X-Ray Powder Diffraction Study of Layer Compounds. The Crystal Structure of α-$Ti(HPO_4)_2 \cdot H_2O$ and a Proposed Structure for γ-$Ti(H_2PO_4)(PO_4) \cdot 2H_2O$

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α-$Ti(HPO_4)_2 \cdot H_2O$ was investigated by X-ray powder diffraction methods. A profile least-squares analysis of the X-ray data proved the substance to be isostructural with α-$Zr(HPO_4)_2 \cdot H_2O$. The lattice parameters are a = 8.630(2), b = 5.006(1), c = 16.189(3) Å, β = 110.20(1)°, Z = 4, space group $P2_1/c$ (No. 14).

The basic features of the structure of γ-$TiH_2P_2O_8 \cdot 2H_2O$ were found by a combination of direct methods and packing considerations. A partial model was refined. The model is in accordance with NMR results and shows that the compound shall be formulated $Ti(H_2PO_4)(PO_4) \cdot 2H_2O$. The lattice parameters for the partial model are a = 5.181(1), b = 6.347(1), c = 11.881(1) Å, β = 102.59(1)°, Z = 2, space group $P2_1$ (No. 4).

Since the first preparative studies by Clearfield and Stynes[1] and by Alberti and Torracca[2] of α-$Zr(HPO_4)_2 \cdot H_2O$, many phosphates and arsenates of tetravalent metals (Zr, Ti, Ce, Sn, Th) have been synthesized and investigated. It was discovered that there are two different structures of the layers (usually named the alpha and gamma layers).[3,4] An extremely large number of different phases have been obtained either by exchange of the protons of α- and γ-compounds with other cations or by intercalation of polar molecules (water, amines, alcohols, etc.) in the interlayer region. This number has been further increased with the discovery that many organic derivatives of α-zirconium phosphate can be synthesized[5] and that asymmetric layers are usually present[6] in mixed compounds (e.g. zirconium phosphate–phosphite, zirconium phosphate–phosphonate, etc.). Many of these compounds are of interest for practical application in various fields (ion exchange, intercalation, proton conduction, heterogenous catalysis, molecular sorption, etc.); therefore they have been intensely studied and hundreds of publications have appeared in the literature (for recent reviews see Refs. 4 and 7–9). However, only few papers deal with structure determinations, and the structure of the γ-layer is yet unknown. The reason for that is that the compounds are usually obtained as microcrystalline powders, and it is, with few exceptions, difficult to obtain single crystals large enough for X-ray structure determination. Another complication is that when the salt forms are obtained by ion exchange, the crystal quality is reduced to such an extent that detailed structure investigations are difficult.

The materials for which the structures have been solved by single-crystal methods are α-$Zr(NH_4PO_4)_2 \cdot H_2O$[10] and α-$Zr(HPO_4)_2 \cdot H_2O$.[11]

The structures of α-$ZrKH(PO_4)_2$,[12] α-$ZrNaH(PO_4)_2$,[13] α-$ZrNaH(PO_4)_2 \cdot H_2O$,[14] $Zr(HPO_3)_2$,[6] $Zr(HPO_4)_{0.85}(HPO_3)_{1.15} \cdot 0.5H_2O$ [6] and α-$Zr(HPO_4)_2 \cdot H_2O$ [15] have been investigated by powder diffraction methods, the latter by neutrons, the first five by X-rays. All the structure determinations have shown the compounds to have a characteristic layer structure.

Clayden[16] investigated the ^{31}P-MASNMR spectra of α-zirconium phosphate and γ-zirconium phosphate. The former showed only one ^{31}P resonance, the latter showed two resonances of equal integrated intensity. Clayden interpreted his observations as follows: "A rather large difference in chemical shift of 18 ppm is observed for these two resonances, which suggests two chemically distinct types of phosphate group rather than two similar but crystallographically inequivalent phosphorus atoms. Additional support for this interpretation is provided by the chemical shift anisotropies of these two resonances." Clayden gave further support to this interpretation by studies of incorporation of phenyl phosphate in the γ-zirconium phosphate. In conclusion, Clayden considers the phase to contain terti-

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ary phosphate groups and dihydrogen phosphate groups in equal amounts. Therefore the formula for γ-ZrP should be written γ-$Zr(H_2PO_4)(PO_4)\cdot 2H_2O$.

The present report is concerned with further investigations of the nature of layer compounds by application of powder diffraction techniques. The compounds we have investigated are hydrates of α-titanium phosphate and of γ-titanium phosphate. The formula for the α-compound is α-$Ti(HPO_4)_2\cdot H_2O$ (in the following it is called α-TiP). The formula for the γ-compound has previously been written as γ-$Ti(HPO_4)_2\cdot 2H_2O$, but in view of Clayden's investigation we prefer to formulate our compound as γ-$Ti(H_2PO_4)(PO_4)\cdot 2H_2O$ (in the following it is called γ-TiP). The crystal structure of α-TiP was refined by a profile least-squares analysis[17] using X-ray powder diffraction data, and the structure is shown to be isostructural with that of α-ZrP

Table 1. Unit cell parameters in Å and ° of titanium and zirconium phosphates.

