

## A case of polytypism in hydrated oxysalts: the crystal structure of $\text{Mg}_3(\text{PO}_4)_2 \cdot 22 \text{H}_2\text{O-II}$

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**Abstract.**  $\text{Mg}_3(\text{PO}_4)_2 \cdot 22 \text{H}_2\text{O-II}$  crystallizes in space group  $P\bar{1}$ , with  $a = 6.937(3)$ ,  $b = 6.932(3)$ ,  $c = 16.132(5)$  Å,  $\alpha = 82.15(3)$ ,  $\beta = 89.72(3)$ ,  $\gamma = 119.49(3)^\circ$ ,  $Z = 1$ . The structure was solved (direct methods) and refined anisotropically (least squares) to  $R = 0.042$ , using 1826 observed reflections measured on a single-crystal diffractometer ( $\text{MoK}\alpha$  radiation). All hydrogen atoms were located from difference maps and included in the refinement. (001) layers formed by  $\text{Mg}(\text{H}_2\text{O})_6$  and  $\text{PO}_4$  polyhedra and by lattice water molecules are linked by hydrogen bonds and stacked with the  $\dots ABB'A \dots$  scheme. A structure previously studied by other authors has been recognized as a polytype,  $\text{Mg}_3(\text{PO}_4)_2 \cdot 22 \text{H}_2\text{O-I}$ , where the pair of layers  $AB$  is nearly identical as in II, but the  $B'$  layer is oriented differently with respect to  $B$ . The two orientations are related by a mirror pseudo-symmetry of the  $B$  layer. Differences of the hydrogen bonding scheme in the two cases are pointed out.

### Introduction

In the frame of a structural research on hydrogen bonding in crystalline oxysalts, the compound  $\text{Mg}_3(\text{PO}_4)_2 \cdot 22 \text{H}_2\text{O}$  has been considered, as a member of the family of hydrates characterized by a  $z/xn$  ratio (= number of water molecules/number of cations  $\times$  coordination number) greater than one. The following hydrated crystals of this type have been studied structurally till now:  $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$  (epsomite) (Baur, 1964b),  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  (melanterite) (Baur, 1964a),  $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  (Herpin and Sudarsanan, 1965),  $\text{Al}_2(\text{SO}_4)_3 \cdot 17 \text{H}_2\text{O}$  (alunogen) (Menchetti and Sabelli, 1974),  $\text{CrH}(\text{SO}_4)_2 \cdot 7 \text{H}_2\text{O}$  (Gustafsson, Lundgren, and Olovsson, 1977) and  $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  (Hair and Beattie, 1977). All these structures show fully hydrated hexacoordinated cations, without sharing of  $\text{H}_2\text{O}$  molecules between  $\text{M}(\text{H}_2\text{O})_6$  coordination polyhedra; the excess water molecules are

accommodated as “lattice water” hydrogen bonded to the polyhedra and to the oxyanions. This structural type was called “AI” by Wells (1975) in his classification of hydrates; in principle, however, other structural types might be observed in hydrates with  $z/xn > 1$ , e.g. with condensation of  $\text{M}(\text{H}_2\text{O})_n$  polyhedra and more lattice water molecules. A purpose of the present work is to check the observed rule that all the hydrates with stoichiometric excess water crystallize in the AI structural type.

When the present crystal structure had already been solved and refined, the authors learnt of a structural paper on the same type of compound (Schroeder, Mathew, and Brown, 1978). After examining them carefully, it was concluded that the two structures, though partly similar, belonged to different crystal phases of the same compound related by polytypism, since the essential difference was found in the orientation of layers. As distinct symbols cannot be assigned to the two polytypes according to the classification suggested by Bailey (1977), we propose to call  $\text{Mg}_3(\text{PO}_4)_2 \cdot 22 \text{H}_2\text{O}$ -I that studied by Schroeder et al. (1978), and  $\text{Mg}_3(\text{PO}_4)_2 \cdot 22 \text{H}_2\text{O}$ -II that studied in the present work.

### Experimental and analysis of data

The crystals of  $\text{Mg}_3(\text{PO}_4)_2 \cdot 22 \text{H}_2\text{O}$  were obtained by preparing solutions of  $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$  (19.4 g in  $1000 \text{ cm}^3$  of water) and of  $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$  (20.0 g in  $2000 \text{ cm}^3$  of water) and mixing them at  $5^\circ \text{C}$  (de Schulten, 1903). A single crystal with dimensions  $0.24 \times 0.10 \times 0.04 \text{ mm}$ , tabular  $\{001\}$ , was chosen for the measurements on a Philips PW 1100 four-circle automatic diffractometer [ $\lambda(\text{MoK}\alpha) = 0.71069 \text{ \AA}$ , graphite monochromator]. By least-squares refinement of 25 measured  $\theta$  values, the following unit-cell constants were obtained:  $a = 6.937(3)$ ,  $b = 6.932(3)$ ,  $c = 16.132(5) \text{ \AA}$ ,  $\alpha = 82.15(3)$ ,  $\beta = 89.72(3)$ ,  $\gamma = 119.49(3)^\circ$ . The symmetry is then triclinic, and not monoclinic as reported in an old paper (Haushofer, 1882) on the basis of morphological data. Other physical data are:  $V = 666.6 \text{ \AA}^3$ ,  $M = 659.206$ ,  $Z = 1$ ,  $D_c = 1.642 \text{ g cm}^{-3}$ ,  $D_m = 1.640 \text{ g cm}^{-3}$  (de Schulten, 1903), space group  $P\bar{1}$ ,  $F(000) = 350$ ,  $\mu(\text{MoK}\alpha) = 3.35 \text{ cm}^{-1}$ .

