & Åstrom, 1972) is also present in the α polymorph, although in a more distorted form.

References

ANDERSSON, S. & ÅSTROM, A. (1972). *Solid State Chemistry*, NBS Spec. Publ. 364, pp. 3–13.

CHEETHAM, A. K. & TAYLOR, J. C. (1976). *J. Solid State Chem.* In the press.

DIHLSTROM, K. (1938). *Z. anorg. Chem.* **239**, 57–64.

GALY, J. (1972). *Solid State Chemistry*, NBS Spec. Publ. 364, pp. 29–39.

KAFALAS, J. A. (1972). *Solid State Chemistry*, NBS Spec. Publ. 364, pp. 287–292.

NEUTRON DIFFRACTION COMMISSION (1972). *Acta Cryst.* **A28**, 357–358.

RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.

ROGERS, D. & SKAPSKI, A. C. (1964). *Proc. Chem. Soc.* pp. 400–401.

SKAPSKI, A. C. & ROGERS, D. (1965). *Chem. Commun.* pp. 611–613.

SWANSON, H. E., COOK, M. I., EVANS, E. H. & DE GROOT, S. H. (1960). *Natl. Bur. Stand. (US), Circ.* 539, **10**, 8–10.

The Hydrogen Bonding of Hydromagnesite

BY M. AKAO AND S. IWAI

Research Laboratory for Engineering Materials, Tokyo Institute of Technology, Tokyo 152, Japan

Abstract. Mg$_5$(CO$_3$)$_4$(OH)$_2$(H$_2$O)$_4$ (Dovez, Iran), monoclinic, $P2_1/c$, $a = 10.105$ (5), $b = 8.954$ (2), $c = 8.378$ (4) Å, $\beta = 114.44$ (5)°, $Z = 2$, D_m (flotation) = 2.25, $D_x = 2.25$ g cm^{-3}. The H positions have been determined from three-dimensional X-ray data. The H atoms in the water molecules take part in a hydrogen-bond system, while those in the hydroxyl groups do not.

Introduction. Crystals of hydromagnesite were kindly provided by Professor P. Bariand, Laboratoire de Minéralogie et Cristallographie, Université de Paris VI. Although the crystals were strongly twinned on (100), a twin-free specimen of dimensions 0.23 × 0.07 × 0.07 mm could be isolated. Intensities were measured on a Philips four-circle diffractometer with Mo $K\alpha$ radiation, monochromated by a graphite plate, by the ω–2θ scan technique with a scan speed of 4° min^{-1} in ω. 2598 independent reflexion data were obtained for $2\theta \leq 100°$. Intensities were corrected for Lorentz and polarization factors but not for extinction. No correc-

tions were made for absorption, since μR of the crystal is less than 0.07 [μ(Mo $K\alpha$) = 5.3 cm^{-1}]. The systematic absences were $h0l$ for l odd and $0k0$ for k odd.

With the atomic coordinates given by Stephan (1974) and anisotropic thermal parameters the structure without H atoms was refined to an R value of 0.063. The positions of the H atoms were found from a difference Fourier synthesis. The structure was refined by the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970) to a conventional R value of 0.052, with anisotropic thermal parameters for non-hydrogen atoms and isotropic for H. The weighting scheme employed was $w = 1/(A + B|F_o| + C|F_o|^2 + D|F_o|^3)$. The parameters A, B, C and D were varied so that $\langle w||F_o| - |F_c||^2 \rangle$ was independent of the magnitude of F_o. The values of A, B, C and D for the last cycles were 14.8, -1.31, 0.043, and -0.00029 respectively. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974) for the heavy atoms, and for H those of Stewart, Davidson & Simpson (1965) were used. Final atomic parameters are

given in Table 1.* Selected interatomic distances and bond angles are given in Table 2.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32351 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final atomic parameters in hydromagnesite*

	x	y	z
Mg(1)	0·34502 (9)	0·06865 (10)	0·35897 (10)
Mg(11)	0·34474 (9)	0·43518 (10)	0·49177 (10)
Mg(2)	0·0	0·0	0·0
O(H)	0·22455 (17)	0·97967 (20)	0·11721 (21)
O(W1)	0·24791 (24)	0·61189 (28)	0·30117 (28)
O(W11)	0·23813 (24)	0·92381 (30)	0·45921 (29)
O(1)	0·00878 (27)	0·17176 (35)	0·16220 (45)
O(11)	0·01677 (27)	0·37440 (37)	0·30587 (37)
O(2)	0·22288 (19)	0·25692 (22)	0·35464 (25)
O(3)	0·43075 (19)	0·19566 (19)	0·21587 (22)
O(4)	0·49221 (18)	0·40165 (19)	0·37848 (21)
O(44)	0·49778 (18)	0·39688 (20)	0·11400 (20)
C(1)	0·08223 (27)	0·26599 (32)	0·27463 (36)
C(2)	0·47277 (21)	0·33128 (23)	0·23558 (25)

	x	y	z	B (Å^2)
H(1)	0·230 (7)	0·896 (7)	0·116 (8)	3·4 (8)
H(2)	0·163 (7)	0·633 (7)	0·278 (8)	3·5 (8)
H(3)	0·289 (7)	0·684 (7)	0·356 (9)	3·3 (8)
H(4)	0·145 (7)	0·911 (7)	0·385 (9)	4·2 (9)
H(5)	0·243 (7)	0·915 (7)	0·566 (9)	4·3 (9)

