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The Crystal Structure of $Mg_3(PO_4)_2$

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The crystal structure of $Mg_3(PO_4)_2$ has been determined from three-dimensional X-ray data. The structure is monoclinic, space group $P2_1/n$. The elementary cell contains two formula units and has the dimensions:

$a = 7.5957 \pm 8$ Å
$b = 8.2305 \pm 5$ Å
$c = 5.0775 \pm 5$ Å
$\beta = 94.05 \pm 1°$

The structure may be described in terms of somewhat distorted MgO_6 octahedra, MgO_5 polyhedra, and nearly regular PO_4 tetrahedra. The groups are linked together by sharing corners and edges to give a three-dimensional framework. The structure is discussed and the coordination of the metal ions is compared with the arrangement in the isostructural compound γ-$Zn_3(PO_4)_2$ reported by Calvo.

During the course of crystal structure studies on phosphate compounds at this Institute reports have been published on the structures of the phases $MoOPO_4$ [1] and $NbOPO_4$.[2] In continuation of this work crystal structure studies were started on the compounds α-$Sr_2P_2O_2$ and $Mg_3(PO_4)_2$. A report of the results obtained for the former phase will shortly appear elsewhere. This article describes the investigation of the structure of $Mg_3(PO_4)_2$.

Single crystals of $Mg_3(PO_4)_2$ were prepared by sealing of equivalent mixtures of magnesium diphosphate and magnesium oxide into thin-walled platinum tubes, which were subsequently heated to 1400°C. After a slow decrease of the temperature to 1100°C—over a period of 10 h—the heating was continued for about two weeks. The product thus obtained consisted of colourless irregularly shaped small crystals.

X-RAY DIFFRACTION DATA AND COMPUTING METHODS

The *d*-values and relative intensities obtained from a powder pattern of $Mg_3(PO_4)_2$ agreed with those reported [3] in the literature. The cell parameters of the monoclinic unit cell were calculated from a photograph taken with

strictly monochromatized Cu$K\alpha_1$ radiation ($\lambda = 1.54056$ Å) in a focusing camera of Guinier-Hägg type. Potassium chloride ($a = 6.29288$ Å) [4] was used as an internal standard. Least-squares refinement gave the following unit-cell dimensions (see Table 1) at 25°C:

$$\begin{aligned} a &= 7.5957 \pm 8 \text{ Å} \\ b &= 8.2305 \pm 5 \text{ Å} \\ c &= 5.0775 \pm 5 \text{ Å} \\ \beta &= 94.05 \pm 1° \\ V &= 316.6 \text{ Å}^3 \end{aligned}$$

Table 1. X-Ray powder data observed for $Mg_3(PO_4)_2$. Cu$K\alpha_1$ radiation. $\lambda(\text{Cu}K\alpha_1) = 1.54050$ Å.

hkl	$10^5\sin^2\theta$ obs	$10^5\sin^2\theta$ calc	*I* obs	*d* (Å) obs	*hkl*	$10^5\sin^2\theta$ obs	$10^5\sin^2\theta$ calc	*I* obs	*d* (Å) obs
110	1905	1909	vw	5.575	$23\bar{1}$	13888	13893	vw	2.067
$10\bar{1}$	3125	3128	vw	4.356	040	14023	14013	vvw	2.058
011	3188	3189	w	4.313	202	14250	14257	w	2.040
020	3499	3503	w	4.116	140	15033	15046	vvw	1.986
101	3563	3564	m	4.080	$22\bar{2}$	16021	16015	vvw	1.925
$11\bar{1}$	4000	4004	st,(d)*	3.850	041	16325	16326	vvw	1.906
111	4441	4440	m	3.655	330	17186	17184	vvw	1.858
120	4529	4537	vvw	3.616	141	17584	17578	vvw,(d)*	1.837
210	5009	5010	vst	3.441	$13\bar{2}$	17737	17730	vvw	1.829
021	5812	5816	vw	3.194	132	18601	18603	vvw	1.786
$12\bar{1}$	6622	6631	w	2.993	$33\bar{1}$	18830	18842	m,(d)*	1.774
121	7061	7067	vvw	2.897	420	20029	20039	vw,(d)*	1.721
220	7630	7637	vw	2.787	$24\bar{1}$	20029	20023	»	1.721
002	9250	9251	w	2.532	411	20603	20596	vw	1.697
$22\bar{1}$	9509	9514	m	2.497	312	20745	20736	w	1.692
310	10184	10177	m,(d)*	2.414	$32\bar{2}$	20745	20747	w	1.691
031	10184	10195	»	2.412	241	20897	20896	vvw	1.685
$13\bar{1}$	11008	11004	vw	2.322	$11\bar{3}$	22075	22070	w	1.640
131	11447	11447	vvw	2.277	150	22927	22928	vw	1.609
$31\bar{1}$	11832	11836	vvw	2.239	$33\bar{2}$	25130	25126	m	1.537
$20\bar{2}$	12503	12512	vvw	2.178	250	26031	26029	vw	1.510
311	13144	13144	w	2.125	341	26279	26281	vw	1.502
$12\bar{2}$	13347	13351	vw	2.108					

