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Crystal Structure of Sodium Zirconium Phosphate, $Zr_2(NaPO_4)_4·6H_2O$, from X-ray Powder Diffraction Data

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The crystal structure of the completely sodium ion exchanged phase of α-zirconium phosphate, $Zr_2(NaPO_4)_4·6H_2O$, has been determined by using X-ray powder diffraction data. The partial structural model for the full-pattern refinement was derived from a combination of direct methods and heavy atom methods. The crystals belong to the triclinic space group $P1$ with $a = 8.9192(3)$ Å, $b = 10.5824(4)$ Å, $c = 5.4045(3)$ Å, $\alpha = 94.238(3)°$, $\beta = 90.164(4)°$, $\gamma = 111.013(3)°$, and $Z = 1$. The final agreement factors are $R_p = 0.101$, $R_{wp} = 0.135$, and $R_F = 0.037$. The layer structure is similar to that of the parent α-zirconium phosphate in terms of metal coordination and bridging nature of the phosphate group. The complete exchange of the protons in the parent compound, $Zr(HPO_4)_2·H_2O$, affected the arrangement of the layers sufficiently to lower the symmetry from monoclinic to triclinic. The sodium ions are surrounded by oxygen atoms of both the water molecules and the phosphate groups. Electron diffraction studies show superlattice points along the smallest axis, which is not apparent in the powder diffraction data.

Introduction

Zirconium bis(hydrogen orthophosphate) hydrate $Zr(HPO_4)_2·H_2O$ (α-ZrP), is an insoluble ion exchanger with a layer structure.[1] The structure consists of octahedral metal atoms situated nearly in a plane which are bridged by phosphate oxygens.[2,3] Three oxygens of each phosphate are bonded to three different metal atoms while the fourth bonds to a proton and points away from the layer. The water molecules reside between the layers. Adjacent layers are arranged in such a way as to create zeolite-like cavities with rather restricted entrance to the cavity. There is just one cavity per zirconium atom. The layers are held together by van der Waals forces, as all the hydrogen bonds are intralayer.[3,4]

Ion exchange occurs by replacement of the orthophosphate proton by a variety of alkali metal, alkaline earth metal, and transition metal cations.[1] These cations then occupy positions between the layers accompanied by layer expansion to accommodate the ions and water molecules. α-ZrP crystals exchange Na^+ ions to form both mono- and diexchanged phases.[5] When the crystals are titrated with sodium hydroxide, two solid phases are present up to 50% exchange. They are the unexchanged α-ZrP and a half-exchanged phase with composition $Zr(NaPO_4)(HPO_4)·5H_2O$. The composition of the fully exchanged phase is $Zr(NaPO_4)_2·3H_2O$. The water content in these phases depends on the relative humidity and temperature. Although large single crystals of α-ZrP can be prepared, the crystals shatter and disorder during ion exchange as the layers expand to accommodate the cations. Therefore the only way to solve the structure of these ion exchanged phases is by using powder diffraction data. We have earlier determined the structures of $Zr(NaPO_4)(HPO_4)$,[6] $Zr(NaPO_4)(HPO_4)·H_2O$,[7] and $Zr(KPO_4)(HPO_4)·H_2O$[8] by powder methods. In this paper, we describe the powder structure of the fully sodium ion exchanged phase of α-ZrP.

Experimental Section

Sample Preparation. Crystalline α-ZrP was prepared by refluxing a zirconium phosphate gel in 12 M phosphoric acid. The fully exchanged sodium salt was prepared by potentiometric titration using 0.1 M NaOH/NaCl at pH 6. At the completion of the titration, the solid was recovered by filtration and blotted dry. This compound was identified as $Zr(NaPO_4)_2·3H_2O$ by its X-ray powder pattern. Complete details of the preparation and analytical data for the compound have been presented.[5]

X-ray Data Collection. Step-scanned X-ray powder diffraction data for the sample (packed into a flat aluminum sample holder) were collected by means of a Rigaku computer-automated diffractometer. The X-ray source was a rotating anode operating at 50 kV and 180 mA with a copper target and graphite-monochromated radiation. Data were collected between 2 and 80° in 2θ with a step size of 0.01° and a count time of 10 s per step. Data were mathematically stripped of the $K\alpha_2$ contribution, and peak picking was conducted by a modification of the double-derivative method.[9] The powder pattern was indexed by Ito methods[10] on the basis of the first 20 observed lines. The best solution which indexed all the lines (figure of merit = 118) indicated a triclinic unit cell with lattice parameters $a = 8.912$ Å, $b = 10.575$ Å, $c = 5.404$ Å, $\alpha = 94.277°$, $\beta = 90.1°$, and $\gamma = 111.03°$.

Electron diffraction patterns were taken on a JEOL JEM-2010 TEM operating at 200 kV. The sample for diffraction was prepared by dispersing gently ground powder under dry acetone on holey carbon-filmed grids.

