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The crystal structure of β-Mg_2PO_4OH, a synthetic hydroxyl analogue of wagnerite

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β-Mg_2PO_4OH / *Crystal structure / Hydrogen bonding / IR spectrum / Cell parameters for the series* Mg_2PO_4F *(wagnerite)* – β-Mg_2PO_4OH

Abstract. The crystal structure of β-Mg_2PO_4OH ($P2_1/c$, $a = 9.656(3)$, $b = 12.859(3)$, $c = 12.069(4)$ Å, $\beta = 108.49(3)°$, $Z = 16$) has been refined isotropically to a final R-value of 0.052 for 1863 high-angle reflections. Fairly regular PO_4 tetrahedra, distorted *cis*-$MgO_4(OH)_2$ octahedra, and distorted $MgO_4(OH)$ trigonal bipyramids are sharing either edges or vertices to build up a complex three-dimensional network. The variation in cell parameters for the solid-solution series $Mg_2PO_4F - Mg_2PO_4OH$ with wagnerite structure is shown graphically. There are indications of preferred substitution of OH for F in the two 'largest' F/OH sites. Low valence sums in the bond-strength calculation are correlated with long Mg–O distances. Hydrogen bonding is relatively weak with strongly bent $O-H\cdots O$ bonds. The infra-red spectrum is briefly discussed.

Introduction

Hydrothermal syntheses in the system $Mg_2PO_4F - Mg_2PO_4OH$ by the first author (essentially unpublished) have revealed the existence of five polymorphs of the compound Mg_2PO_4OH. A brief summary of the experimental work was published by Raade (1980), and the phase diagram for Mg_2PO_4OH is presented in the preceding paper (Raade and Rømming, 1986). Two of these phases were originally described as minerals, namely althausite, δ-Mg_2PO_4OH (Raade and Tysseland, 1975; Raade, 1979) and holtedahlite, γ-Mg_2PO_4OH (Raade and Mladeck, 1979). The crystal structure of natural althausite was reported by Rømming and Raade (1980). The accompanying paper by Raade and Rømming (1986) describes the crystal structure of the synthetic high-temperature ε-phase and gives powder data for the synthetic low-temperature α-phase, which is isostructural with the libethenite group of minerals. Attempts to determine the structure of holtedahlite have failed for both natural and synthetic material, probably because of submicroscopic twinning.

Mg_2PO_4F was encountered only as the wagnerite structure modification over the investigated range of 250 – 750 °C and 1 – 7 kbar. The hydroxyl analogue of wagnerite, β-Mg_2PO_4OH, was synthesized at 5.5 kbar, 350 °C. Being obtained in only one hydrothermal run, the stability field of the β-phase is not known, except that it is a low-temperature, high-pressure phase relative to the four others (Fig. 1 in Raade and Rømming, 1986).

Natural wagnerite is normally close to the F end-member in composition. Recently, more hydroxyl-rich wagnerites were described by Novák and Povondra (1984) and Irouschek and Armbruster (1984). We can confirm the suggestion made by the two former authors, that there exists a series between wagnerite and its hydroxyl analogue.

The crystal structure of wagnerite from the type locality at Werfen, Austria, was solved by Coda et al. (1967). Crystals of our synthetic hydroxyl analogue were well suited for single-crystal work, and the result of the structure determination is presented in this paper.

X-ray powder data

Powder diffraction data for natural wagnerites are given in a number of papers (Henriques, 1956; Finko, 1962; Staněk, 1965; Sheridan et al., 1976; Propach, 1976). A calculated pattern based on the structure determination of Coda et al. (1967) together with observed data for a sample from Colorado were tabulated by Sheridan et al. (1976). However, we find that except for the strongest reflections, there is poor agreement between calculated and observed intensities. The method of calculation or the computer program employed is not stated. We have calculated a new set of intensities with the program LAZY PULVERIX by Yvon et al. (1977), and find an excellent agreement with those observed by Sheridan et al. (1976). Calculated powder diffraction data for β-Mg_2PO_4OH for the case of a Guinier-de Wolff camera and Fe$K\alpha_1$ radiation, using the same program, are in good agreement with the visually estimated intensities. A table of these powder data has been deposited.[1]

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[1] Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 51379, the names of the authors and the title of the paper.