(d)* = diffuse

The density was determined experimentally by the apparent loss of weight in benzene. It was found to be 2.74 g/cm³ which compares favourably with the theoretical value of 2.76 g/cm³ based on two formula units in the unit cell.

Rotation and Weissenberg photographs (*hk*0—*hk*2) of a single crystal — a somewhat irregularly shaped plate with the dimensions 0.08 mm in the ($11\bar{1}$) direction × 0.02 mm × 0.02 mm — were taken with CuK radiation. The reflections systematically absent in the photographs are *h*0*l* with $h+l$ odd and 0*k*0 with *k* odd, which is characteristic of the space group $P2_1/n$.

The reflections were recorded photographically with the multiple film technique. The relative intensities were estimated visually by comparison

with an intensity scale obtained by photographing a reflection with different exposure times. A total of 346 independent reflections of non-zero intensity were measured.

The computational work involved in the refinement of lattice constants (Program No. 6018), absorption correction (No. 6019), Lorentz-polarization correction (No. 6024), Fourier summation (No. 6015), least-squares refinement (No. 6023), and calculation of interatomic distances (No. 6016) was performed on the electronic computers FACIT EDB and TRASK. (The program members refer to the list of crystallographic computer programs.[5])

The linear absorption coefficient, $\mu = 93.1$ cm^{-1}, was used in the calculation of the absorption factor for each reflection. However, this correction may be somewhat uncertain due to the irregular shape of the crystal.

STRUCTURE DETERMINATION

In $P2_1/n$ the following point positions exist:

2(*a*): 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
2(*b*): $\frac{1}{2}00$; $0\frac{1}{2}\frac{1}{2}$
2(*c*): $00\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$
2(*d*): $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}0$
4(*e*): $\pm(xyz)$; $\pm(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$

From the three-dimensional Patterson function $P(uvw)$, within the limits $0 \leq u \leq \frac{1}{2}$, $0 \leq v \leq \frac{1}{2}$, $0 \leq w \leq 1$, approximate parameter values were derived for the six magnesium atoms (situated in point positions 2(*c*) and 4(*e*)), and the four phosphorus atoms (in 4(*e*)). Assuming P—O distances of about 1.5 Å approximate coordinates for the sixteen oxygens (in 4 × 4(*e*)) were obtained from peaks in $P(uvw)$ ascribed to P—O vectors.

A refinement of the coordinates so obtained was then performed using the least-squares technique. Initially all of the 346 independent reflections

Table 2. Weight analysis obtained in the final cycle of the least-squares refinement of $Mg_3(PO_4)_3$. w = weighting factor, $\Delta = ||F_{obs}|-|F_{calc}||$.