Chemical formula	Notation	*a*	*b*	*c*	β	Space group
α-$Zr(HPO_4)_2\cdot H_2O$	α-ZrP	9.062(1)	5.288(1)	16.255(2)	111.38(1)	$P2_1/c$
α-$Ti(HPO_4)_2\cdot H_2O$	α-TiP	8.630(2)	5.006(1)	16.189(3)	110.20(1)	$P2_1/c$
γ-$Ti(HPO_4)_2\cdot 2H_2O$	γ-TiP	5.181(1)	6.347(1)	11.881(1)	102.59(1)	$P2_1$
γ-$Ti(HPO_4)_2\cdot 2H_2O$	γ-TiP	5.178(2)	23.149(4)	6.343(2)		*Cmcm*

Table 2. X-Ray powder pattern of α-$Ti(HPO_4)_2\cdot H_2O$.

d_{obs}/Å	d_{calc}			I/I_0	*h* *k* *l*					
7.604	7.569			80	0 0 2					
4.261	4.258			35	1 1 0					
4.232	4.231			30	2 0 −2					
4.046	4.041			20	1 1 −2					
3.457	3.457			90	1 1 2					
3.422	3.422			75	2 0 −4					
3.150	3.149			5	2 1 0					
3.026	3.026			5	0 1 4					
2.876	2.877			10	3 0 −2					
2.611	2.609			35	1 1 4					
2.585	2.586			10	2 0 −6					
2.533	2.532			45	0 0 6					
2.503	2.503			90	0 2 0					
2.494	2.494			100	3 1 −2					
2.390	2.389			5	2 0 4					
2.374	2.374			15	1 1 −6					
2.244	2.244	2.246		40	0 2 3	3 1 1				
2.157	2.156			10	2 1 4					
2.022	2.021	2.020	2.025	50	1 1 6	2 2 −4			4 0 0	
1.960	1.960			35	2 2 2					
1.942	1.942			5	4 0 −6					
1.875	1.876			10	2 0 6					
1.865	1.865	1.862		25	1 1 −8	2 1 −8				
1.728	1.728			45	2 2 4					
1.711	1.711			40	4 0 −8					
1.575	1.574	1.575		85	4 2 0	1 3 2				
1.565	1.564			55	5 1 −6					
1.527	1.528			10	0 3 4					
1.518	1.517			5	3 1 6					
1.504	1.504			5	3 1 −10					
1.501	1.501			5	2 2 6					
1.465	1.465	1.465		5	1 3 4	4 2 2				
1.443	1.444			5	3 3 −2					
1.439	1.438			5	6 0 −4					
1.418	1.419	1.419		5	1 3 −6	1 2 8				
1.412	1.413			5	4 2 −8					
1.252	1.252			5	0 4 0					
1.247	1.247			5	2 3 6					
1.175	1.175			5	4 1 −13					
1.173	1.172			5	5 3 −6					

Table 3. Atomic coordinates for the structure of α-Ti(HPO$_4$)$_2$·H$_2$O. a = 8.630(2), b = 5.006(1), c = 16.189(3) Å, β = 110.20(1)°, $P2_1/c$. R = 3.4 %, R_w = 4.7 %,[a] $R_{expected}$ = 3.0 %.

Atom	x	y	z
Ti	0.755(26)	0.242(48)	0.518(23)
P1	0.039(47)	0.719(65)	0.622(34)
P2	0.473(47)	0.295(79)	0.597(35)
O1	0.105	0.806	0.560
O2	−0.066	0.486	0.601
O3	−0.131	0.941	0.589
O4	0.104	0.760	0.716
O5	0.344	0.443	0.562
O6	0.418	−0.014	0.569
O7	0.625	0.314	0.590
O8	0.512	0.243	0.705
O9	0.254	0.235	0.759

[a]Isotropic temperature factor parameters B/Å^2 were not refined, but the values reported for the atoms in Ref. 15 were used in the calculations, and only the positional parameters for Ti, P1 and P2 were refined. The R-values are defined as follows:

$$R = 100\Sigma|y_{obs} - y_{calc}|/\Sigma y_{obs}$$

$$R_w = 100(\Sigma(y_{obs} - y_{calc})^2 W/\Sigma y^2_{obs} W)^{\frac{1}{2}}$$

$$R_{expected} = 100[(N-P)\Sigma w y^2_{obs}]^{\frac{1}{2}}.$$

[α-Zr(HPO$_4$)$_2$ · H$_2$O]. The crystal chemistry of γ-TiP was investigated by X-ray powder diffraction data. The basic features of the structure were established by direct methods using integrated intensities from a synchrotron X-ray diffraction pattern and from packing considerations. The partial model for γ-TiP was refined by a least-squares profile analysis.[17]