Table 1. Cell parameters refined from powder data for the series $Mg_2PO_4F-Mg_2PO_4OH$ with wagnerite structure.

OH:F	n	a(Å)	b(Å)	c(Å)	β(°)	V(Å^3)
0:1	3	9.641(3)	12.657(6)	11.918(2)	108.23(3)	1381(1)
1:3	3	9.653(3)	12.699(5)	11.959(11)	108.33(2)	1392(2)
1:1	3	9.656(3)	12.757(4)	12.002(7)	108.37(4)	1403(2)
10:7*	3	9.657(3)	12.781(8)	12.015(5)	108.42(3)	1407(2)
3:1	3	9.659(4)	12.816(7)	12.044(7)	108.35(3)	1415(2)
7:1	1	9.659(2)	12.836(3)	12.064(3)	108.40(2)	1419.2(4)
1:0	1	9.658(3)	12.854(4)	12.079(4)	108.48(3)	1422.2(6)

Guinier-de Wolff quadruple focusing camera, Fe$K\alpha$ radiation (λ = 1.93728 Å), Internal standard: lead nitrate.

n: number of measurements (for n = 1, the estimated standard deviations from the least-squares calculation are given in parentheses; for n = 3, the standard errors of the mean are given).

* Corrected value inferred from the curves in Figure 1.

Cell parameters refined from powder data for the whole series $Mg_2PO_4F-Mg_2PO_4OH$ with wagnerite structure are given in Table 1 and are plotted in Figure 1. Considering the small error bars for the individual points, smooth curves can be drawn through them, except for the composition that was meant to be OH:F = 5:3. An error was obviously made in the preparation of this mixture, and its true composition must be corrected to OH:F = 10:7.

The c and especially the b parameters are seen to increase markedly with increased OH content, whereas a is practically unaffected. There is an increase of ca. 3% in cell volume from the F to the OH end-member.

Single-crystal X-ray data

A crystal with dimensions 0.05 × 0.05 × 0.10 mm was selected for the X-ray experiments. Data were collected on a Nicolet $P3/F$ diffractometer at room temperature, using graphite crystal monochromatized Mo$K\alpha$ radiation. Cell parameters were determined by a least-squares fit to the diffractometer settings for 25 general reflections with $2\theta > 32°$. The crystal data are shown in Table 2. There is good agreement with the cell parameters refined from powder data (Table 1).

Intensity data were collected by the $\theta/2\theta$ scan technique, scan speed $3°\,\mathrm{min}^{-1}$, scan width 2° with an additional dispersion term; background counts were taken for 0.35 times the scan time at each of the scan limits. All reflections within a quadrant of reciprocal space out to a $\sin\theta/\lambda$ value of 0.8 Å^{-1} were measured. Three standard reflections were measured at regular intervals during the data collection; the variation in intensity was less than 0.5% and no correction for drift was applied. Out of 4273 meas-

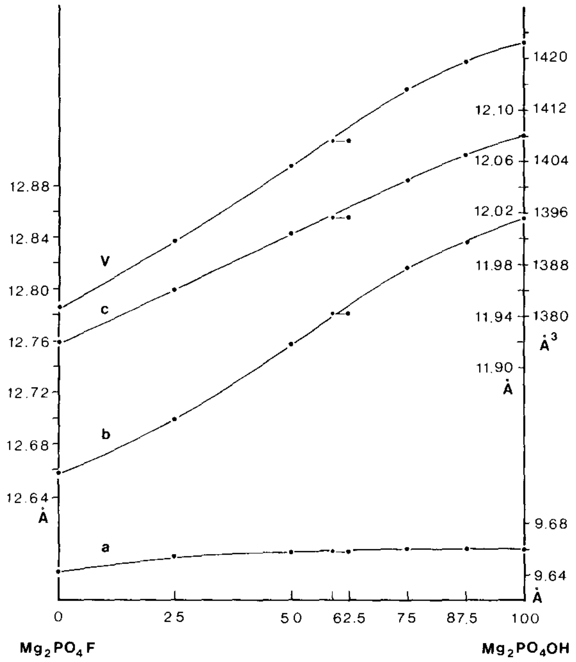

Fig. 1. Plot of cell parameters versus composition for the series $Mg_2PO_4F-Mg_2PO_4OH$ with wagnerite structure (mol%). Based on data in Table 1.