A powder diffraction pattern was obtained from a Guinier camera (4 mm =  $1^\circ \theta$ ,  $\text{CuK}\alpha$  radiation) and indexed with the reported cell constants, taking into account the single crystal intensities (Table 1).

The intensities of 2345 reflections with  $\theta \leq 25^\circ$  were measured on the same single-crystal used for the cell determination, using the following conditions:  $\omega$  scan,  $\Delta\omega = 1.5^\circ$ , scanning speed  $0.025^\circ \text{ s}^{-1}$ , background time = (scan time/2)  $(I_{\text{bkg}}/I_{\text{pk}})^{1/2}$ , attenuating filter inserted for intensities higher than  $60000 \text{ counts s}^{-1}$ , three reference reflections. A final set of 1826 independent observations was obtained, by removing the reflections with  $I < 2\sigma(I)$ .

**Table 1.** Powder pattern of  $\text{Mg}_3(\text{PO}_4)_2 \cdot 22 \text{H}_2\text{O}$ -II. Observed and calculated  $d$  spacings, indices and intensities (on an arbitrary scale) of the reflexions

$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$I_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$I_{\text{obs}}$
7.97	7.96	002	50	2.901	2.899	$\bar{2}13$	20
6.03	6.02	100	35	2.865	2.870	$\bar{2}22$	100
5.75	5.74	$\bar{1}11$	10	2.846	2.847	$0\bar{2}1$	90
5.47	{ 5.48 5.46	{ 101 $\bar{1}\bar{1}1$	10	2.795	{ 2.795 2.795	{ $\bar{1}24$ 023	10
5.32	{ 5.31 5.31	{ 003 011	35	2.658	{ 2.654 2.654	{ 006 022	45
4.96	4.96	112	40	2.523	{ 2.527 2.521	{ 115 $\bar{2}\bar{2}3$	15
4.63	{ 4.62 4.61	{ 102 $\bar{1}\bar{1}2$	5	2.309	2.309	$\bar{2}04$	20
4.12	4.13	113	40	2.246	{ 2.248 2.247	{ 017 $\bar{1}30$	10
3.985	3.981	004	15	2.027	2.028	$\bar{1}27$	10
3.467	3.468	$\bar{2}10$	10	1.802	1.803	$0\bar{1}8$	10
3.266	3.266	$\bar{1}\bar{2}1$	5	1.731	{ 1.733 1.732	{ $\bar{1}19$ $\bar{2}41$	20
3.186	{ 3.185 3.184	{ 005 $\bar{2}\bar{1}2$	40	1.415	{ 1.417 1.413	{ $\bar{4}03$ $\bar{3}29$	10
3.005	{ 3.007 3.002	{ $\bar{1}\bar{2}2$ $\bar{2}01$	10				
2.905	2.905	$\bar{1}15$	15				

**Table 2.** Atomic fractional coordinates of the polytypes II (this work) and I (Schroeder, Mathew, and Brown, 1978) of  $\text{Mg}_3(\text{PO}_4)_2 \cdot 22 \text{H}_2\text{O}$ , for non-hydrogen atoms

	II			I		
	$x$	$y$	$z$	$x$	$y$	$z$
P	0.0031(2)	-0.0368(2)	0.24028(6)	0.0953	0.0530	0.2408
Mg(1)	0	$\frac{1}{2}$	0	0	$\frac{1}{2}$	0
Mg(2)	0.6483(2)	0.2510(2)	0.34371(7)	0.7832	0.3871	0.3431
O(1)	-0.0261(4)	-0.0707(4)	0.3369(1)	0.0995	0.0519	0.3378
O(2)	0.1470(4)	0.2165(4)	0.2077(2)	0.2136	0.2940	0.2102
O(3)	0.1173(4)	-0.1628(4)	0.2137(2)	0.2149	-0.0696	0.2139
O(4)	-0.2263(4)	-0.1265(4)	0.2056(2)	-0.1492	-0.0641	0.2040
W(1)	-0.2235(6)	0.3162(6)	0.1055(2)	-0.1823	0.3651	0.1050
W(2)	0.1703(6)	0.7771(6)	0.0582(2)	0.1937	0.8023	0.0577
W(3)	0.2045(6)	0.3862(6)	0.0472(2)	0.2232	0.4040	0.0496
W(4)	0.7473(6)	0.0684(6)	0.4254(2)	0.9256	0.2476	0.4261
W(5)	0.7613(5)	0.5082(5)	0.4116(2)	0.8728	0.6745	0.4110
W(6)	0.9686(5)	0.4124(5)	0.2855(2)	1.0903	0.5440	0.2920
W(7)	0.5721(5)	0.4165(5)	0.2404(2)	0.6553	0.5012	0.2405
W(8)	0.3408(4)	0.1484(5)	0.4078(2)	0.5056	0.2634	0.4098
W(9)	0.5020(5)	-0.0328(5)	0.2855(2)	0.6339	0.0924	0.2799
W(10)	0.6450(6)	0.8168(6)	0.0488(2)	0.6670	0.8383	0.0460
W(11)	0.2786(7)	0.5280(6)	0.4150(2)	0.4950	0.7496	0.4163