Experimental

Investigation of α-TiP. The compound was made from titanium powder (Fluka) and 5 M H$_3$PO$_4$ as described by Tegehall.[18] A Guinier diagram was taken with a Guinier–Hägg camera, using Cu $K\alpha_1$ radiation (λ = 1.540 51 Å) and quartz as an internal standard. The 2θ values of the photograph were measured with an optical photometer and on an Abbé comparator. The powder pattern was indexed with a monoclinic cell.[19] The lattice constants reported in Table 1 are in good agreement with the values reported by Clearfield.[20] The indexed pattern is listed in Table 2. The compound was assumed to be isostructural with α-ZrP [α-Zr(HPO$_4$)$_2$·H$_2$O]. The intensities of the powder photograph were calculated using atomic coordinates from Ref. 15 and the space group $P2_1/c$. These calculations, performed with the program LAZY-PULVERIX,[21] showed that the calculated intensities were in qualitative agreement with the intensities observed in the Guinier photograph. It was then very likely that α-TiP is isostructural with α-ZrP.[8]

The powder pattern of α-TiP was also measured on a Stoe diffractometer with a position sensitive detector, using Cu $K\alpha_1$ radiation. The diffractometer was calibrated with a standard $Ag_6Ge_{10}P_{12}$ sample (a = 10.318 Å). This powder pattern was used in a profile refinement[17] of the structure. The atomic coordinates from the structure of α-ZrP were used as starting parameters, and only the positions of titanium and two phosphorus atoms were refined. The least-squares program EDINP[22] was used with scattering factors for neutral atoms.[23] The coordinates for the atoms are listed in Table 3, and Fig. 1 shows the observed and calculated profiles of the powder pattern and a difference plot.

Investigation of γ-TiP. Microcrystalline γ-TiP was prepared by a slow decomposition of titanium fluorocomplexes at 60 °C as described by Alberti *et al.*[24] Many attempts have been made to obtain larger crystals of γ-TiP. In a special preparation thin, plate-shaped crystals were obtained by the following procedure. An amount of amorphous titanium phosphate containing 0.0062 mol titanium was placed in a glass vial. After addition of 30 ml of 8 M phosphoric acid the vial was sealed and placed in an automatic shaker for 24 h. Then the vial was placed in a hydrothermal bomb. The bomb was placed in an oven and heated to 250 °C for 24 h. After cooling in air the vial was opened and the crystals were separated by centrifugation. They were washed with water until the pH was 4 and dried in air at room temperature.

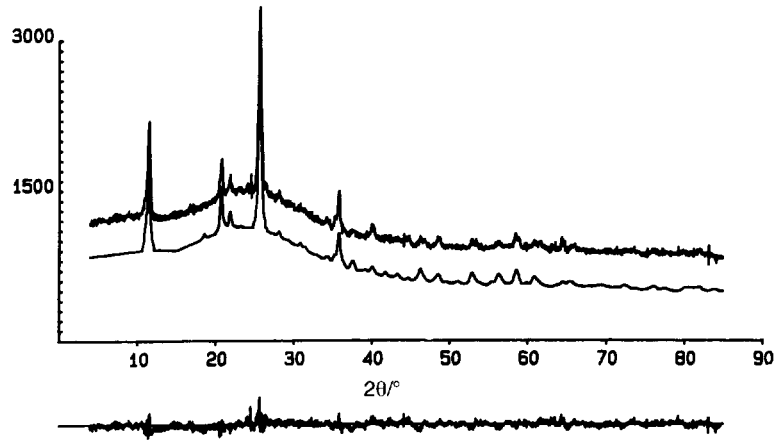

Fig. 1. Stoe X-ray diffraction pattern of α-Ti(HPO$_4$)$_2$·H$_2$O. Upper curve, observed, and lower curve, calculated, pattern, with data listed in Table 3. Below: a difference plot. λ(Cu $K\alpha_1$) = 1.540 51 Å.

This material was used in an attempt to determine the crystal system and space group of γ-TiP (see below). The larger crystals in this preparation had a size of 0.5×0.1×0.01 mm. They were, however, all composed of several extremely thin plates in slightly different orientations.