Interval sin θ	Number of independent reflections	$\overline{w\Delta^2}$	Interval F_{obs}	Number of independent reflections	$\overline{w\Delta^2}$
0.00—0.46	61	1.89	0— 5	11	0.29
0.46—0.58	50	0.98	5—20	65	1.42
0.58—0.67	38	0.98	10—15	70	0.93
0.67—0.74	37	0.44	15—20	65	0.79
0.74—0.79	32	0.76	20—25	31	0.78
0.79—0.84	28	0.50	25—30	36	1.00
0.84—0.89	21	0.69	30—35	18	0.74
0.89—0.93	31	0.44	35—40	16	0.80
0.93—0.97	25	1.48	40—45	13	1.93
0.97—1.00	15	1.10	45—50	13	1.09

measured were included in the calculations, but after a few cycles eight strong, low-angle reflections were omitted as suffering from extinction. The atomic scattering curves applied in these calculations were those for ionized atoms P^{1+} Mg^{2+} and O^-. Correction was made for the real part of the anomalous dispersion.[6] The refinement was considered to be complete when the parameter

Table 3. Observed and calculated structure factors of $Mg_3(PO_4)_2$.

h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}
0	2	0	45·6	46·3	0	2	1	29·9	32·3	-4	2	1	20·9	18·4
0	4	0	41·7	42·1	1	2	1	16·1	17·8	-4	3	1	16·7	14·3
0	6	0	50·8	49·9	2	2	1	6·4	6·1	-4	4	1	19·4	18·0
0	8	0	5·1	5·5	3	2	1	6·4	7·3	-4	5	1	9·6	7·4
0	10	0	11·7	11·0	4	2	1	25·9	23·0	-4	6	1	24·1	25·3
1	1	0	16·0	15·6	5	2	1	44·8	47·6	-4	7	1	28·8	30·3
1	2	0	18·1	18·1	6	2	1	15·3	15·3	-4	8	1	14·2	11·8
1	3	0	7·1	5·4	8	2	1	9·3	8·8	-5	0	1	16·9	14·2
1	4	0	22·8	22·5	9	2	1	7·2	6·2	-5	2	1	33·9	34·3
1	5	0	44·8	44·0	0	3	1	54·6	60·0	-5	3	1	13·2	11·1
1	6	0	51·8	56·5	1	3	1	22·4	22·0	-5	4	1	11·6	11·6
1	8	0	24·2	28·1	2	3	1	7·8	7·8	-5	5	1	8·9	8·7
1	9	0	11·6	12·4	3	3	1	19·2	17·2	-5	6	1	6·2	6·5
1	10	0	18·2	19·8	4	3	1	10·1	9·6	-5	8	1	21·5	22·6
2	0	0	25·6	28·2	5	3	1	5·6	5·7	-6	1	1	13·6	15·0
2	1	0	73·8	80·6	6	3	1	32·4	31·2	-6	2	1	19·6	17·5
2	2	0	43·9	39·5	7	3	1	7·3	6·1	-6	3	1	6·2	4·9
2	3	0	25·2	25·4	9	3	1	15·5	16·9	-6	4	1	18·3	17·9
2	4	0	12·5	11·4	0	4	1	23·4	20·9	-6	5	1	6·1	6·8
2	5	0	44·1	46·8	1	4	1	22·7	21·9	-6	6	1	22·0	22·6
2	6	0	7·2	6·5	2	4	1	33·7	31·7	-6	7	1	28·6	30·8
2	7	0	20·8	21·2	3	4	1	50·0	54·4	-6	8	1	11·8	12·0
2	8	0	26·1	28·8	4	4	1	40·6	38·9	-7	0	1	34·8	36·2
2	9	0	5·5	4·7	5	4	1	26·9	24·5	-7	1	1	20·5	21·5
2	10	0	11·0	11·4	6	4	1	14·0	16·4	-7	4	1	18·8	17·4
3	1	0	34·4	32·6	8	4	1	4·4	4·4	-7	5	1	5·3	5·6
3	2	0	7·7	8·6	1	5	1	25·8	22·8	-7	6	1	7·2	7·4
3	3	0	39·6	36·1	2	5	1	56·9	59·7	-7	7	1	12·0	10·8
3	4	0	14·7	15·5	3	5	1	36·2	34·9	-7	8	1	17·4	18·0
3	5	0	32·9	32·3	4	5	1	22·4	21·5	-8	2	1	37·5	42·6
3	6	0	8·4	7·8	5	5	1	34·8	36·0	-8	3	1	16·4	17·4
3	7	0	32·0	32·4	6	5	1	6·0	5·8	-8	4	1	18·6	18·0
4	0	0	16·9	16·4	7	5	1	15·5	14·2	-8	5	1	27·2	27·6