**Table 3.** Atomic fractional coordinates of hydrogen atoms of  $\text{Mg}_3(\text{PO}_4)_2 \cdot 22 \text{H}_2\text{O-II}$ 

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	−0.278(6)	0.351(6)	0.134(2)
H(2)	−0.244(11)	0.195(11)	0.130(4)
H(3)	0.130(9)	0.790(9)	0.107(4)
H(4)	0.237(6)	0.895(6)	0.033(2)
H(5)	0.190(8)	0.328(8)	0.098(3)
H(6)	0.249(7)	0.324(7)	0.022(2)
H(7)	0.820(6)	0.018(6)	0.402(2)
H(8)	0.717(6)	0.021(6)	0.470(2)
H(9)	0.850(9)	0.655(9)	0.388(3)
H(10)	0.762(6)	0.504(6)	0.459(2)
H(11)	1.000(6)	0.524(6)	0.264(2)
H(12)	1.038(8)	0.352(8)	0.257(3)
H(13)	0.432(8)	0.356(8)	0.232(3)
H(14)	0.629(6)	0.552(6)	0.237(2)
H(15)	0.207(7)	0.059(7)	0.384(3)
H(16)	0.332(6)	0.260(6)	0.412(2)
H(17)	0.588(6)	−0.067(6)	0.256(2)
H(18)	0.384(8)	−0.068(7)	0.259(3)
H(19)	0.519(8)	0.747(8)	0.055(3)
H(20)	0.692(10)	0.843(9)	0.095(3)
H(21)	0.361(7)	0.655(7)	0.393(3)
H(22)	0.174(8)	0.489(8)	0.390(3)

**Table 4.** Vibrational parameters ( $\text{Å}^2$ ), with significant figures of the e.s.d.'s in parentheses

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
P	1.22(4)	1.34(4)	1.27(4)	0.65(3)	−0.12(3)	−0.28(3)
Mg(1)	2.13(8)	1.98(7)	1.26(7)	1.03(6)	−0.15(6)	−0.23(6)
Mg(2)	1.52(5)	1.43(5)	1.37(5)	0.70(4)	−0.05(4)	−0.16(4)
O(1)	2.0(1)	1.4(1)	1.7(1)	0.71(9)	0.00(8)	−0.01(8)
O(2)	1.7(1)	2.7(1)	2.2(1)	1.09(9)	−0.41(9)	−0.88(9)
O(3)	1.9(1)	1.8(1)	1.9(1)	1.10(9)	−0.02(8)	−0.41(8)
O(4)	1.9(1)	1.7(1)	1.4(1)	0.76(9)	−0.14(8)	−0.30(8)
W(1)	5.2(2)	1.9(1)	1.8(1)	1.1(1)	0.4(1)	−0.3(1)
W(2)	4.7(2)	4.9(2)	1.9(1)	3.9(2)	−0.1(1)	0.0(1)
W(3)	3.8(2)	3.2(2)	2.1(1)	1.7(1)	0.8(1)	−0.1(1)
W(4)	1.8(1)	2.8(1)	3.2(1)	1.3(1)	−0.5(1)	−1.4(1)
W(5)	1.8(1)	1.9(1)	1.8(1)	0.9(1)	0.13(8)	−0.24(9)
W(6)	3.8(2)	1.8(1)	1.4(1)	0.6(1)	0.0(1)	−0.4(1)
W(7)	1.7(1)	1.8(1)	2.2(1)	0.6(1)	−0.38(9)	0.13(9)
W(8)	2.1(1)	1.7(1)	2.4(1)	1.0(1)	0.40(9)	0.2(1)
W(9)	4.9(2)	4.7(2)	1.7(1)	4.0(2)	0.6(1)	0.6(1)
W(10)	2.6(2)	3.3(1)	2.3(1)	1.3(1)	−0.3(1)	−0.3(1)
W(11)	3.1(2)	3.1(2)	2.1(1)	1.3(1)	−0.7(1)	−0.4(1)

The structure was solved by direct methods, using the program Multan (Germain, Main, and Woolfson, 1971). Statistical tests on the intensities showed clearly the presence of the symmetry centre. All the atoms of the asymmetric unit appeared on the E-map, with one Mg atom on the symmetry centre. The isotropic refinement (least-squares) converged to  $R = 0.083$ ; by refining anisotropic thermal factors,  $R = 0.065$  was obtained. At this stage, a Fourier difference map revealed all the hydrogen atoms, and a full matrix cycle (unitary weights) with isotropic thermal factors for hydrogen atoms led to  $R = 0.042$ . The final atomic fractional coordinates are reported in Tables 2 and 3, and the anisotropic thermal parameters coefficients of the expression

$$\exp\left(-\frac{1}{4}\sum_{i=1}^3\sum_{j=1}^3B_{ij}h_ih_ja_i^*a_j^*\right)$$

in Table 4. The main calculations were performed with the Shelx package of crystallographic programs (Sheldrick, 1976), using the scattering factors for neutral atoms reported in the International Tables for X-ray Crystallography (1974). Copies of the list of observed and calculated structure factors may be obtained from the authors.