X-Ray diffraction of 'single' crystals. No truly 'single' crystals large enough for diffraction experiments were found in the samples. Several of the thin plate-shaped crystals mentioned earlier in this section were, despite their imperfection, used for obtaining oscillation, Weissenberg and precession photographs. From the oscillation diagrams (taken with the long dimensions of the crystals as oscillation axis) a repeat distance of 6.3 Å was measured (this axis was called *c*). The oscillation diagrams showed a mirror plane perpendicular to the oscillation axis. A precession zero-layer photograph taken with the *c* axis as dial axis and with the beam perpendicular to the plate face of the crystal showed, in addition to the *c* axis already found (measured now as 6.3), and axis of 5.1 Å (this axis was called *a*). There were mirror lines in this photograph along the a^* and c^* axes. Furthermore, systematic extinctions of $h00$ ($h = 2n+1$) and $00l$($l = 2n+1$) were observed. The Weissenberg diagrams of all the crystals showed strongly extended reflections, and they also showed some weak reflections in positions not compatible with only one reciprocal lattice. If, however, only strong reflections were taken into account, two mirror lines along a^* and b^* were observed. The reflections $h00$ ($h = 2n+1$), $0k0$ ($k = 2n+1$) and $0k1$ ($k = 2n+1$) were probably extinct.

Table 4. X-Ray powder patterns.

γ-Ti(HPO$_4$)$_2$·2H$_2$O[a]						γ-Ti(HPO$_4$)$_2$	
d_{obs}	d_{calc}[b]	I/I_0	h	k	l	d	I/I_0
11.60	11.59	100	0	0	1	9.210	65
5.560	5.567	50	0	1	1	5.205	60
4.297	4.303	20	1	0	−2	4.486	15
3.951	3.955	5	1	1	−1	3.419	85
3.854	3.865	5	0	0	3	3.156	100
3.558	3.562	5	1	1	−2	2.989	5
3.450	3.456	20	1	0	−3	2.415	5
3.300	3.301	10	0	1	3		
3.170	3.174	15	0	2	0		
3.058	3.061	10	0	2	1		
3.031	3.035	5	1	1	−3		
2.786	2.784	1	1	0	−4		
2.590	2.591	10	2	0	−1		
2.552	2.555	10	1	1	−4		
2.526	2.528	10	2	0	0		
2.450	2.453	10	0	2	3		
2.336	2.337	10	1	2	−3		
2.315	2.319	1	0	0	5		
2.304	2.307	5	1	0	4		
2.217	2.216	5	2	1	−3		
2.169	2.169	5	1	1	−5		
2.150	2.152	5	2	0	2		
2.094	2.096	5	1	2	−4		
2.080	2.081	10	0	3	1		
1.986	1.988	5	0	3	2		
1.951	1.952	5	1	3	0		
1.930	1.932	5	2	0	3		
1.896	1.896	1	2	2	1		
1.846	1.849	5	0	1	6		
1.804	1.804	5	1	3	2		
1.726	1.728	5	2	0	4		
1.685	1.686	10	1	3	3		
1.665	1.667	10	2	1	4		
1.654	1.656	5	0	0	7		
1.650	1.650	5	2	2	3		
1.618	1.619	10	3	0	−4		
1.586	1.587	10	0	4	0		
1.576	1.577	5	2	3	−3		
1.572	1.572	10	0	4	1		
1.558	1.559	10	1	3	−5		

						1	0	1
						1	0	2
						1	1	2
						1	2	2
						1	0	−5
						0	2	4
						1	0	−6
						2	0	−5
						1	3	−3
						1	3	−4
						1	2	−6
						3	0	1
						2	3	1
						3	1	−4
						0	3	5

[a] Monoclinic indexing. a = 5.181(1), b = 6.347(1), c = 11.881(1) Å, β = 102.59(1)°. [b] d_{calc} is made in space group $P2_1$.

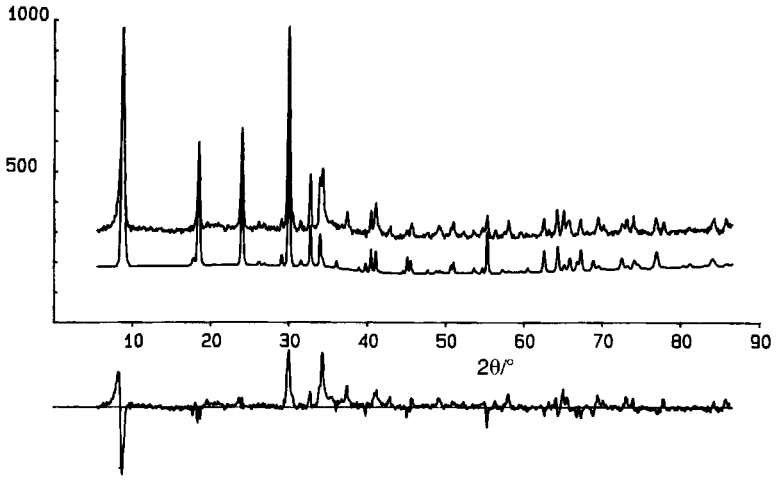

Fig. 2. Stoe X-ray diffraction pattern of γ-$Ti(H_2PO_4)(PO_4)\cdot 2H_2O$. Upper curve, observed, and lower curve, calculated, pattern, using space group *Cmcm*, R = 8.3 %. $R_{expected}$ = 7.9 %. λ(Co $K\alpha_1$) = 1.7889 Å.