4	1	0	7·4	3·4	8	5	1	24·7	26·5	-9	0	1	17·1	16·1
4	2	0	16·0	15·0	0	6	1	10·1	11·3	-9	1	1	18·4	17·8
4	3	0	35·8	35·6	2	6	1	8·2	7·8	-9	2	1	4·1	4·7
4	4	0	25·1	23·1	3	6	1	11·7	11·4	-9	3	1	22·1	22·1
4	5	0	14·4	13·1	4	6	1	27·4	27·7	4	0	2	33·7	34·6
4	6	0	12·2	12·5	5	6	1	13·1	13·5	6	0	2	15·8	14·2
4	7	0	18·9	19·3	6	6	1	30·1	32·2	8	0	2	23·6	24·0
4	8	0	9·9	9·8	7	6	1	14·2	14·3	0	1	2	8·1	10·4
4	9	0	30·8	30·0	0	7	1	23·2	23·0	1	1	2	11·9	9·6
5	1	0	42·0	40·0	1	7	1	20·5	19·2	2	1	2	10·0	8·1
5	2	0	10·7	9·5	2	7	1	20·5	22·2	3	1	2	42·9	48·9
5	3	0	32·9	28·5	3	7	1	19·9	18·7	4	1	2	38·7	40·5
5	4	0	7·5	7·3	4	7	1	29·7	29·0	5	1	2	33·8	33·0
5	5	0	28·0	25·5	6	7	1	9·0	7·2	6	1	2	23·6	24·8
5	6	0	11·4	11·1	7	7	1	10·4	11·9	7	1	2	12·9	12·7
5	7	0	13·0	11·4	2	8	1	12·8	12·5	8	1	2	16·3	17·5
5	8	0	11·7	12·1	3	8	1	17·8	16·2	0	2	2	9·3	9·5
6	0	0	7·3	0·2	4	8	1	11·1	9·6	2	2	2	41·1	45·1
6	1	0	9·8	8·6	5	8	1	23·9	25·8	3	2	2	8·7	7·5
6	2	0	15·6	14·2	6	8	1	15·2	17·5	4	2	2	19·2	18·2
6	3	0	8·6	6·7	0	9	1	16·2	16·2	5	2	2	18·1	15·0
6	4	0	32·0	32·5	1	9	1	37·8	41·9	6	2	2	15·9	14·8
6	5	0	11·9	11·3	2	9	1	10·1	9·8	7	2	2	16·3	15·2
6	6	0	4·9	4·9	3	9	1	5·6	4·4	8	2	2	17·8	18·0
6	7	0	12·2	12·0	1	10	1	13·1	12·6	0	3	2	9·3	9·0
6	8	0	13·6	14·7	2	10	1	7·4	7·1	1	3	2	23·7	24·3
7	1	0	12·2	11·6	-1	2	1	32·8	40·9	2	3	2	7·3	5·9
7	2	0	35·4	38·7	-1	3	1	29·3	30·9	3	3	2	18·8	17·1
7	3	0	29·4	31·9	-1	4	1	27·7	25·2	4	3	2	8·3	7·0
7	4	0	19·2	20·5	-1	5	1	19·3	18·6	5	3	2	19·4	18·1
7	5	0	3·3	2·8	-1	6	1	18·6	15·7	6	3	2	14·6	13·4
7	6	0	11·7	11·6	-1	7	1	9·9	9·6	7	3	2	38·0	39·1
7	7	0	11·5	11·4	-1	8	1	35·1	35·4	8	3	2	12·7	11·9
8	0	0	11·3	11·8	-1	9	1	9·2	8·7	1	4	2	9·0	7·2
8	1	0	20·5	21·3	-1	10	1	20·5	19·2	2	4	2	36·8	38·9
8	2	0	17·3	18·0	-2	1	1	6·9	6·6	3	4	2	37·0	38·0
8	4	0	4·1	4·6	-2	2	1	40·5	55·0	4	4	2	22·1	19·6
8	5	0	2·4	3·5	-2	3	1	37·1	40·7	5	4	2	30·0	30·6
9	1	0	2·6	2·5	-2	4	1	48·3	53·4	7	4	2	13·9	13·0
9	2	0	10·4	10·8	-2	5	1	27·8	24·6	8	4	2	18·2	19·4
9	3	0	12·7	13·4	-2	6	1	13·5	11·6	1	5	2	19·3	18·0
9	4	0	19·5	22·2	-2	7	1	19·9	19·1	2	5	2	16·5	16·2
3	0	1	10·7	10·7	-2	8	1	19·2	17·5	3	5	2	5·2	4·0
5	0	1	57·4	62·4	-2	9	1	6·2	5·8	4	5	2	26·3	26·7
7	0	1	45·6	49·9	-2	10	1	9·1	8·4	5	5	2	27·1	28·1
9	0	1	19·1	18·6	-3	0	1	20·7	19·9	6	5	2	14·2	12·6
2	1	1	15·4	17·2	-3	1	1	29·2	31·9	7	5	2	14·8	14·5
3	1	1	62·4	66·4	-3	2	1	9·1	10·4	0	6	2	18·5	17·8
4	1	1	42·7	40·3	-3	3	1	12·8	11·0	1	6	2	43·8	47·5
5	1	1	29·7	27·9	-3	4	1	19·9	17·2	2	6	2	19·1	18·4
6	1	1	7·6	6·9	-3	5	1	29·5	27·8	3	6	2	22·5	21·5
7	1	1	27·1	28·2	-3	6	1	36·3	34·8	4	6	2	26·5	27·2
8	1	1	6·8	5·6	-3	9	1	11·0	10·0	5	6	2	9·9	10·1
9	1	1	10·1	8·1	-4	1	1	46·3	51·8	6	6	2	10·7	10·0