## Discussion

### *Description of the structure and hydrogen bonding*

The crystal structure is built up by coordination octahedra Mg(H<sub>2</sub>O)<sub>6</sub> and tetrahedra PO<sub>4</sub> and by lattice water molecules, all held together by hydrogen bonding only. Distances and angles of coordination and hydrogen bonds are reported in Tables 5 and 6, respectively. The polyhedra are arranged on (001) layers which are stacked according to the . . . *ABB'A* . . . scheme (Fig. 1). The *A* layer is formed by the Mg(1)<sup>1</sup> octahedra and by the lattice water molecules W(10) and W(10'), and is centrosymmetric; the *B* layer contains the Mg(2) octahedra, the PO<sub>4</sub> tetrahedra (at a slightly lower level) and the lattice water W(11); the *B'* layer is centrosymmetrically related to *B*. All three layers are shown in Figure 2. Because of the values of *a*, *b* and  $\gamma$ , the polyhedra are arranged on each layer with a rough hexagonal pseudo-symmetry: but, to a better approximation, the *B* and *B'* layers are characterized by a pseudo-mirror plane parallel to  $[\bar{1}10]$  and to  $\mathbf{c}^*$ .

Internal cohesion of the *A* layer is provided by the two hydrogen bonds which W(2') and W(3') donate to W(10), and by the bifurcated hydrogen bond donated by W(10) to W(2) and W(3) (and also by the centrosymmetri-

<sup>1</sup> A single figure in parentheses denotes an atom of the asymmetric unit; primed figures mean the centrosymmetrically related position  $\bar{x}, \bar{y}, \bar{z}$ . Roman numerals represent the following translations: I, +**b**; II, +**a**+**b**; III, +**a**; IV, -**a**; V, +**a**+**c**; VI, +**a**+**b**+**c**; VII, **a**+2**b**; VIII, +**b**+**c**.

**Table 5.** Interatomic distances, O–P–O and W–Mg–W angles in the coordination polyhedra

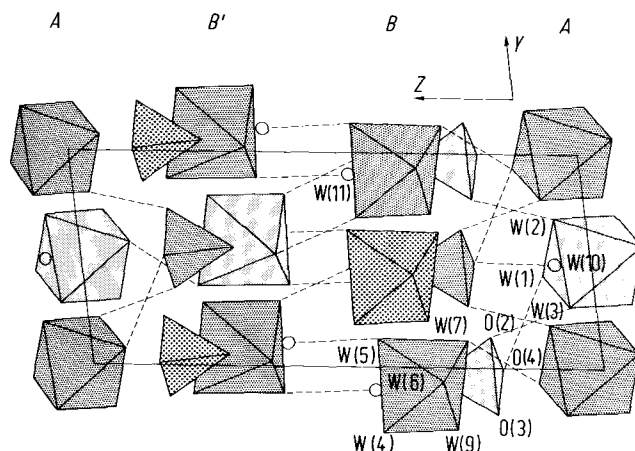
P–O(1)	1.541(2) Å	O(1) ... O(2)	2.497(3) Å	108.3(2)°
P–O(2)	1.540(3)	O(1) ... O(3)	2.509(4)	109.4(2)
P–O(3)	1.534(3)	O(1) ... O(4)	2.506(4)	109.1(2)
P–O(4)	1.536(3)	O(2) ... O(3)	2.521(4)	110.2(2)
Average	1.538	O(2) ... O(4)	2.514(4)	109.6(2)
		O(3) ... O(4)	2.518(4)	110.2(2)
		Average	2.511	109.5
Mg(1)–W(1)	2.089(3) Å	W(1) ... W(2)	2.996(6) Å	92.5(1)°
Mg(1)–W(2)	2.058(4)	W(1) ... W(3)	2.893(6)	88.9(2)
Mg(1)–W(3)	2.041(4)	W(2) ... W(3)	2.863(6)	88.6(2)
Average	2.063	W(1) ... W(2) <sup>j</sup>	2.868(5)	87.5(1)
		W(1) ... W(3) <sup>j</sup>	2.947(5)	91.1(2)
		W(2) ... W(3) <sup>j</sup>	2.933(5)	91.4(2)
		Average	2.917	90.0
Mg(2)–W(4)	2.054(4) Å	W(4) ... W(5)	2.979(5) Å	93.4(2)°
Mg(2)–W(5)	2.039(3)	W(4) ... W(6)	2.833(5)	86.6(2)
Mg(2)–W(6)	2.077(3)	W(4) ... W(8)	3.138(5)	98.1(1)
Mg(2)–W(7)	2.112(3)	W(4) ... W(9)	2.788(5)	84.8(1)
Mg(2)–W(8)	2.100(3)	W(5) ... W(6)	2.816(5)	86.3(1)
Mg(2)–W(9)	2.089(3)	W(5) ... W(7)	3.074(4)	95.6(1)
Average	2.077	W(5) ... W(8)	2.759(5)	83.6(1)
		W(6) ... W(7)	2.861(5)	86.2(1)
		W(6) ... W(9)	3.189(6)	100.1(1)
		W(7) ... W(8)	2.996(4)	90.7(1)
		W(7) ... W(9)	2.890(5)	87.2(1)
		W(8) ... W(9)	2.960(4)	90.1(1)
		Average	2.940	90.2
		W(4) ... W(7)		168.1(1)
		W(5) ... W(9)		173.2(1)
		W(6) ... W(8)		169.1(2)