From the Weissenberg films axes a = 5.2 and b = 23.5 Å were measured. The conclusions from this investigation by 'single-crystal' methods are that the material is most likely orthorhombic, C-centred and has axes a = 5.2, b = 23.5 and c = 6.3 Å.

X-Ray diffraction of powders. Powder patterns of anhydrous and dihydrated γ-TiP were recorded with a Guinier–Lenné camera, using Cu $K\alpha_1$ radiation (λ = 1.540 51 Å) and silicon as an internal standard. The powder patterns were also measured on a Stoe diffractometer with a position-sensitive detector, using Co $K\alpha_1$ (λ = 1.7889 Å) radiation. The diffractometer was calibrated with a standard $Ag_6Ge_{10}P_{12}$ sample (a = 10.318 Å).

The powder patterns are listed in Table 4. They are in agreement with the previously reported patterns for anhydrous γ-TiP[25] and for the dihydrate of γ-TiP.[24,26] The pattern of γ-TiP is displayed in Fig. 2.

The powder pattern of γ-TiP was also measured at the W1 wiggler beam line at Hamburg Synchrotron Strahlungslabor (HASYLAB) with a general purpose diffractometer[27] modified for powder diffraction measurements. A linear detector covering an angular range 2.7° was used in a step scanning mode to measure the powder pattern at room temperature. Details of the experimental set-up are described elsewhere.[28] The sample was kept in a 0.3 mm diameter capillary and was rotated during the measurement to reduce the effect of preferred orientation. Fig. 3 shows the powder pattern.

Indexing of the powder pattern. The Guinier photograph and the pattern from the Stoe diffractometer showed a strong reflection at 11.6 Å. The synchrotron X-ray powder pattern from HASYLAB had a great number of sharp diffraction peaks, but the first reflection at 11.6 Å was unfortunately not included. This latter pattern was indexed using the program FZON,[19] with a C-centred cell a = 5.178, b = 23.149, c = 6.343 Å. The volume of this cell is 760 $Å^3$. When the reflection at d = 11.6 Å was added to the pattern, FZON gave a monoclinic solution to the indexing in addition to the orthorhombic. The de Wolff figures of merit M_{20} for the two solutions to the indexing of the powder patterns were 46 and 20, respectively. The unit cell parameters for the monoclinic cell are a = 5.181, b = 6.347, c = 11.881 Å and β = 102.59°. This cell has a volume of 380 $Å^3$, and is related to the orthorhombic cell. The

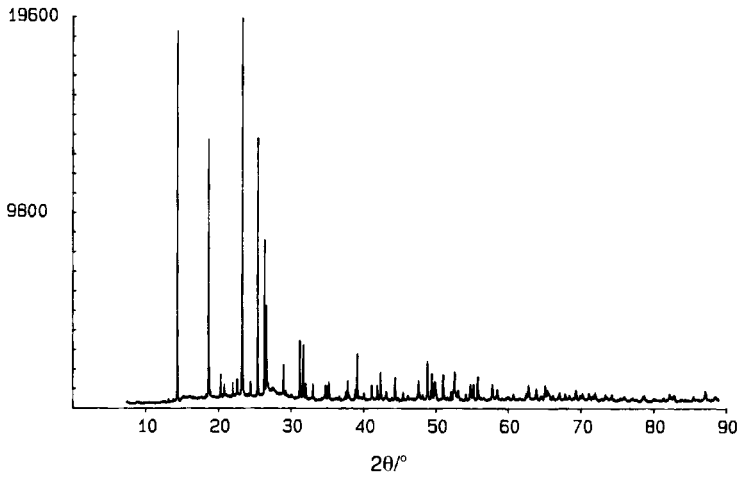

Fig. 3. Synchrotron X-ray pattern of γ-$Ti(H_2PO_4)(PO_4)\cdot 2H_2O$ (HASYLAB). λ = 1.392 Å.

diagonal in the *ab*-plane of the orthorhombic cell is twice the *c* axis in the monoclinic cell. A monoclinic cell has been suggested by Kobayashi.[29] This cell is close to that derived by Alberti[4] on the basis of the γ-ZrP cell determined by Yamanaka and Tanaka.[30]

In the following, attempts to find a model for the structure using both orthorhombic and monoclinic space groups are described.