Table 2. Crystal data for β-Mg_2PO_4OH (synthesized at 5.5 kbar, 350 °C).

Space group $P2_1/c$		Molecular weight	$= 160.59$
($h0l$ absent for l odd)		Z	$= 16$
($0k0$ absent for k odd)		D_{cal}	$= 3.002$ g cm^{-3}
		$F(000)$	$= 1218$
a	$= 9.656(3)$ Å	λ(Mo$K\alpha$)	$= 0.71069$ Å
b	$= 12.859(3)$ Å	R	$= 0.052$
c	$= 12.069(4)$ Å	R_w	$= 0.039$
β	$= 108.49(3)°$		
V	$= 1421.2(8)$ Å^3	1863 applied observations	
(T	$= 19 \pm 1$ °C)		

ured reflections, 2190 with $I > 2.5\,\sigma(I)$ were retained for the structure analysis. The estimate of the standard deviation was based on counting statistics with an additional term of 2% of the net intensity. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Description of the computer programs applied is given by Groth (1973). Atomic form factors were those of Doyle and Turner (1968) for the heavy atoms and of Stewart et al. (1965) for hydrogen.

Structure determination

The parameters of Coda et al. (1967) for wagnerite were used as a starting set for the refinements, substituting the fluorine atoms of wagnerite with oxygen. The model refined well and the hydrogen positions were found from a difference Fourier map. An attempt to refine the structure with anisotropic thermal parameters failed to give physically meaningful results, probably because an absorption correction had not been made. This was also experienced by Coda et al. (1967). Irouschek and Armbruster (1984, abstract only) report that they have succeeded in refining anisotropically the structure of a Swiss wagnerite with composition $(Mg_{1.84}Fe_{0.16})$-$PO_4(F_{0.7}OH_{0.3})$ to a final R-value of 0.025.

The full-matrix least-squares refinements, varying all positional parameters and the isotropic thermal parameters for the non-hydrogen atoms converged to a conventional R-value of 0.052, R_w of 0.039 and a goodness of fit, $S = [\Sigma w \Delta F^2/(m-n)]^{\frac{1}{2}}$, of 1.44. For the last stage of refinement, only high-angle diffraction data with $\sin\theta/\lambda > 0.35$ Å^{-1} were used, reducing the number of applied observations to 1863.

Final atomic parameters are listed in Table 3 and bond lengths and ranges of angles in Table 4. Tables of observed and calculated structure factors are available from the authors.

Description of the structure

The structure of β-Mg_2PO_4OH is rather complex, involving 36 unique atoms in the asymmetric unit (Table 3). Three kinds of coordination polyhedra are present. These are fairly regular PO_4 tetrahedra, distorted $MgO_4(OH)_2$ octahedra with the OH groups in *cis* configuration, and distorted trigonal bipyramids $MgO_4(OH)$. These polyhedra are sharing either edges or vertices to build up a three-dimensional network. The isotypic wagnerite structure is described and pictured in detail by Coda et al. (1967), and the particulars are not repeated here. To facilitate a comparison, we have adopted the same numbering scheme of the P and Mg atoms (four Mg atoms with odd numbers are in 5-coordination, the other four with even numbers are in 6-coordination). The reader is also referred to the structure descriptions of the isostructural minerals triploidite $(Mn,Fe)_2PO_4OH$ (Waldrop, 1970), which forms a series with wolfeite $(Fe,Mn)_2PO_4OH$, and sarkinite Mn_2AsO_4OH (Dal Negro et al., 1974). In the wagnerite and sarkinite papers, projections of various parts of the structures are shown to clarify the connections between the polyhedra. In the present paper we have therefore restricted ourselves to include only a stereoview of the β-Mg_2PO_4OH structure (Fig. 2).