Table 3. Continued.

h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}
7	6	2	6·6	6·9	- 2	2	2	23·2	29·7	- 5	1	2	33·1	33·3
0	7	2	5·8	5·6	- 2	3	2	21·5	21·5	- 5	2	2	43·8	49·3
1	7	2	19·3	18·7	- 2	4	2	11·4	9·6	- 5	3	2	32·6	35·5
3	7	2	28·0	30·2	- 2	5	2	9·1	8·9	- 5	4	2	15·3	14·6
4	7	2	11·0	10·1	- 2	6	2	14·5	13·3	- 5	5	2	36·3	39·4
5	7	2	6·3	5·5	- 2	7	2	18·7	16·5	- 5	6	2	8·7	8·4
6	7	2	15·3	16·5	- 2	8	2	28·1	28·6	- 5	7	2	4·8	4·1
0	8	2	5·4	6·0	- 2	9	2	11·9	11·2	- 5	8	2	7·3	8·0
1	8	2	28·7	28·3	- 3	1	2	12·2	11·0	- 6	0	2	18·7	18·0
2	8	2	11·6	11·3	- 3	2	2	26·6	31·2	- 6	1	2	17·2	16·2
4	8	2	4·1	3·9	- 3	3	2	67·4	79·7	- 6	3	2	17·4	18·0
0	9	2	6·3	5·4	- 3	4	2	25·5	22·6	- 6	4	2	31·4	33·3
1	9	2	10·7	9·3	- 3	5	2	16·5	15·4	- 6	5	2	8·5	8·9
2	9	2	12·5	11·9	- 3	6	2	4·0	4·9	- 6	7	2	15·2	15·4
0	10	2	13·0	15·1	- 3	7	2	9·8	8·4	- 7	1	2	5·7	4·8
- 1	1	2	3·2	2·7	- 3	9	2	8·4	7·8	- 7	2	2	25·3	28·4
- 1	3	2	28·5	36·2	- 4	0	2	11·3	10·8	- 7	3	2	10·2	10·2
- 1	4	2	15·6	13·8	- 4	1	2	10·6	9·3	- 7	4	2	22·0	24·0
- 1	5	2	27·8	26·0	- 4	2	2	6·3	6·3	- 7	6	2	18·8	19·9
- 1	6	2	16·8	15·7	- 4	3	2	39·6	44·0	- 8	0	2	20·1	20·0
- 1	7	2	15·3	13·7	- 4	4	2	17·7	17·1	- 8	1	2	13·3	14·5
- 1	8	2	5·4	5·1	- 4	5	2	12·1	11·4	- 8	2	2	26·8	29·5
- 1	9	2	12·2	11·5	- 4	6	2	11·5	11·4	- 8	3	2	12·3	12·4
- 1	10	2	12·2	11·4	- 4	7	2	23·3	24·1	- 8	5	2	6·5	7·6
- 2	0	2	35·5	31·7	- 4	8	2	9·0	9·1	- 9	1	2	12·4	13·2
- 2	1	2	6·7	8·4	- 4	9	2	29·9	32·4	- 9	2	2	9·7	4·7