Structure model in space group Cmcm. The powder pattern recorded on the Stoe diffractometer is shown in Fig. 2. The first five strong reflections are the 020, 021, 130, 150 and 002 (orthorhombic indexing). The scattering contribution per atom of the compound is Ti, 31 %; P, 14 %; O, 4 %, and the strong reflections 020 and 002 indicate a certain layer character of the structure in the (010) and (001) directions. In the space group *Cmcm* possible sites for the titanium and phosphorus atoms would be the 4*c* site 0, $-y$, $\frac{1}{4}$; 0, y, $\frac{3}{4}$; $\frac{1}{2}$, $\frac{1}{2}+y$, $\frac{1}{4}$; $\frac{1}{2}$, $\frac{1}{2}-y$, $\frac{3}{4}$; this would account for the layer nature along the *b* and *c* directions. The reflections 150 and 130 will have large contributions for y equal to 0.20 and 0.17, respectively. Thus a position for the Ti atom would be 0, 0.185, $\frac{1}{4}$.

The observed reflections of the powder pattern correspond well with the space group *Cmcm*. However, of the first 45 reflections in the pattern recorded at HASYLAB no reflection of the type *h0l* was found. This is possibly an indication that *Cmcm* is not the correct space group.

In the packing considerations described in the following the dimensions of TiO_6 octahedra were taken from the structure of rutile[31] and dimensions of PO_4 tetrahedra from the structure of potassium dihydrogen phosphate.[32] These dimensions are for the titanium–oxygen octahedron Ti–O distances 1.95–1.98 Å and O–O distances of 2.54–2.96 Å, and for the phosphate group P–O distances of 1.54 Å and O–O distances of 2.52 Å.

The *a* axis of γ-TiP (5.178 Å) corresponds well with the O–O distance of an TiO_6 octahedron and a PO_4 tetrahedron stacked on top of each other. The *c* axis corresponds to two Ti–O distances of an TiO_6 octahedron and the O–O distance of a PO_4 tetrahedron. These considerations and the assumed Ti atom position (at 0, 0.185, $\frac{1}{4}$) gave the model of the structure shown in Fig. 4.

A total of 204 structure factors were extracted from the synchrotron data using the program ALLHKL[33] with the unit cell a = 5.178, b = 23.149, c = 6.343 Å. Of these structure factors 132 have $F > 3\sigma(F)$ and these were used with the MULTAN programs.[34] Forty-five structure factors had E-values > 1.20, and they combined with 15 of the structure factors with the smallest E-values to give 119 phase relations. The number of phases with a probability > 0.95 or a number of contributions > 3 was 18. The solution obtained is listed in Table 5. It is observed that the highest peak corresponds to the expected position of the titanium atom.

A series of structure-factor and Fourier-map calculations gave the positions of the remaining atoms in the two phos-

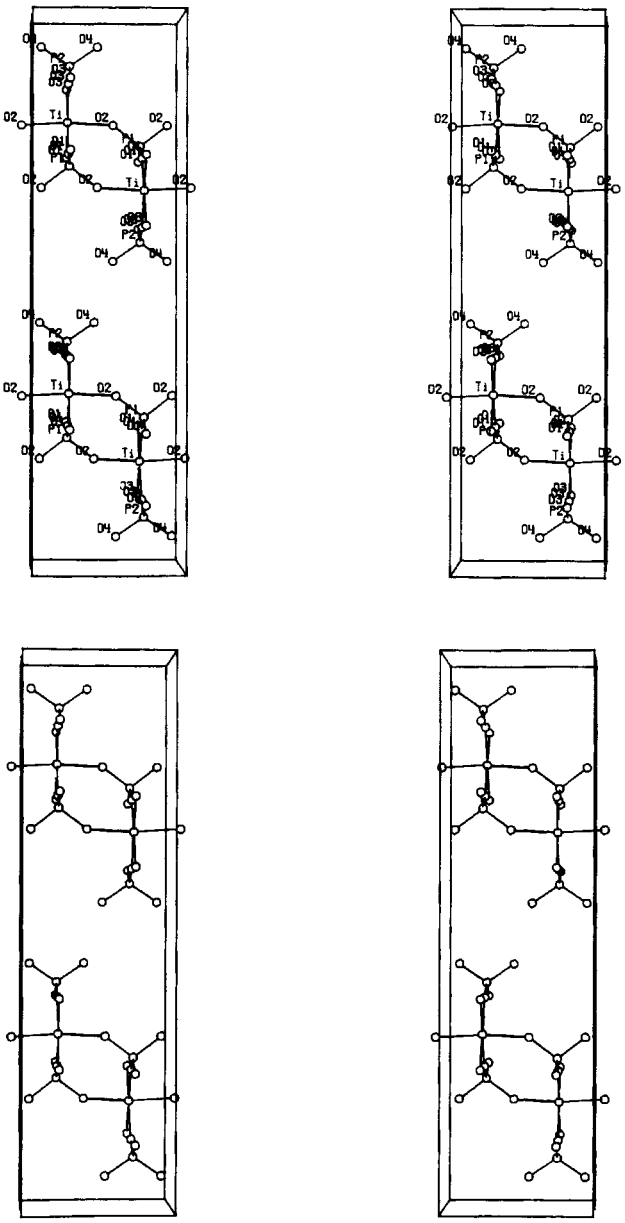

Fig. 4. Projection of proposed structure of γ-Ti(H_2PO_4)(PO_4)·2H_2O, space group *Cmcm*.