Structure Solution and Refinement. Integrated intensities were extracted from the profile over the range $8 < 2\theta < 62°$ by decomposition (MLE) methods as described earlier.[7] This procedure produced 97 reflections of which 75 were nonoverlapping. The intensities of the overlapping peaks were divided by the number of contributors (in most cases 2) and included in the data set for structure analysis in the TEXSAN[11] series of single-crystal programs. Structure solution was attempted in the centric space group $P\bar{1}$. The two strong peaks in the electron density map (MITHRIL) were identified as Zr positions. One of them was at (0, 0, 0) (Zr1), and the other, at (0.51, 0.09, 0.5) (Zr2). If the structure were centrosymmetric, the second position would be at another inversion center, (0.5, 0.0, 0.5). Although this was an indication of the lower symmetry, it was ignored at this stage primarily due to the quality of the powder diffraction data. The electron density map also contained the positions of two P (P1 and P2) atoms and six oxygen atoms bonded to both P and Zr atoms. A Patterson map computed using the same data set confirmed the positions of the Zr and P atoms. The vector corresponding to two Zr atoms was at (0.51, 0.086, 0.5), which again

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Table 1. Crystallographic Data for $Zr_2(NaPO_4)_4 \cdot 6H_2O$

pattern range (2θ)	11.5–80°
step scan increment (2θ)	0.01°
step scan time	10 s
radiation source	rotating anode
λ	1.5406, 1.5444 Å
fw	762.3
space group	*P*1 (No. 1)
a	8.9192(3) Å
b	10.5824(4) Å
c	5.4045(3) Å
α	94.238(3)°
β	90.164(4)°
γ	111.013(3)°
V	474.65(7) Å^3
Z	1
β_{calcd}	2.66 g cm^{-3}
μ	144.1 cm^{-1}
T	23 °C
no. of contributing reflns	448
no. of geometric observns	23
P–O distances and tolerance	1.53(1) Å
ZrO_6 distances and tolerance	2.03(1) Å
O–O distances for PO_4	2.55(1) Å
O–O distances for ZrO_6	2.66(1) Å
no. of structural params	27
no. of profile params	11
statistically expected R_{wp}[a]	0.02
R_{wp}[b]	0.135
R_p[c]	0.101
R_F[d]	0.037

[a] Expected $R_{wp} = R_{wp}/(\chi^2)^{1/2}$; $\chi^2 = \sum w(I_o - I_c)^2/(N_{obs} - N_{var})$. [b] $R_{wp} = [\sum w(I_o - I_c)^2/\sum wI_o^2]^{1/2}$. [c] $R_p = \sum|I_o - I_c|/\sum I_c$. [d] $R_F = \langle |F_o| - |F_c| \rangle / \langle |F_o| \rangle$.

indicated the lower symmetry. The positions of the remaining oxygen atoms of the phosphate groups were calculated on the basis of the known geometry. These positions completed the layer structure in the space group $P\bar{1}$. This model was used for Rietveld refinement in GSAS.[12]

The raw data were transferred to the GSAS program package for full-profile refinement. In the early stages of refinement, the atomic positions were refined with soft constraints consisting of both Zr–O and P–O bond distances and O–O nonbonded distances. During refinement, the geometry about the Zr2 atom at (0.5, 0.0, 0.5) worsened, and no reasonable positions for Na and water molecules could be identified in the difference Fourier map. At this stage, it was decided to switch the structure analysis to the noncentric space group. The new layer for the space group *P*1 was obtained by generating the centrosymmetrically related atoms, and Zr2 was included as obtained in the *E* map. The refinement then progressed well, and the positions of the Na and water oxygen atoms were identified from the difference Fourier maps. All the atoms were refined isotropically. The final difference Fourier map contained some residual density peaks (<0.3 e/Å^3) close to the positions of some of the water molecules. The Na and lattice water molecules were refined without any geometrical constraints. In the final cycles of refinement, the shifts in all the parameters were less than their estimated standard deviations. Neutral atomic scattering factors were used for all atoms. No corrections were made for anomalous dispersion, absorption, or preferred orientation.

Results and Discussion

Crystallographic and experimental parameters are given in Table 1, final positional and thermal parameters, in Table 2, and bond lengths and angles, in Table 3; the final Rietveld refinement difference plot is in Figure 4. The arrangement of Na^+ ions between the layers of zirconium phosphate is shown in Figure 2, and the coordination geometry of Na^+ ions, in Figure 3.