The four OH groups are engaged in weak hydrogen bonding. Interatomic distances and angles for the hydrogen bonds are given in Table 4.

Table 3. Fractional atomic coordinates and isotropic thermal parameters (Å^2) for β-Mg_2PO_4OH (with estimated standard deviations in parentheses).

Atom	*x*	*y*	*z*	*B*
P(1)	0.1137(3)	0.0773(2)	0.4248(1)	0.26(5)
P(2)	0.8791(3)	0.0702(2)	0.0751(2)	0.32(5)
P(3)	0.3821(3)	0.1750(2)	0.0747(2)	0.29(5)
P(4)	0.6218(3)	0.1798(2)	0.4226(2)	0.28(5)
Mg(1)	0.5511(3)	0.0723(1)	0.9154(2)	0.42(4)
Mg(2)	0.4710(2)	0.0696(2)	0.6007(2)	0.50(5)
Mg(3)	0.0429(2)	0.1805(2)	0.9220(2)	0.48(5)
Mg(4)	0.9710(2)	0.1772(2)	0.6096(2)	0.51(5)
Mg(5)	0.1893(3)	0.0223(2)	0.1871(2)	0.51(5)
Mg(6)	0.7855(3)	0.0013(2)	0.3037(2)	0.56(5)
Mg(7)	0.3057(2)	0.2297(2)	0.3183(2)	0.46(5)
Mg(8)	0.7095(2)	0.2503(2)	0.1949(2)	0.54(5)
O(11)	0.1664(6)	0.1160(4)	0.3223(4)	0.77(8)
O(12)	0.2447(8)	0.0476(5)	0.5295(8)	0.78(12)
O(13)	0.9868(9)	0.0162(7)	0.6200(7)	0.70(16)
O(14)	0.0283(6)	0.1642(4)	0.4585(4)	0.46(9)
O(21)	0.7952(5)	0.0924(4)	0.1615(4)	0.72(9)
O(22)	0.7684(6)	0.0533(4)	0.9520(5)	0.70(11)
O(23)	0.0238(8)	0.0270(6)	0.8854(6)	0.51(15)
O(24)	0.9845(6)	0.1593(4)	0.0683(5)	0.48(9)
O(31)	0.3198(5)	0.1425(3)	0.1719(4)	0.28(7)
O(32)	0.2592(6)	0.2049(4)	0.9625(4)	0.42(10)
O(33)	0.4838(9)	0.2320(6)	0.6182(6)	0.59(15)
O(34)	0.4677(6)	0.0840(4)	0.0459(4)	0.67(10)
O(41)	0.6893(4)	0.1532(3)	0.3273(3)	0.25(7)
O(42)	0.7429(6)	0.2042(4)	0.5363(4)	0.36(9)
O(43)	0.5188(9)	0.2257(6)	0.8804(6)	0.66(16)
O(44)	0.5205(6)	0.0912(4)	0.4394(5)	0.71(11)
O(H1)	0.4344(4)	0.0330(4)	0.7542(3)	0.60(7)
O(H2)	0.6888(5)	0.0812(3)	0.7005(4)	0.70(7)
O(H3)	0.1902(5)	0.1632(3)	0.7092(4)	0.67(7)
O(H4)	0.9280(5)	0.2191(3)	0.7592(3)	0.53(7)
H(1)	0.453(12)	−0.027(9)	0.751(8)	1.0
H(2)	0.708(11)	0.078(7)	0.632(8)	1.0
H(3)	0.223(11)	0.167(7)	0.660(8)	1.0
H(4)	0.964(11)	0.286(8)	0.775(8)	1.0

The O – O distances vary from 2.7 to 3.0 Å and the hydrogen bonds are strongly bent with O – H – O angles from 116 to 144°. The O – H(4) group can be considered to form a bifurcated bond with the acceptor oxygen atoms O(11) and O(14).