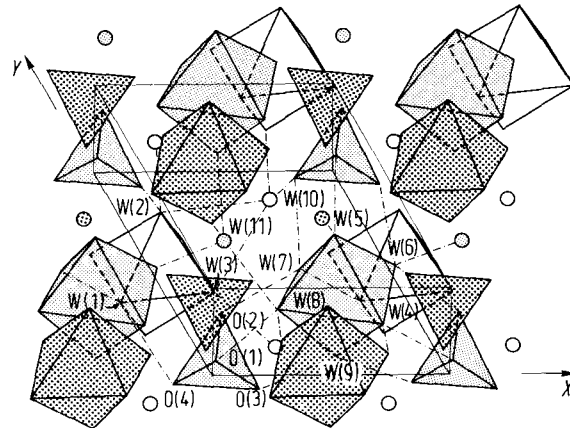
cally related bonds). The peculiar configuration of the last bond is proved by H(19) being nearly equidistant from W(2) and W(3) (Table 6), and by the small values of the angles  $\angle \text{W}(2)–\text{W}(10)–\text{W}(3)$  and  $\angle \text{W}(2)–\text{H}(19)–\text{W}(3)$ , which are 54.8(1) and 71(1)° respectively. The other hydrogen bonds donated by W(1), W(2), W(3) and W(10) link the *A* and *B* layers together; in particular the W(1) ... O(4) contact (3.250 Å long) is at about the distance limit for a significant interaction, even if the bond angles  $\angle \text{W}(1)–\text{H}(2)–\text{O}(4)$  and  $\angle \text{W}(7)^{\text{IV}}–\text{W}(1)–\text{O}(4)$  are quite regular for a normal hydrogen bond.

Within the *B* layer, nine hydrogen bonds donated by the six water molecules of the Mg(2) octahedron to the oxygen atoms of the PO<sub>4</sub> tetrahedron are present, and also the hydrogen bonds which the lattice water

**Table 6.** Interatomic distances and angles in the hydrogen bonds

<i>D</i>	<i>H</i>	<i>A</i>	<i>DA</i>	<i>ADA'</i>	<i>DH</i>	<i>HA</i>	<i>DHA</i>	<i>HDH'</i>
W(1)	H(1) ... W(7) <sup>IV</sup>		2.929(4) Å	99.0(1)°	0.73(4) Å	2.21(4) Å	169(4)°	104(6)°
	H(2) ... O(4)		3.258(5)					
W(2)	H(3) ... O(3) <sup>I</sup>		2.651(4)	109.9(2)	0.87(6)	1.80(6)	166(6)	108(5)
	H(4) ... W(10) <sup>VIII</sup>		2.765(5)					
W(3)	H(5) ... O(2)		2.635(4)	111.8(2)	0.85(5)	1.80(5)	175(5)	105(5)
	H(6) ... W(10) <sup>VI</sup>		2.738(5)					
W(4)	H(7) ... O(1) <sup>III</sup>		2.699(5)	109.4(2)	0.86(4)	1.84(4)	172(4)	111(4)
	H(8) ... W(8) <sup>V</sup>		2.802(4)					
W(5)	H(9) ... O(1) <sup>II</sup>		2.633(4)	112.2(2)	0.92(6)	1.73(6)	170(6)	107(5)
	H(10) ... W(11) <sup>VI</sup>		2.775(4)					
W(6)	H(11) ... O(3) <sup>III</sup>		2.673(4)	112.2(1)	0.72(4)	1.95(4)	173(4)	110(5)
	H(12) ... O(2) <sup>III</sup>		2.657(4)					
W(7)	H(13) ... O(2)		2.661(4)	112.6(1)	0.87(6)	1.80(6)	174(5)	111(5)
	H(14) ... O(4) <sup>II</sup>		2.730(5)					
W(8)	H(15) ... O(1)		2.606(4)	93.8(1)	0.95(5)	1.66(5)	174(5)	102(4)
	H(16) ... W(11)		2.885(6)					
W(9)	H(17) ... O(4) <sup>III</sup>		2.655(4)	112.3(1)	0.90(4)	1.76(4)	174(4)	106(4)
	H(18) ... O(3)		2.688(4)					
W(10)	H(19) ... W(2)		3.167(6)	103.8(2)	0.76(5)	2.53(5)	143(5)	108(6)
	H(20) ... W(3)		3.048(6)	112.4(1)				
	H(20) ... O(4) <sup>II</sup>		2.702(4)					
W(11)	H(21) ... W(9) <sup>I</sup>		3.102(5)	78.5(1)	0.80(5)	2.36(5)	156(4)	105(5)
	H(22) ... W(6) <sup>IV</sup>		2.905(5)					