shifts in one cycle were less than 3 % of the standard deviations, at which stage the discrepancy index, R, was down to 0.076. Hughes' weighting function $w = h^{-2}|F_{obs},\min|^{-2}$ for $|F_{obs}| \leq h/F_{obs},\min|$ and $w = |F_{obs}|^{-2}$ for $F_{obs} > |F_{obs},\min|$ with $h = 3.5$ was used in the input cycle of the refinement. A weight analysis obtained in the last cycle is given in Table 2.

A list of the observed and calculated structure factors is presented in Table 3.

A three-dimensional difference synthesis calculated over the asymmetric part of the unit cell at points 0.2 Å apart showed no maxima higher than about 20 % of the heights of the oxygen peaks in the electron density functions. From these calculations as well as from a computation of the interatomic

Table 4. The structure of $Mg_3(PO_4)_2$.

Space group: No. 14, $P2_1/n$.
Unit-cell dimensions: $a = 7.5957 \pm 8$ Å
$b = 8.2305 \pm 5$ Å
$c = 5.0775 \pm 5$ Å
$\beta = 94.05° \pm 0.01°$

Cell content: 2 $Mg_3(PO_4)_2$.

4 P, 4 Mg_1, 4 O_1, 4 O_2, 4 O_3, and 4 O_4 in $6 \times 4(e)$:

$\pm (x,y,z)$; $\pm (\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$

2 Mg_2 in $2(c)$: $(0,0,\frac{1}{2})$; $(\frac{1}{2},\frac{1}{2},0)$

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B)$ Å^2
Mg_1	0.6095 ± 3	0.1432 ± 3	0.0920 ± 8	0.47 ± 0.04
Mg_2	0	0	$\frac{1}{2}$	0.37 ± 0.05
P	0.1996 ± 2	0.1946 ± 2	0.0355 ± 6	0.33 ± 0.03
O_1	0.0589 ± 6	0.1446 ± 6	0.8188 ± 18	0.51 ± 0.08
O_2	0.1262 ± 6	0.1995 ± 6	0.3036 ± 16	0.56 ± 0.08
O_3	0.2592 ± 6	0.3629 ± 6	0.9470 ± 16	0.37 ± 0.08
O_4	0.3545 ± 6	0.0759 ± 6	0.0459 ± 16	0.27 ± 0.07

distances which were found to be of reasonable lengths (see below), further evidence was obtained that the atomic parameters arrived at in the last cycle and listed in Table 4 represent an adequate description of the structure of $Mg_3(PO_4)_2$.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure of $Mg_3(PO_4)_2$ may be described as consisting of PO_4 tetrahedra held together by magnesium ions to give a three-dimensional array. The magnesium ion in the twofold position (Mg(2)) coordinates oxygen