Table 5. Atomic coordinates of γ-TiP and peak heights obtained from MULTAN and from Fourier calculations and packing considerations in space group *Cmcm* (No. 63).

Atom	*x*	*y*	*z*	Peak height
Ti	0.000	0.184	0.250	4600
P1	0.000	0.772	0.250	2100
P2	0.000	0.592	0.250	1400
O1	0.250	0.746	0.250	
O2	0.000	0.811	0.063	
O3	0.250	0.618	0.250	1600
O4	0.000	0.557	0.063	

Table 6. Atomic coordinates of γ-TiP in monoclinic cells.[a]

Atom	Least-squares distance calculation in $P2_1$			Coordinates from refinements of HASYLAB data, $R_{expected}$ = 4.0 %					
				$P2_1/m$ (R = 14.4 %)			$P2_1$ (R = 12.4 %)		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Ti	0.790	0.250	0.626	0.771(2)	0.250	0.616(1)	0.804(2)	0.250	0.628(1)
P1	0.175	0.250	0.444	0.211(4)	0.250	0.453(1)	0.234(3)	0.251(3)	0.444(1)
P2	0.397	0.228	0.804	0.396(3)	0.250	0.816(1)	0.418(4)	0.147(3)	0.801(1)
O1	−0.108	0.250	0.472	−0.068(5)	0.250	0.471(2)	−0.015(5)	0.274(6)	0.509(2)
O2	0.208	0.059	0.372	0.216(7)	0.088(2)	0.376(2)	0.216(6)	0.059(6)	0.359(2)
O3	0.207	0.441	0.372	[0.216(7)	0.412(2)	0.376(2)]	0.164(6)	0.408(5)	0.371(2)
O4	0.401	0.250	0.551	0.425(5)	0.250	0.526(2)	0.438(5)	0.250(7)	0.529(2)
O5	0.683	0.249	0.778	0.625(5)	0.250	0.749(2)	0.658(4)	0.199(6)	0.757(3)
O6	0.181	0.252	0.694	0.081(5)	0.250	0.731(2)	0.107(5)	0.180(5)	0.661(2)
O7	0.363	−0.033	0.844	0.346(4)	0.037(2)	0.872(2)	0.387(8)	−0.133(3)	0.799(2)
O8	0.352	0.450	0.882	[0.346(4)	0.463(2)	0.872(2)]	0.388(7)	0.413(4)	0.857(2)

[a]The coordinates in square brackets are obtained by the symmetry operations of the space group.

phate groups and yielded the solution also arrived at by packing considerations (Fig. 4). The model was then used in a profile refinement of the synchrotron radiation data with the program EDINP.[22] The resulting R-value was 30 %. This rather high value possibly indicates that the space group for γ-TiP is not *Cmcm*. The model arrived at is consistent with a layer structure and with the fact that only the two oxygen atoms O4 per formula unit can belong to hydroxyl groups.

Structure model in the monoclinic space groups $P2_1/m$ *and* $P2_1$. As the refinements in the space group *Cmcm* did not converge, solutions in the monoclinic space groups $P2_1/m$ and $P2_1$ were tried. The unit cell has in the monoclinic case a volume half that of the unit cell in the orthorhombic case. The coordinates of the atoms were transformed and renamed for the monoclinic setting as listed in Table 6. A distance angle least-squares refinement was then made in the space group $P2_1$ using the program DALS.[35] The distances for the TiO_6 octahedra and the PO_4 tetrahedra were constrained to the values listed above. In addition, the distance between hydroxyl groups belonging to different but adjacent layers (O7 and O8) were constrained to 3.0 Å. The distance angle least-squares refinement yielded the set of coordinates listed in Table 6. The coordinates found deviate slightly from the symmetry of space group $P2_1/m$. The synchrotron X-ray pattern was then refined with the program EDINP[22] using this model. This gave the coordinates listed in Table 6 for the space groups $P2_1/m$ and $P2_1$. It was not possible in a difference Fourier map to locate the positions of the water molecules. As the average scattering contribution for an oxygen atom is only 4 % of the total scattering, it is to be expected that the coordinates of the heavy atoms Ti, P1 and P2 could be compared. The *y*-coordinate found for the P2 atom in the $P2_1$ calculations deviates significantly from the 0.250 used in the calculation in $P2_1/m$. Fig. 5 is a stereoscopic drawing of the proposed