**Fig. 1.** Projection of the structure of  $\text{Mg}_3(\text{PO}_4)_2 \cdot 22 \text{H}_2\text{O-II}$  onto the (100) plane. Coordination polyhedra, lattice water molecules (circles) and inter-layer hydrogen bonds (dashed lines) are emphasized



**Fig. 2.** Projection of the structure of  $Mg_3(PO_4)_2 \cdot 22 H_2O$ -II onto the (001) plane. Only hydrogen bonds donated by water molecules of the asymmetric unit (dashed-dotted lines) are shown

W(11) donates to W(6) and W(9) and receives from W(8). The layers  $B$  and  $B'$  are tied to each other by the two hydrogen bonds  $W(4) \dots W(8')^V$  and  $W(5) \dots W(11')^{VI}$ , and by those centrosymmetrically related; then every  $Mg(2)$  octahedron of layer  $B$  is linked to its equivalent one of layer  $B'$  by the pair of bonds  $W(4) \dots W(8')^V$  and  $W(4')^V \dots W(8)$ .

A key role is played by the two lattice water molecules in determining the stability of the structure, since they provide both the internal cohesion of the  $A$  and  $B$  layers, and the  $A \dots B$  and  $B \dots B'$  linking. W(10) is tied to three water molecules and an oxygen atom, whereas W(11) forms all its four hydrogen bonds with  $H_2O$  molecules, and behaves then as "ice-like" water. However, some distortion is observed with respect to the bonding configuration in ice phases stable at room pressure, since the two hydrogen bonds donated by W(11) are substantially longer than the values 2.75–2.80 Å typical of those cases (Franks, 1972), and besides they show a very small  $A \dots D \dots A'$  angle ( $78.5^\circ$ ). This unusual value cannot be accounted for by the acceptors forming an edge of coordination polyhedron, as it occurs in other cases (Catti, 1979).

Hydrogen bonds of the type  $W \dots O$  range from 2.606 to 2.730 Å of length [with the exception of  $W(1) \dots O(4)$ ] and are then short and strong, while those of type  $W \dots W$  are longer (2.738–3.176 Å). The bonding between  $B$  and  $B'$  layers seems to be a little weaker than between  $A$  and  $B$ , as it is provided by medium-strength  $W \dots W$  bonds (2.775 and 2.802 Å).

#### *Comparison with the structure of $Mg_3(PO_4)_2 \cdot 22 H_2O$ -I*

In order to compare the structures of phase II and I, the unit cell of the latter (Schroeder, Mathew and Brown, 1978) should be transformed according to



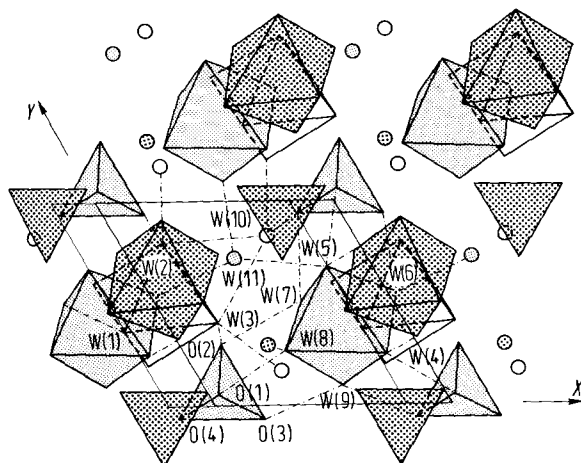


Fig. 3. Projection of the structure of  $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ -I onto the (001) plane

the matrix  $100/\bar{0}\bar{1}0/00\bar{1}$ , obtaining the following cell constants:  $a = 6.902$ ,  $b = 6.961$ ,  $c = 15.982 \text{ \AA}$ ,  $\alpha = 87.66^\circ$ ,  $\beta = 94.78^\circ$ ,  $\gamma = 119.19^\circ$ . A close similarity with the cell II for  $a$ ,  $b$ , and  $\gamma$ , but substantial differences for  $c$ ,  $\alpha$  and  $\beta$  are observed. Taking into account that the  $d_{001}$  values ( $15.926 \text{ \AA}$  for I and  $15.925 \text{ \AA}$  for II) are the same, the two lattices can be thought to differ by a sliding of the (001) planes which causes  $\alpha$ ,  $\beta$  and  $c$  to change while the interplanar distance is kept unvaried. By transforming the atomic fractional coordinates of phase I (Schroeder et al., 1978) according to  $x' = x$ ,  $y' = \frac{1}{2} - y$ ,  $z' = -z$ , a qualitative correspondence is obtained with the asymmetric unit of phase II, with following scheme: P→P, Mg(1)→Mg(1), Mg(2')→Mg(2), O(1)→O(1), O(2)→O(2), O(3)→O(3), O(4')→O(4), O(W1')→W(4), O(W2')→W(5), O(W3)→W(6), O(W4)→W(1), O(W5)→W(2), O(W6)→W(3), O(W7')→W(7), O(W8')→W(10), O(W9')→W(9), O(W10')→W(8), O(W11')→W(11). The transformed atomic coordinates reported in Table 2 are close to the corresponding ones of phase II, using the same atomic symbols. Very similar  $z$  values, but fairly different  $x$  and  $y$  coordinates are shown by atoms of the two asymmetric units; this discrepancy is related to the differences in the  $\alpha$  and  $\beta$  angles, so that with respect to  $(\mathbf{a}, \mathbf{b}, \mathbf{c}^*)$  reference systems the corresponding atoms would show quite similar  $x$  and  $y$  values as well. Both phases are then characterized by practically isostructural double layers  $AB$  (for small differences in the  $B$  layers, cf. below); but because of the different  $\alpha$  and  $\beta$  angles the symmetry centres at  $z = \frac{1}{2}$  are rather shifted in the two cases, and the atoms of the upper layer  $B'$  take on quite different positions in I and II. This appears clearly by comparing Figures 2 and 3. The  $B'$ (I) and  $B'$ (II) layers can be thought to be related either by the pseudo-mirror plane parallel to  $[110]$  and  $\mathbf{c}^*$  and passing through the P atom, or by the shift vector