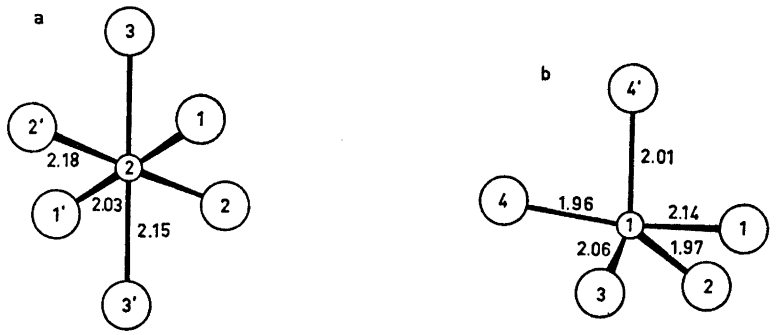

Fig. 1. The coordination of oxygen atoms (large circles) around the magnesium atoms (small circles) in $Mg_3(PO_4)_2$. The atoms have been numbered as in Tables 4 and 5. a) The MgO_6 octahedron. b) The MgO_5 polyhedron.

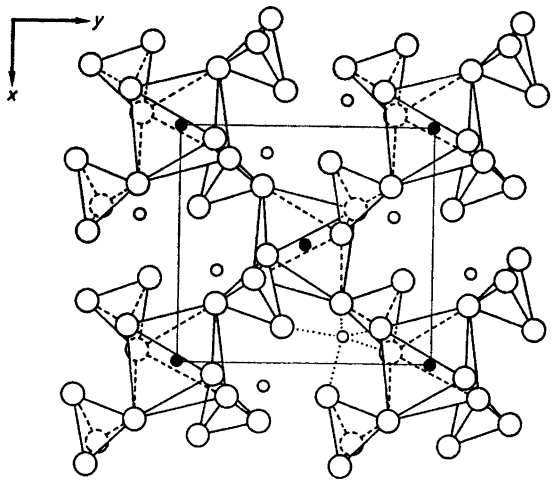

Fig. 2. The structure of $Mg_3(PO_4)_2$. Schematic drawing showing the links between MgO_6 octahedra and PO_4 tetrahedra. Large open circles denote oxygen atoms and small filled ones the magnesium (Mg(2)) atoms, octahedrally surrounded by six oxygen atoms. Small open circles denote the magnesium (Mg(1)) atoms which have five oxygen atom neighbours. One of the MgO_5 polyhedra thus formed is indicated.

atoms of six different PO_4 tetrahedra while the magnesium in the fourfold position (Mg(1)) has five oxygen atom neighbours belonging to four different PO_6 tetrahedra. The coordination numbers of the magnesium atoms are thus six and five corresponding to a somewhat distorted MgO_6 octahedron and a rather irregular MgO_5 polyhedron. The magnesium-oxygen polyhedra are shown in Fig. 1 and the linking between the PO_4 tetrahedra and the magnesium-oxygen polyhedra is represented in Fig. 2.

The interatomic distances and standard deviations (σ) and also some angles are listed in Table 5. The average P—O distance within the phosphate group is 1.52_6 Å and the average angle O—P—O is 109.5°. These values are in good agreement with those found in other well-refined orthophosphates.[7-8]

Table 5. Interatomic distances (Å) and standard deviations ($\pm$ σ in Å) and some angles in $Mg_3(PO_4)_2$.