Infra-red spectrum

Infra-red spectra of the different synthetic members of the series $Mg_2PO_4F - Mg_2PO_4OH$ with wagnerite structure have been recorded and

Table 4. Bond lengths (Å) with e.s.d.'s in parentheses and ranges of angles (°) with e.s.d.'s from 0.2 to 0.5° for β-Mg$_2$PO$_4$OH.

P(1)−O(11)	1.561(6)
P(1)−O(12)	1.526(7)
P(1)−O(13)	1.531(10)
P(1)−O(14)	1.520(7)
O−P(1)−O	107.5−111.3
P(2)−O(21)	1.536(6)
P(2)−O(22)	1.546(6)
P(2)−O(23)	1.543(10)
P(2)−O(24)	1.552(7)
O−P(2)−O	105.7−113.2
P(3)−O(31)	1.537(5)
P(3)−O(32)	1.539(6)
P(3)−O(33)	1.530(10)
P(3)−O(34)	1.535(7)
O−P(3)−O	108.1−111.1
P(4)−O(41)	1.529(5)
P(4)−O(42)	1.527(6)
P(4)−O(43)	1.550(10)
P(4)−O(44)	1.556(7)
O−P(4)−O	104.6−111.7
Mg(1)−O(22)	2.017(6)
Mg(1)−O(34)	1.989(6)
Mg(1)−O(34)	2.084(7)
Mg(1)−O(43)	2.021(9)
Mg(1)−O(H1)	1.979(5)
O−Mg(1)−O	79.0−104.2 114.4−123.4 axial 165.8
Mg(2)−O(12)	2.099(8)
Mg(2)−O(33)	2.099(9)
Mg(2)−O(44)	2.164(7)
Mg(2)−O(44)	2.131(7)
Mg(2)−O(H1)	2.048(6)
Mg(2)−O(H2)	2.071(6)
O−Mg(2)−O	81.5−101.3 169.0−173.7
Mg(3)−O(14)	2.059(6)
Mg(3)−O(23)	2.019(9)
Mg(3)−O(24)	2.035(6)
Mg(3)−O(32)	2.013(7)
Mg(3)−O(H4)	1.989(5)
O−Mg(3)−O	83.5−102.8 111.2−132.0 axial 170.9
Mg(4)−O(13)	2.077(10)
Mg(4)−O(14)	2.072(7)
Mg(4)−O(24)	2.174(6)
Mg(4)−O(42)	2.126(6)
Mg(4)−O(H3)	2.084(6)
Mg(4)−O(H4)	2.050(6)
O−Mg(4)−O	79.9−103.9 165.8−169.3
Mg(5)−O(11)	2.096(6)
Mg(5)−O(22)	2.090(7)
Mg(5)−O(23)	2.064(8)
Mg(5)−O(31)	2.039(6)
Mg(5)−O(H2)	1.995(6)
O−Mg(5)−O	81.7−99.7 108.6−139.1 axial 171.4
Mg(6)−O(12)	2.215(8)
Mg(6)−O(13)	2.109(10)
Mg(6)−O(21)	2.105(6)
Mg(6)−O(41)	2.221(5)
Mg(6)−O(H1)	2.062(5)
Mg(6)−O(H3)	2.139(5)
O−Mg(6)−O	76.2−117.3 160.0−162.2
Mg(7)−O(11)	1.997(6)
Mg(7)−O(31)	2.134(5)
Mg(7)−O(32)	2.105(6)
Mg(7)−O(43)	2.037(9)
Mg(7)−O(H3)	1.986(6)
O−Mg(7)−O	81.7−97.5 106.4−143.8 axial 168.8

Table 4. Continued.