[0.400.400]. Using the (**a**, **b**, **c**\*) reference system with the origin on P, corresponding atomic coordinates of the two  $B'$  layers are transformed according to the relationships  $x_{\text{II}} = -y_{\text{I}}$ ,  $y_{\text{II}} = -x_{\text{I}}$ ,  $z_{\text{II}} = z_{\text{I}}$ , or  $x_{\text{II}} = x_{\text{I}} + 0.40$ ,  $y_{\text{II}} = y_{\text{I}} + 0.40$ ,  $z_{\text{II}} = z_{\text{I}}$ .

Slightly different mirror-related configurations, however, are observed also for the  $B$  layers. As for the P tetrahedron, the pseudo-mirror operation, which transforms the II polytype into I, exchanges O(2) with O(4), causing the P–O(4) bond to lengthen from 1.536 to 1.546 Å; also the W(1) . . . O(4) contact lengthens from 3.258 to 3.421 Å, which becomes too long a distance for a hydrogen bond. In the Mg(2) octahedron the largest deviation from  $m$  symmetry is observed for the face W(4)–W(5)–W(8), so that by the II → I transformation the crystal-chemical roles of W(5) and W(8) are exchanged. The distances Mg(2)–W(5), Mg(2)–W(8), W(4)–W(5) and W(4)–W(8) become 2.103, 2.052, 3.163 and 2.943 Å, and the angles W(4)–Mg(2)–W(5) and W(4)–Mg(2)–W(8) change into 98.7 and 91.2°. Besides, in the polytype I the three hydrogen bonds donated by each of W(4), W(5) and W(8) to as many water molecules become W(4) . . . W(5')<sup>VIII</sup>, W(5) . . . W(11) and W(8) . . . W(11')<sup>VI</sup> [2.790(6), 2.907(8) and 2.776(6) Å long, respectively]. The second of these bonds replaces W(8) . . . W(11), forming the only substantial difference between the  $B$  layers in the two polytypes. The other two bonds substitute W(4) . . . W(8')<sup>V</sup> and W(5) . . . W(11')<sup>VI</sup> of polytype II in the linking of  $B$  and  $B'$  layers.

### Conclusions

The structures of the two polytypes of  $\text{Mg}_3(\text{PO}_4)_2 \cdot 22 \text{H}_2\text{O}$  confirm two important crystal-chemical observations: (i)  $\text{Mg}^{2+}$  and other hexacoordinated cations of similar ionic radius prefer the  $\text{M}(\text{H}_2\text{O})_6$  configuration, when there are enough water molecules for all cations; (ii) the fully hydrated coordination polyhedra are normally isolated with no sharing between vertices, edges of faces, both when  $z/xn > 1$  (AI structural type, with excess lattice water) and when  $z/xn = 1$  (AII type, no lattice water). In both AI and AII structures the polyhedra are usually arranged on layers, which often show a pseudo-hexagonal symmetry as in the salt studied here: cf.  $\text{Zn}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$  (Ghosh and Ray, 1977) and  $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$  (Catti, Ferraris, and Ivaldi, 1978); in several cases the layer symmetry is exactly hexagonal, as in  $\text{MgSO}_3 \cdot 6 \text{H}_2\text{O}$  (Flack, 1973),  $\text{Sm}(\text{BrO}_3)_3 \cdot 9 \text{H}_2\text{O}$  (Sikka, 1969),  $\text{NaAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$  (Cromer, Kay, and Larson, 1967),  $\text{Al}(\text{IO}_3)_2\text{NO}_3 \cdot 6 \text{H}_2\text{O}$  (Cradwick and de Endredy, 1975) and  $\text{AlH}_2(\text{IO}_3)_5 \cdot 6 \text{H}_2\text{O}$  (Cradwick and de Endredy, 1977). Probably, the hydrogen bonding configuration is optimized by this type of polyhedra packing.

