The Crystal Structure of Hydromagnesite

By M. Akao, F. Marumo and S. Iwai

*Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Oh-okayama 2–12,
Meguro-ku, 152 Tokyo, Japan*

Crystals of hydromagnesite, $4MgCO_3.Mg(OH)_2.4H_2O$, are monoclinic, $P2_1/c$, with $a=10\cdot11$ (1), $b=8\cdot97$ (1), $c=8\cdot39$ (1) Å, $\beta=114\cdot6$ (9)°, $Z=2$, and have a strong pseudo-orthorhombic character. The structure of the mineral has been determined from three-dimensional X-ray data collected by photographic methods on the assumption of an orthorhombic space group *Bbcm* (No. 64). The structure was solved by Patterson and Fourier methods, and refined by the least-squares method to a conventional R value of 0·15 for 282 observed reflexions. Both independent magnesium atoms have octahedral coordinations with average Mg–O distances of 2·10 and 2·04 Å, respectively. The structure is based on a three-dimensional framework of MgO_6 octahedra and triangular carbonate ions. There are large cavities with dimensions of about $4\cdot6 \times 4\cdot6 \times 4\cdot1$ Å in the structure.

Introduction

The following magnesium carbonates are known in nature: magnesite ($MgCO_3$), nesquehonite ($MgCO_3.3H_2O$), lansfordite ($MgCO_3.5H_2O$), artinite [$MgCO_3.Mg(OH)_2.3H_2O$], hydromagnesite, and dypingite [$4MgCO_3.Mg(OH)_2.5H_2O$]. Among these minerals hydromagnesite is the only species stable under atmospheric conditions. Two chemical formulae were proposed for hydromagnesite:

$4MgCO_3.Mg(OH)_2.4H_2O$ (Winchell & Winchell, 1951) and $3MgCO_3.Mg(OH)_2.3H_2O$ (Palache, Berman & Frondel, 1951). Recently the true stoichiometric formula was revealed to be the former on the basis of a chemical analysis of specimens from Dovez, Minab district, Iran by Bariand, Cesbron, Vachey & Sadrzadeh (1973). The crystals of hydromagnesite are always finely twinned with twinning planes parallel to (100). The first reliable X-ray study with the single-crystal method was carried out by Murdoch (1954), and showed that the crystal is monoclinic, having pseudo-orthorhombic nature with cell dimensions $a=18\cdot58$, $b=9\cdot06$, and $c=8\cdot42$ Å. This cell is *B*-centred and gives $a=10\cdot20$, $b=9\cdot06$, $c=8\cdot42$, and $\beta=114°$ of the monoclinic cell in reduced-cell representation. The more accurate values were recently determined by H. T. Evans Jr., D. Appleman and M. Morse (Hemingway & Robie, 1972) to be $a=10\cdot106$, $b=8\cdot951$, $c=8\cdot388$ Å, and $\beta=114\cdot61°$. Bariand *et al.* (1973) confirmed these cell dimensions and obtained $P2_1/c$ for the space group of this mineral.

Little has been known about the structure of hydromagnesite, although it has considerable industrial importance. Its structure determination was undertaken to obtain a better knowledge of the crystal chemistry of the magnesium carbonates.

Experimental

The specimens used were platy crystals from Fort Point, San Francisco, California. Because of the fine lamellar twinning on (100), a single crystal suitable for structure determination could not be isolated. X-ray experiments were therefore carried out with a twinned specimen of dimensions $0\cdot01 \times 0\cdot09 \times 0\cdot22$ mm. The cell dimensions and the space group were determined from Weissenberg photographs taken with Cu $K\alpha$ radiation. They are in agreement with the previously reported results and are given in Table 1 together with other crystallographic data.

Table 1. *Crystal data for hydromagnesite*

Space group	Monoclinic cell $P2_1/c$	Pseudo-orthorhombic cell *Bbcm*
a	10·11 (1) Å	18·371 (9) Å
b	8·97 (1)	8·961 (9)
c	8·38 (1)	8·384 (8)
β	114·6 (9)°	90·2 (4)°
U	690·8 Å³	1380 Å³
Z	2	4

Chemical formula $4MgCo_3.Mg(OH)_2.4H_2O$
F.W. 467·6; $D_m=2\cdot24$, $D_x=2\cdot25$ g cm⁻³
μ(Cu $K\alpha$)$=39\cdot7$ cm⁻¹

Although the true symmetry is monoclinic, the X-ray photographs showed a strong pseudo-orthorhombic character close to the symmetry of the space group *Bbcm*. The relation of the pseudo-orthorhombic unit-cell vectors (**a′**, **b′** and **c′**) to those of the true cell is: **a′**$=2$**a**$-$**c**, **b′**$=$**b**, and **c′**$=$**c**. The angle β' is 90·2°. Consequently, most of reflexions overlapped those from the twin counterpart on the Weissenberg photographs. Only reflexions with large I' were separately

recorded (the prime means the index is referred to the pseudo-orthorhombic cell). From a close examination of those reflexions with large l's, the deviation from the orthorhombic symmetry was found to be small. The difference in intensities between $h'k'l'$ and $h'k'\bar{l}'$ was about 8% on average. Because of the strong orthorhombic character as well as the overlapping of reflexions from twin components, the structure determination was carried out by assuming $Bbcm$ crystal symmetry. The density of 2·24 g cm^{-3} obtained by the flotation method agrees well with the calculated value, if Z is assumed to be 4 in the pseudo-orthorhombic cell.