Discussion. The crystal structure of hydromagnesite was independently determined by Akao, Marumo & Iwai (1974) and Stephan (1974). The former reported an averaged structure on the assumption of the orthorhombic space group *Bbcm*, with $a = 18·371$, $b = 8·961$, $c = 8·384$ Å, and $\beta = 90·2°$; the latter, a monoclinic structure with space group $P2_1/c$, $a = 10·092$, $b = 8·960$, $c = 8·376$ Å, and $\beta = 114·36°$. However, no description has been reported to date for the H positions. The atomic coordinates of non-hydrogen atoms in the present study are close to those given by Stephan (1974).

The structure has a strong pseudo-orthorhombic character and shows a pseudo mirror plane parallel to (Ī02). The deviations from the pseudosymmetry are very small with respect to the heavy atoms, the maximum deviation being 0·16 Å in atomic coordinates. In the orthorhombic structure, Mg(1), O(1), O(4) and O(W1) are crystallographically equivalent to Mg(11), O(11), O(44) and O(W11) respectively. Only the H atoms remarkably disturb the pseudosymmetry.

The structure is based on corrugated layers of MgO$_6$ octahedra and carbonate groups parallel to (100). The hydroxyl group is shared by three MgO$_6$ octahedra. The water molecule is located at an unshared corner of an MgO$_6$ octahedron. The locations of the water and the hydroxyl group predicted in the previous works have been confirmed by the H positions obtained in the present study.

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Symmetry code

(None)	$x,\quad y,\quad z$	(iii)	$\bar{x}, -\frac{1}{2} + y, \frac{1}{2} - z$	(vi)	$x, 1 - y, \quad z$
(i)	$\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$	(iv)	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$	(vii)	$1 - x, 1 - y, 1 - z$
(ii)	$x, \frac{3}{2} - y, \frac{1}{2} + z$	(v)	$x, \quad \frac{1}{2} - y, \frac{1}{2} + z$		

Carbonate group

C(1)–O(1)	1·254 (4)	C(2)–O(4)	1·294 (3)	O(2)–C(1)–O(11)	119·8 (3)
C(1)–O(11)	1·262 (5)	C(2)–O(44)	1·288 (3)	O(3)–C(2)–O(4)	119·9 (2)
C(1)–O(2)	1·299 (3)	O(1)–C(1)–O(11)	118·4 (3)	O(3)–C(2)–O(44)	119·7 (2)
C(2)–O(3)	1·274 (3)	O(2)–C(1)–O(1)	121·8 (3)	O(4)–C(2)–O(44)	120·4 (2)

MgO$_6$ octahedron

Mg(1)–O(H^{vi})	2·044 (2)	Mg(1)–O(44^{iv})	2·155 (2)	Mg(11)–O(4)	2·093 (2)
Mg(1)–O(W11^{vi})	2·075 (3)	Mg(11)–O(H^v)	2·054 (2)	Mg(11)–O(4^{vii})	2·133 (2)
Mg(1)–O(2)	2·081 (2)	Mg(11)–O(W1)	2·172	Mg(2)–O(11^i)	2·041 (3) [×2]
Mg(1)–O(3)	2·083 (2)	Mg(11)–O(2)	2·053 (2)	Mg(2)–O(H^{vi})	2·074 (2) [×2]
Mg(1)–O(44^v)	2·077 (2)	Mg(11)–O(3^v)	2·074 (2)	Mg(2)–O(1)	2·030 (3) [×2]

Hydrogen bonds

		O(W)–H	H···O	O···O	O(W)–H–O
O(W1)–H(2)···O(1^i)		0·82 (7)	2·03 (8)	2·787 (4)	154 (6)
O(W1)–H(3)···O(W11)		0·80 (6)	2·44 (7)	3·110 (4)	141 (6)
O(W11)–H(4)···O(11^i)		0·89 (6)	1·78 (6)	2·651 (3)	178 (6)
O(W11)–H(5)···O(W1^{ii})		0·88 (8)	1·97 (8)	2·844 (4)	164 (8)