Since they show layer structures so frequently, the hydrates of this class are likely to be affected by polytypism more commonly than is realized. In the

case of  $\text{Mg}_3(\text{PO}_4)_2 \cdot 22 \text{H}_2\text{O}$  this was discovered by chance, but more general results could be obtained by systematic studies. The difficult point is to ascertain what is the driving force for selective formation of polytypes, i.e. whether the kind of chemical preparation, or the thermodynamic conditions, or just the crystal growth mechanism.

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## References

- Bailey, S. W.: Report of the I.M.A. – I.U.Cr. Joint Committee on Nomenclature. *Am. Mineral.* **62**, 411–415 (1977)
- Baur, W. H.: On the crystal chemistry of salt hydrates. III. The determination of the crystal structure of  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  (melanterite). *Acta Crystallogr.* **17**, 1167–1174 (1964)
- Baur, W. H.: On the crystal chemistry of salt hydrates. IV. The refinement of the crystal structure of  $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$  (epsomite). *Acta Crystallogr.* **17**, 1361–1369 (1964)
- Catti, M.: Pseudo-symmetry and hydrogen bonding in the crystal structure of  $\text{NaH}_2\text{PO}_2 \cdot \frac{4}{5} \text{H}_2\text{O}$ . *Acta Crystallogr.* **B35**, 1041–1046 (1979)
- Catti, M., Ferraris, G., Ivaldi, G.: Disorder of  $\text{HPO}_4^{2-}$  and of hydrogen bonds in the structure of  $\beta\text{-Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$ . *Acta Crystallogr.* **B34**, 369–373 (1978)
- Cradwick, P. D., de Endredy, A. S.: Crystal structure of aluminium iodate nitrate hexahydrate. *J. Chem. Soc. (Dalton Trans.)* **19**, 1926–1929 (1975)
- Cradwick, P. D., de Endredy, A. S.: Crystal structure of aluminium iodate-hydrogen iodate-water (1/1/6) and preparation of anhydrous aluminium iodate. *J. Chem. Soc. (Dalton)*, 146–149 (1977)
- Cromer, D. T., Kay, M. L., Larson, A. C.: Refinement of the alum structures. II. X-ray and neutron diffraction of  $\text{NaAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ ,  $\gamma$  alum. *Acta Crystallogr.* **22**, 182–187 (1967)
- de Schulten, M. A.: Recherches sur le phosphate et l'arséniate trimagnésien. Reproduction artificielle de la bobierite et de la hoernésite. *Bull. Soc. fr. Minéral.* **5**, 81–86 (1903)
- Flack, H.: Etude de la structure cristalline du sulfite de magnésium hexahydraté,  $\text{MgSO}_3 \cdot 6 \text{H}_2\text{O}$ . *Acta Crystallogr.* **B29**, 656–658 (1973)
- Franks, F.: The properties of ice. In: *Water, a comprehensive treatise* (Ed. F. Franks), vol. 1, p. 118–123. New York: Plenum Press 1972
- Germain, G., Main, P., Woolfson, M. M.: The application of phase relationships to complex structures III. The optimum use of phase relationships. *Acta Crystallogr.* **A27**, 368–376 (1971)
- Ghosh, M., Ray, S.: Twinning and disorder in zinc perchlorate hexahydrate crystals. *Z. Kristallogr.* **145**, 146–154 (1977)
- Gustafsson, T., Lundgren, J. O., Olovsson, I.: Hydrogen bond studies. CXVII. The crystal structure of  $\text{CrH}(\text{SO}_4)_2 \cdot 7 \text{H}_2\text{O}$ . *Acta Crystallogr.* **B33**, 2373–2376 (1977)
- Hair, N. J., Beattie, J. K.: Structure of hexaaquairon(III) nitrate trihydrate. Comparison of iron(II) and iron(III) bond lengths in high-spin octahedral environments. *Inorg. Chem.* **16**, 245–250 (1977)
- Haushofer, K.: Kristallographische Untersuchungen. *Z. Kristallogr.* **6**, 113–141 (1882)
- Herpin, P., Sudarsanan, K.: Structure cristalline du nitrate d'aluminium hydraté. *Bull. Soc. fr. Minéral. Cristallogr.* **88**, 595–601 (1965)
- International Tables for X-ray Crystallography. Vol. IV. Birmingham: Kynoch Press 1974
- Menchetti, S., Sabelli, C.: Alunogen: its structure and twinning. *Tschermaks Min. Petr. Mitt.* **21**, 164–178 (1974)

- Schroeder, L. W., Mathew, M., Brown, W. E.:  $XO_4^-$  ion hydration. The crystal structure of  $Mg_3(PO_4)_2 \cdot 22 H_2O$ . *J. Phys. Chem.* **82**, 2335–2340 (1978)
- Sheldrick, G. M.: SHELX 76. Program for crystal structure determination. England: Univ. of Cambridge 1976
- Sikka, S. K.: The use of neutron resonance scattering in the structure determination of  $Sm(BrO_3)_3 \cdot 9 H_2O$ . *Acta Crystallogr.* **A25**, 621–626 (1969)
- Wells, A. F.: *Structural Inorganic Chemistry*, 4th Ed., p. 548–554. Oxford: Clarendon Press 1975