Intensity data were collected on multiple-film equi-inclination Weissenberg photographs taken with Cu $K\alpha$ radiation around the b' ($=b$) and c' ($=c$) axes up to the fifth layer. They were visually estimated with an intensity scale, and corrected for Lorentz, polarization, and spot-shape factors. Correction for absorption factors was also made during the structure refinement. When the two component reflexions from the twin individuals did not overlap on the films, intensities for both reflexion spots were measured separately and summed. 282 independent intensities were obtained and used for the determination of the averaged structure. The accuracy of the measurement was low owing to the twinning.

Structure determination

The averaged structure with orthorhombic symmetry was solved by the heavy-atom method. One of the independent magnesium atoms was located on the three-dimensional Patterson function. The positions of all the remaining atoms other than hydrogen were found on Fourier maps synthesized with phases determined by the magnesium atom. The structure was refined by a local version of the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970), employing isotropic thermal and secondary extinction parameters. The final R value was 0·15 for 282 observed reflexions. The corrections for absorption and secondary extinction factors were made by assuming that the crystal shape was a rectangular parallelepiped with dimensions 0·01 × 0·09 × 0·22 mm. The computed extinction factor was 0·5 × 10^{-4} and the largest correction was about 17% of F. The following weighting scheme was employed: $w=0\cdot3$ if $|F_o|=0$, $w=1\cdot0$ if $0<|F_o|\le10$, $w=0\cdot5$ if $10<|F_o|\le50$, and $w=0\cdot1$ if $50<|F_o|$. The atomic scattering factors used were those for neutral atoms given in *International Tables for X-ray Crystallography* (1968). In view of low accuracy of the intensity data, refinement was terminated at this point. The final positional and thermal parameters are listed in Table 2.*

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30563 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Final positional and thermal parameters for hydromagnesite*

	x	y	z	B [Å²]
Mg(1)	0·1726 (4)	0·0668 (8)	0·1825 (13)	0·8 (2)
Mg(2)	0·0	0·0	0·0	0·9 (3)
C(1)	0·0436 (18)	0·25	0·25	1·3 (6)
C(2)	0·2363 (13)	0·3292 (32)	0·0	0·2 (5)
OH	0·3867 (11)	0·4770 (24)	0·0	0·5 (4)
H₂O	0·3799 (11)	0·0982 (22)	0·1694 (28)	2·9 (4)
O(1)	0·0052 (13)	0·1515 (24)	0·1779 (31)	3·8 (5)
O(2)	0·1109 (13)	0·25	0·25	2·0 (5)
O(3)	0·2148 (12)	0·1960 (26)	0·0	0·9 (4)
O(4)	0·2479 (9)	0·1039 (16)	0·3646 (20)	0·9 (3)

The water molecule was distinguished from the hydroxyl group by consideration of the number of molecules in the unit cell.

Discussion

The projection of the structure along the c' axis is shown in Fig. 1. The structure is based on a three-dimensional framework of MgO$_6$ octahedra and triangles of carbonate ions. Mg(1)O$_6$ octahedra are arranged in strings parallel to the c' axis by sharing edges. Four such strings run through the B-centred unit cell. The strings are further combined into rugged sheets parallel to (100) sharing apices of the octahedra. The Mg(2)O$_6$ octahedra join these layers in the a' direction by sharing apices with the Mg(1)O$_6$ octahedra. All the oxygen atoms in the crystal participate in the construction of the framework; two thirds of them belong to carbonate ions. The framework is reinforced by the strong C–O bonds of the carbonate ions. There are large cavities around $(0,0,\frac{1}{2})$ and its equivalents. The distances from $(0,0,\frac{1}{2})$ to the surrounding atoms are given in Table 3. If the van der Waals radius of an oxygen atom is assumed to be 1·40 Å, the size of the cavity is about 4·6 × 4·6 × 4·1 Å.

The bond distances and angles are given in Table 3. The Mg(1) atom is surrounded by four oxygen atoms from carbonate ions, one hydroxyl group and one water molecule, while the Mg(2) atom is surrounded by four oxygen atoms from carbonate ions and two hydroxyl groups. As seen in Table 3, the Mg(1)O$_6$ octahedron is more distorted than the Mg(2)O$_6$ octahedron owing to the edge-sharing. In view of the rather large standard deviations of positional parameters, both independent carbonate ions can be considered to have a normal shape. The C(1)O$_3$ ion is approximately parallel to (011) or (01$\bar{1}$) of the pseudo-orthorhombic cell. The plane of the C(2)O$_3$ ion is parallel to the c' axis and makes an angle of 15° with (100). From the infrared absorption spectra of hydromagnesite White (1971) concluded that distinct kinds of carbonate ions should be contained in the mineral. Actually, the C(1)O$_3$ ion has a quite different environment from that around the C(2)O$_3$ ion. All oxygen atoms in the C(2)O$_3$ ion coordinate to two Mg atoms,

Fig. 1. Crystal structure of hydromagnesite viewed along the c' axis. Heights of atoms from the $a' - b'$ plane are indicated as percentages of the c' length. Only atoms between $z = 0$ and $\frac{1}{2}$ are shown.