Mg(8)−O(21)	2.227(6)
Mg(8)−O(33)	2.093(9)
Mg(8)−O(41)	2.085(5)
Mg(8)−O(42)	2.121(6)
Mg(8)−O(H2)	2.179(6)
Mg(8)−O(H4)	2.042(5)
O−Mg(8)−O	74.3−122.7 159.1−162.3
O(H1)−H(1)	0.80(12)
O(41)−H(1)	2.14(11) 2.03*
O(H1)−O(41)	2.718(7)
O(H1)−H(1)−O(41)	129
O(H2)−H(2)	0.90(10)
O(42)−H(2)	2.08(10) 2.06*
O(H2)−O(42)	2.712(7)
O(H2)−H(2)−O(42)	126
O(H3)−H(3)	0.76(12)
O(12)−H(3)	2.26(11) 2.12*
O(H3)−O(12)	2.814(7)
O(H3)−H(3)−O(12)	131
O(H4)−H(4)	0.93(10)
O(14)−H(4)	2.20(10) 2.18*
O(H4)−O(14)	2.738(7)
O(H4)−H(4)−O(14)	116
O(11)−H(4)	2.24(10) 2.22*
O(H4)−O(11)	3.042(7)
O(H4)−H(4)−O(11)	144

Mg atoms with odd numbers: 5-coordination.

Mg atoms with even numbers: 6-coordination.

* Corrected H···O (acceptor) bond length assuming an H−O (donor) distance of 0.95 Å.

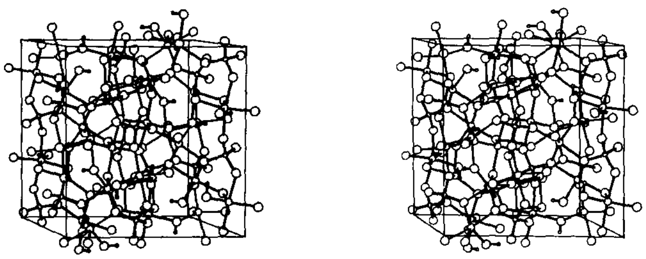

Fig. 2. Stereoview of the unit cell of β-Mg_2PO_4OH as seen approximately down the *a*-axis (*b* is horizontal and *c* vertical). It should be noted that none of the OH groups is oriented along the *a*-direction (cf. Fig. 1).

will be discussed in more detail in a separate paper. The spectrum of β-Mg_2PO_4OH shows two sharp O−H stretching frequencies at 3595 and 3580 cm^{-1}. These are not readily related to the hydrogen bond distances because of the strongly bent configurations of the hydrogen bonds. At least seven ν_3 absorption bands of the $(PO_4)^{3-}$ groups are recognized, at 1145, 1125, 1115, 1090, 1060, 1035, and 1010 cm^{-1}. These are slightly displaced

Table 5. Bond-strength calculation for β-Mg_2PO_4OH (valence units).

	P(1)	P(2)	P(3)	P(4)	Mg(1)	Mg(2)	Mg(3)	Mg(4)	Mg(5)	Mg(6)	Mg(7)	Mg(8)	H(1)	H(2)	H(3)	H(4)	Σ
O(11)	1.163								0.336		0.440					0.08	2.019
O(12)	1.279					0.334				0.244					0.10		1.957
O(13)	1.262							0.354		0.325							1.941
O(14)	1.300						0.372	0.359								0.09	2.121
O(21)		1.245								0.328		0.206					1.779
O(22)		1.212			0.417				0.342								1.971
O(23)		1.221					0.414		0.367								2.002
O(24)		1.192					0.397	0.273	0.066								1.928
O(31)			1.241						0.393		0.304						1.938
O(32)			1.235				0.421				0.328						1.984
O(33)			1.265			0.334						0.339					1.938
O(34)			1.248		0.449 0.348												2.045
O(41)				1.269						0.240		0.347	0.11				1.966
O(42)				1.275				0.310				0.315		0.11			2.010
O(43)				1.199	0.412						0.395						2.006
O(44)				1.179		0.280 0.306					0.054						1.819
O(H1)					0.462	0.383				0.369			0.89				2.104
O(H2)						0.360			0.442			0.269		0.89			1.961
O(H3)								0.348		0.300	0.453				0.90		2.001
O(H4)							0.449	0.381				0.389				0.83	2.049
Σ	5.004	4.870	4.989	4.922	2.088	1.997	2.053	2.025	1.946	1.806	1.974	1.865	1.00	1.00	1.00	1.00	39.539

Computed from the empirical bond-strength/bond-length relations of Brown and Altermatt (1985).

from the frequencies shown by the pure F member. A strong band at 595 cm^{-1} with indistinct shoulders towards higher frequencies are due to $\nu_4(PO_4)$ vibrations. Numerous absorption bands not present in the infrared spectrum of Mg_2PO_4F are found in the spectrum of β-Mg_2PO_4OH. These occur at 980, 960, 930, 875, 770, and 740 cm^{-1}. They become more prominent with increasing OH content and can be interpreted as multiple O–H deformation modes.