PO_4 group	$P-O_1$	1.535 ± 8	O_1-P-O_2	111.77°
	$P-O_2$	1.508 ± 8	O_1-P-O_3	103.72°
	$P-O_3$	1.534 ± 6	O_1-P-O_4	110.43°
	$P-O_4$	1.527 ± 5	O_2-P-O_3	112.08°
	O_1-O_2	2.519 ± 12	O_2-P-O_4	108.61°
	O_1-O_3	2.413 ± 7	O_3-P-O_4	110.19°
	O_1-O_4	2.515 ± 8	Average:	109.47°
	O_2-O_3	2.523 ± 10		
	O_2-O_4	2.465 ± 8		
	O_3-O_4	2.510 ± 7		
MgO_6 group	$Mg_2-2\ O_1$	2 × 2.034 ± 8	$O_1-Mg_2-O_2$	81.03°
	$Mg_2-2\ O_2$	2 × 2.179 ± 6	$O_1-Mg_2-O_2'$	98.97°
	$Mg_2-2\ O_3$	2 × 2.150 ± 5	$O_1-Mg_2-O_3$	85.97°
			$O_1-Mg_2-O_3'$	94.03°
	O_1-O_2	2.739 ± 12	$O_2-Mg_2-O_3$	86.84°
	O_1-O_2'	3.204 ± 7	$O_2-Mg_2-O_3'$	93.16°
	O_1-O_3	2.854 ± 9	Average:	90.00°
	O_1-O_3'	3.062 ± 8		
	O_2-O_3	2.975 ± 7		
	O_2-O_3'	3.144 ± 8		
MgO_5 group	Mg_1-O_1	2.142 ± 7	$O_1-Mg_1-O_2$	83.52°
	Mg_1-O_2	1.965 ± 8	$O_1-Mg_1-O_3$	70.02°
	Mg_1-O_3	2.063 ± 8	$O_1-Mg_1-O_4'$	94.53°
	Mg_1-O_4'	2.012 ± 5	$O_1-Mg_1-O_4$	167.68°
	Mg_1-O_4	1.961 ± 6	$O_2-Mg_1-O_3$	127.34°
			$O_2-Mg_1-O_4'$	101.93°
	O_1-O_2	2.739 ± 12	$O_2-Mg_1-O_4$	108.76°
	O_1-O_3	2.423 ± 7	$O_3-Mg_1-O_4'$	124.16°
	O_1-O_4'	3.052 ± 8	$O_3-Mg_1-O_4$	102.00°
	O_1-O_4	4.078 ± 14	$O_4-Mg_1-O_4'$	82.12°
	O_2-O_3	3.611 ± 20	Average:	106.21°
	O_2-O_4'	3.090 ± 8		
	O_2-O_4	3.192 ± 7		
	O_3-O_4	3.128 ± 10		
	O_3-O_4'	3.601 ± 15		
	O_4-O_4'	2.610 ± 6		

Table 6.

	$Mg_3(PO_4)_2$	γ-$Zn_3(PO_4)_2$	$Co_3(PO_4)_2$	
a	7.557	7.545	7.557	(Å)
b	8.365	8.469	8.365	(Å)
c	5.067	5.074	5.067	(Å)
β	94.05	94.41	94.05	(°)
V	316.6	323.1	319.5	(Å^3)

The lattice parameters of $Mg_3(PO_4)_2$, γ-$Zn_3(PO_4)_2$,[9] and $Co_3(PO_4)_2$[10] are very similar (*cf.* Table 6). As a matter of fact Sarver, Katnack and Hummel[11] as early as 1958 suggested that the two former phases are isomorphous. The crystal structure analysis of γ-$Zn_3(PO_4)_2$ recently reported by Calvo[9] gave atomic parameters rather close to those now found for the magnesium compound. A detailed comparison of the two structures, however, discloses some interesting differences.

Calvo describes the cation-oxygen coordination of γ-$Zn_3(PO_4)_2$ as 6-fold, octahedral for one-third and as 4-fold, tetrahedral for two-thirds of the zinc ions. The Zn—O distances within the tetrahedra are 1.98—2.16 Å. An additional oxygen atom is removed to a distance of >2.4 Å (according to the refinement of the structure reported in Ref. 12). The standard deviations of these distances are given by Calvo as being around ± 0.10 Å. It seems quite reasonable to describe this atomic arrangement as a ZnO_4 tetrahedron. In the magnesium compound, however, the oxygen environment around the Mg(1) atoms is clearly a five-fold one, the Mg—O distances being 1.96—2.14 Å with a standard deviation (σ) of < ± 0.01 Å. In spite of the two phases being clearly isomorphous the coordination conditions are thus markedly different. This, however, might be explained by the assumption that the Zn—O bonds in γ-$Zn_3(PO_4)_2$ are more covalent in character than the five Mg—O bonds in $Mg_3(PO_4)_2$. The kind of MgO_5 polyhedra found in $Mg_3(PO_4)_2$ is a rare coordination group although not a unique one. As a matter of fact Calvo[13] in his structural analysis of α-$Mg_2P_2O_7$ has found MgO_5 polyhedra (with Mg—O distances ranging from 1.985 to 2.120 Å) as well as MgO_6 octahedra.

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