Table 3. *Interatomic distances* (Å) *and bond angles* (°) *with their estimated standard deviations in parentheses*

Mg(1)–OH^{vii}	2·04 (2)	OH^{vii}–Mg(1)–H$_2$O^{ii}	85·6 (8)
Mg(1)–H$_2$O^{ii}	2·16 (2)	OH^{vii}–Mg(1)–O(2)	103·0 (8)
Mg(1)–O(2)	2·07 (2)	OH^{vii}–Mg(1)–O(3)	82·3 (8)
Mg(1)–O(3)	2·07 (2)	OH^{vii}–Mg(1)–O(4^i)	86·3 (8)
Mg(1)–O(4^i)	2·09 (2)	H$_2$O^{ii}–Mg(1)–O(2)	98·1 (7)
Mg(1)–O(4^{ii})	2·15 (2)	H$_2$O^{ii}–Mg(1)–O(4^i)	85·5 (7)
		O(3)—Mg(1)–O(4^{ii})	101·8 (8)
		O(4^i)–Mg(1)–O(4^{ii})	78·3 (7)
Mg(2)–OH^{vii}	2·09 (3)	OH^{vii}–Mg(2)–O(1^i)	91·1 (8)
Mg(2)–O(1^i)	2·02 (3)	O(1^i)–Mg(2)–O(1^v)	95·1 (9)
C(1)—O(1^i)	1·28 (3)	O(1^i)–C(1)—O(1^{iv})	113 (1)
C(1)—O(2)	1·24 (4)	O(1^i)–C(1)—O(2)	123 (1)
C(2)—O(3)	1·26 (4)	O(4^{iv})–C(2)—O(3)	119 (1)
C(2)—O(4^{iv})	1·30 (2)	O(4^{iv})–C(2)—O(4^{iii})	121 (2)
H$_2$O^{ii}–H$_2$O^{vi}	2·84 (3)	H$_2$O^{vi}–H$_2$O^{ii}–H$_2$O^{vii}	116 (1)
H$_2$O^{ii}–H$_2$O^{vii}	3·04 (3)		
X———H$_2$O^{vi}	2·77 (2)	H$_2$O^{vi}–X———O(1^i)	119·6 (6)
X———O(1^i)	3·02 (2)		
(X; 0,0,$\frac{1}{2}$)			

Symmetry code

(i)	x	y	z	(v)	x	y	$\bar{z}$
(ii)	$\frac{1}{2}-x$	$\bar{y}$	$\frac{1}{2}-z$	(vi)	$\frac{1}{2}-x$	$\bar{y}$	$\frac{1}{2}+z$
(iii)	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	(vii)	$\frac{1}{2}-x$	$\frac{1}{2}+y$	z
(iv)	x	$\frac{1}{2}-y$	$\frac{1}{2}-z$				

whereas in the C(1)O$_3$ ion one oxygen atom coordinates to two Mg atoms but the remaining two oxygen atoms coordinate to one Mg atom.

Difference maps based on the final atomic parameters were synthesized in order to examine the deviation of the real structure from the averaged one. The maps verified that the structure obtained was a fairly good approximation to the real structure. Prominent deviations are observed for Mg(2), O(1), and C(1) and for the water molecule. The shifts are approximately restricted to the xz plane.

As already stated, the structure is based on a stack of layers parallel to (100). The layers have mirror planes perpendicular to the c' axis in the averaged structure. The mirror planes are, however, not exact but quasisymmetry planes in the real structure. Accordingly, there is a small difference between the atomic arrangement in a layer and that in its mirror image. Within a single crystal of the mineral the layers should be stacked in a definite way. However, the mirror image of a layer can also be stacked on the preceding layer without introducing large stresses. Thus the observed polysynthetic twinning on (100) can be easily understood from the pseudo-orthorhombic nature and the layer character of the structure.

It is of interest to compare the structure of hydromagnesite with that of nesquehonite, since nesquehonite sluggishly converts to hydromagnesite with liberation of water and CO_2 at room temperature. In the nesquehonite structure, the coordination octahedron around Mg is strongly deformed owing to edge-sharing with a carbonate ion (Stephan & MacGillavry, 1972). The sharing also causes a deformation of the carbonate ion. On the other hand, the MgO$_6$ octahedra share only apices in hydromagnesite, and consequently the deformations are much smaller. This structural difference is probably responsible for the difference between the stabilities of the two minerals.

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