H(2)–O(W1)–H(3)	101 (6)	H(4)–O(W11)–H(5)	107 (7)	O(H)–H(1)	0·75 (6)
H(2)–O(W1)···H(5^{ii})	101 (5)	H(4)–O(W11)···H(3)	87 (5)		
H(3)–O(W1)···H(5^{ii})	118 (6)	H(5)–O(W11)···H(3)	111 (5)	Mg(1)–O(H^{vi})–H(1^{vi})	113 (4)
C(1^i)–O(1^i)···H(2)	103 (2)	C(1^i)–O(11^i)···H(4)	109 (2)	Mg(11)–O(H^v)–H(1^v)	107 (6)
Mg(2^v)–O(1^i)···H(2)	103 (3)	Mg(2^{vi})–O(11^i)···H(4)	105 (3)	Mg(2)–O(H^{vi})–H(1^{vi})	99 (5)

In the structure of hydromagnesite there are two crystallographically distinct carbonate groups. The average C(1)—O distance (1·272 Å) is shorter than the average C(2)—O distance (1·285 Å). The C(1)O$_3$ group is more distorted than the C(2)O$_3$ group, probably owing to the hydrogen bonding. There are three independent MgO$_6$ octahedra. The average Mg(2)—O distance (2·048 Å) is shorter than the average Mg(1)—O and Mg(11)—O distances (2·086 and 2·097 Å respectively).

The O—H distances (Table 2) are shorter than the average O—H distance (0·956 Å) derived from neutron diffraction data (Ferraris & Franchini-Angela, 1972) by 0·1–0·2 Å, as is usually observed in X-ray analysis. The O(H)—H(1) distance (0·75 Å) is shorter than the average O(W)—H distance (0·85 Å) in the water molecules. The infrared spectrum of hydromagnesite reported by White (1971) shows a very sharp band of free OH$^-$ stretching vibration at 3658 cm^{-1}, two sharp intense bands of weak hydrogen bonds at 3525 and 3463 cm^{-1}, and a broad band of a strong hydrogen bond at about 3000 cm^{-1}. In fact, there are three kinds of hydrogen bonds in the structure: (1) The very short O(W11)···O(11^i) distance (2·651 Å) indicates the existence of a strong hydrogen bond between these atoms.

(2) Longer O(W1)···O(1^i) and O(W11)···O(W1^{ii}) distances (2·787 and 2·844 Å respectively) indicate weak hydrogen bonds. (3) The O(W1) water molecule shows a very long (3·110 Å) and bent (141°) O···O contact with O(W11), and this probably lies at the boundary of a very weak hydrogen bond.

In Fig. 1 the hydrogen bonding in hydromagnesite is shown schematically. Two crystallographically independent water molecules have similar environments. Each O atom of the water molecules is tetrahedrally surrounded by two H, one Mg, and one H of a neighbouring water molecule which acts as a donor of a hydrogen bond. Half the H atoms in the water molecules are hydrogen-bonded to neighbouring water molecules, forming an infinite chain running parallel to c. The other half are hydrogen-bonded to O atoms of the C(1)O$_3$ groups. The O(1) and O(11) atoms of the C(1)O$_3$ group have 'trigonal' planar coordinations; in both cases the C—O···H and Mg—O···H angles are smaller than the ideal value of 120°. The O(H) atom is tetrahedrally surrounded by H(1), Mg(1), Mg(11) and Mg(2); the hydroxyl group does not participate in the hydrogen bonding.

Fig. 1. Hydrogen-bonding scheme of hydromagnesite projected along **b**; y coordinates are given in fractions multiplied by 10^3. Hydrogen bonds are marked with dashed lines, and pseudo mirror planes with dotted lines.

References

AKAO, M., MARUMO, F. & IWAI, S. (1974). Acta Cryst. B30, 2670–2672.
COPPENS, P. & HAMILTON, W. C. (1970). Acta Cryst. A20, 71–83.
FERRARIS, G. & FRANCHINI-ANGELA, M. (1972). Acta Cryst. B28, 3572–3582.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 73–74. Birmingham: Kynoch Press.
STEPHAN, G. W. (1974). De Kristalstructuur van Enige Magnesiumcarbonaten, pp. 25–39, Doctoral Thesis, Univ. of Amsterdam, The Netherlands.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). J. Chem. Phys. 42, 3175–3187.
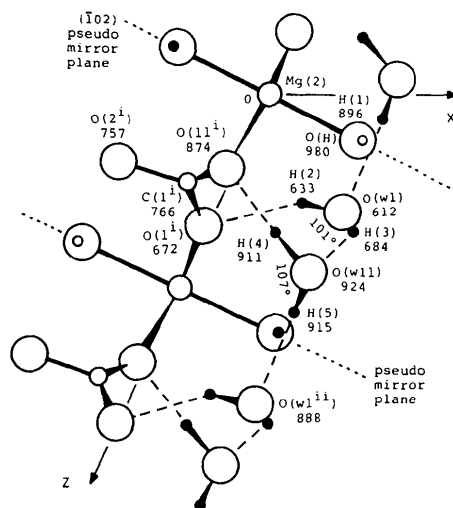WHITE, W. B. (1971). Amer. Min. 56, 46–53.