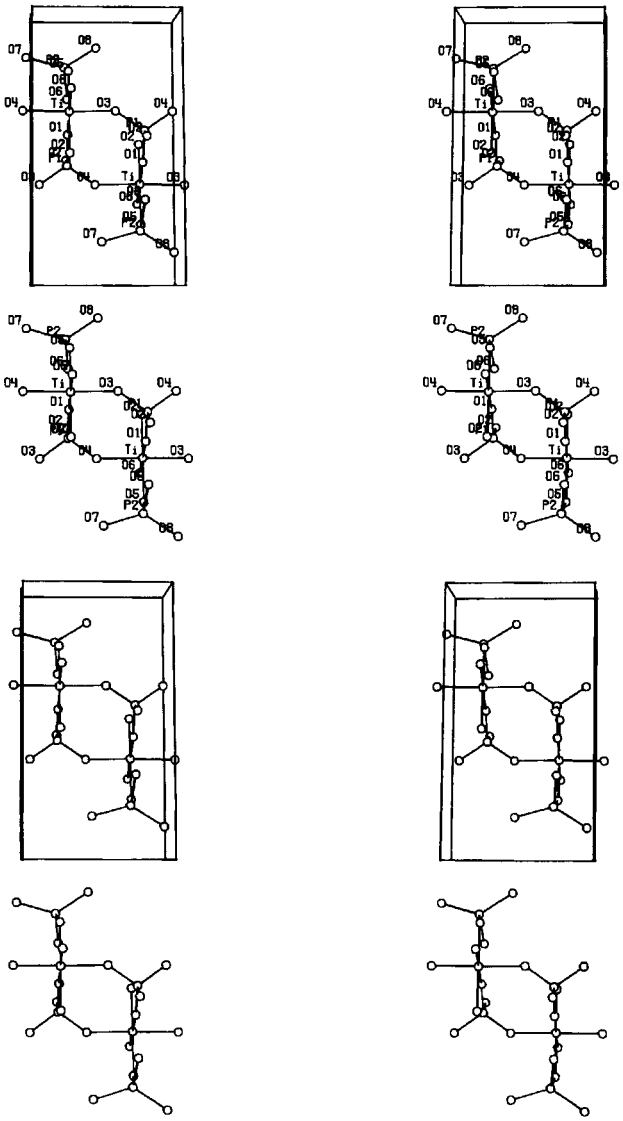

Fig. 5. Projection of proposed structure of γ-$Ti(H_2PO_4)(PO_4)\cdot 2H_2O$, space group $P2_1$.

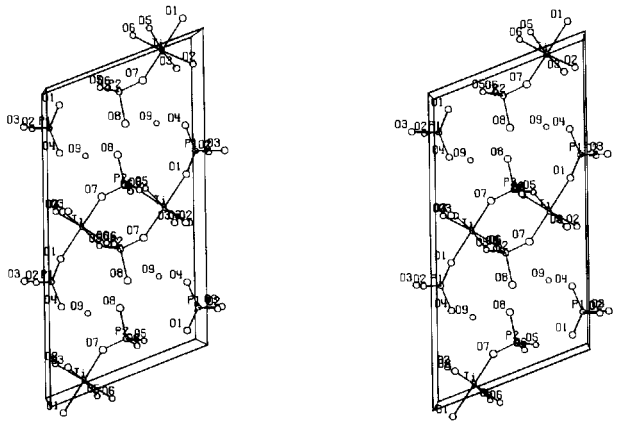

Fig. 6. Projection of structure of α-$Ti(HPO_4)_2 \cdot H_2O$.

structure of γ-TiP with the coordinates listed in Table 6 from the profile refinement of the HASYLAB data in space group $P2_1$. The layer structure is evident, cf. also Fig. 4.

Discussion

The chemical similarity between titanium and zirconium was demonstrated by showing that α-TiP and α-ZrP are isostructural. To compare the structures of the α- and γ-type families a stereoscopic drawing of α-TiP is displayed in Fig. 6, calculated from the coordinates listed in Table 3. The structure models of the γ-TiP are shown in Figs. 4 and 5.

The structure proposed for γ-TiP is incomplete and is not the final one for the compound. There is ambiguity concerning the choice of space group, and only the layers, and not the water molecules between them, have been located. However, the structure proposed for the layer suggests that the layer in γ-TiP is different from the layer in α-TiP, cf. Figs. 5 and 6. In the proposed structure of γ-TiP the phosphate is present as equal numbers of PO_4 and H_2PO_4 groups, while in α-TiP the phosphate is present as HPO_4 groups only. The chemical formula should then be written $Ti(H_2PO_4)(PO_4) \cdot 2H_2O$, in agreement with the findings by Clayden[16] from NMR experiments.

The profile fits with EDINP were not ideal. This indicates that some details of the structure of γ-TiP have not been accounted for, or that the samples investigated were not pure phases. Profile fits have also been tried with neutron diffraction powder data of deuterated γ-TiP. It was not possible with these data to obtain more information concerning the structure than already obtained with the X-ray data.

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