Discussion

Inspection of Figure 2 reveals that none of the four OH groups is oriented along the *a*-axis of the structure. This explains why the *a*-parameter is practically unaffected by the substitution of OH for F in the wagnerite structure (Fig. 1). Only the variation in the *c*-parameter is in close agreement with Vegard's law. It should be pointed out that we are here dealing with an anion substitution involving ionic species with rather different characteristics, e.g. with regard to polarizability and electronegativity. The possibility of partial ordering between OH and F in the wagnerite structure was briefly discussed by Rømming and Raade (1980), based on a bond-strength calculation for natural wagnerite (data from Coda et al., 1967). The F(2) and F(3) atoms were the possible candidates for preferred OH substitution. Each O(H) atom in β-Mg_2PO_4OH is bonded to three Mg atoms, and the average Mg–O distances for O(H2) and O(H3) are distinctly longer (2.082 and 2.070 Å respectively) than for the O(H1) and O(H4) atoms (2.030 and 2.027 Å respectively). The same trend is observed for the Mg–F distances in wagnerite (Coda et al., 1967), and the data clearly corroborate a preferred substitution of OH for F in the two 'largest' F sites of the wagnerite structure.

A bond-strength calculation for β-Mg_2PO_4OH based on the empirical bond-valence parameters of Brown and Altermatt (1985) is presented in Table 5. Satisfactory bond sums for Mg(5) and Mg(7) were achieved by taking into account the longer bond distances Mg(5)–O(24) of 2.697 Å and Mg(7)–O(44) of 2.772 Å. Low bond sums for Mg(5) and Mg(7) in natural wagnerite were shown by Rømming and Raade (1980). Incorporation of the contributions from the second-closest oxygen atoms in the bond-valence calculation was also necessary for the althausite structure (Rømming and Raade, 1980), and is explained by the large degree of distortion of the coordination polyhedra in these structures.

There is still a significant deficiency in the valence sums for Mg(6) and to a lesser degree for Mg(8), and the O(21) atom which is common for these two Mg polyhedra has a sum of only 1.779 v.u. In these cases there are no other oxygen atoms within a distance of 3.2 Å from the Mg atoms. Inspection of the Mg–O bond lengths and O–Mg–O bond angles for Mg(6) and Mg(8) in Table 4 shows a higher degree of distortion for these two pseudo-octahedral polyhedra than for Mg(2) and Mg(4), and each of them also has the two longest Mg—O distances in the structure. Careful study of Table 5 reveals a systematic relationship between low valence sums and long Mg—O distances. The expression used by Brown and Altermatt (1985) to describe the relationship between bond length r and bond valence s ($s = \exp[(r_0 - r)/B]$, where r_0 and B are empirically determined parameters) clearly underestimates the bond strengths for Mg—O bonds longer than about 2.16 Å. This is also the case for the other commonly used expression $s = (r/r_0)^{-N}$ (Brown and Wu, 1976; Brown, 1981), although in this case to a somewhat lesser degree.

Because the X-ray method measures the position of electron density maxima rather than the position of atomic nuclei, the O—H bond lengths in Table 4 should be corrected to 0.95 Å in order to conform with the accepted O—H bond distance. The corresponding shifts in the H···O (acceptor) distances are indicated in Table 4. Using Figure 1 in Brown and Altermatt (1985), which depicts H···O valences as a function of H···O distances, the numbers given in Table 5 were obtained. This approach leads in this particular case to satisfactory valence sums for all the oxygen atoms involved in hydrogen bonding. However, this may not always be the case (cf. Rømming and Raade, 1986; Raade and Rømming, 1986).

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