Table 2. Positional and Thermal Parameters for $Zr_2(NaPO_4)_4 \cdot 6H_2O$

	x	*y*	*z*	U_{iso} ($=B_{iso}/8\pi^2$), Å^2
Zr1	0	0	0	0.015(2)
Zr2	0.5122(8)	0.0802(6)	0.510(1)	0.018(2)
P1	0.117(2)	0.852(2)	0.484(2)	0.020(1)
P2	0.410(2)	0.220(2)	0.029(3)	0.020[a]
P3	0.941(2)	0.196(2)	0.530(3)	0.020[a]
P4	0.570(2)	0.882(2)	0.989(3)	0.020[a]
O1	0.020(2)	0.872(1)	0.255(2)	0.042(2)
O2	0.026(2)	0.856(1)	0.728(2)	0.042[b]
O3	0.270(1)	0.987(2)	0.511(3)	0.042[b]
O4	0.156(3)	0.725(2)	0.428(4)	0.042[b]
O5	0.499(2)	0.219(1)	0.790(2)	0.042[b]
O6	0.498(2)	0.205(1)	0.259(2)	0.042[b]
O7	0.244(1)	0.097(2)	0.005(2)	0.042[b]
O8	0.374(3)	0.359(2)	0.062(4)	0.042[a]
O9	0.988(2)	0.140(2)	0.756(4)	0.042[b]
O10	0.969(2)	0.123(2)	0.280(3)	0.042[b]
O11	0.756(1)	0.169(2)	0.532(3)	0.042[b]
O12	0.039(2)	0.350(1)	0.507(4)	0.042[b]
O13	0.527(2)	0.942(1)	0.236(3)	0.042[b]
O14	0.527(2)	0.935(2)	0.754(3)	0.042[b]
O15	0.758(1)	0.916(2)	0.001(4)	0.042[b]
O16	0.490(3)	0.723(1)	0.999(4)	0.042[b]
O(W1)	0.759(4)	0.259(5)	0.967(5)	0.042[b]
O(W2)	0.734(4)	0.553(3)	0.512(6)	0.042[b]
O(W3)	0.552(5)	0.545(3)	0.816(8)	0.042[b]
O(W4)	0.225(4)	0.684(4)	0.905(6)	0.042[b]
O(W5)	0.994(5)	0.558(4)	0.667(9)	0.042[b]
O(W6)	0.401(4)	0.716(3)	0.571(6)	0.042[b]
Na1	0.815(3)	0.620(2)	0.023(4)	0.018(2)
Na2	0.645(3)	0.724(2)	0.446(4)	0.018[c]
Na3	0.098(3)	0.374(2)	0.058(5)	0.018[c]
Na4	0.354(2)	0.501(2)	0.459(4)	0.018[c]

[a] Constrained to be equal to U_{iso} of P1. [b] Constrained to be equal to U_{iso} of O1. [c] Constrained to be equal to U_{iso} of Na1.

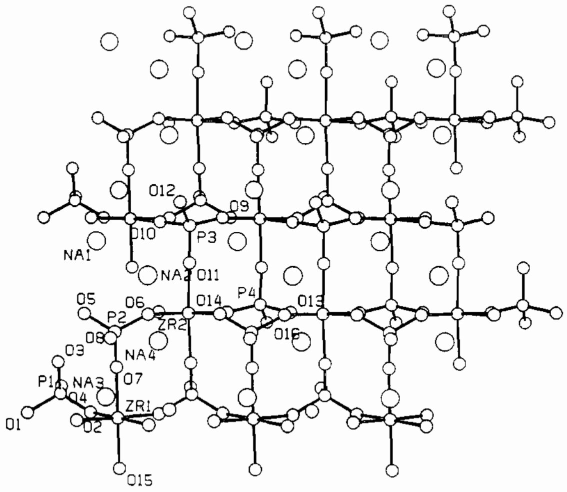

Figure 1. A portion of the structure showing the arrangement of the zirconium phosphate layer. The view is down the *b* axis, and the *c* axis is horizontal.

The unit cell parameters chosen in this case are different from those reported for α-ZrP.[2,3] The *b* axis in α-ZrP corresponds to the *c* axis in the present case. α-ZrP, $Zr(HPO_4)(NaPO_4) \cdot H_2O$,[7] $Zr(HPO_4)(KPO_4) \cdot H_2O$,[8] $Zr(NH_4PO_4)_2 \cdot H_2O$,[13] and $Zr(O_3PC_6H_5)_2$,[14] as well as the amine-intercalated zirconium phosphate phases,[15] crystallize in one of the monoclinic space groups. As indicated above, the fully exchanged sodium phase crystallizes in the triclinic symmetry. The layer structure (Figures 1 and 2) of the fully sodium ion exchanged phase is essentially the same as that of the parent α-ZrP but with differences that will be described below. These differences arise from the need to accommodate two sodium ions and three water molecules in each cavity. The most obvious changes are evident in the symmetry, *P*1 versus $P2_1/c$, and the unit cell parameters. The *a* and *c* axes are very much like those in α-ZrP (*a* and *b*), and the angle between them is very close to 90°. However, the angle between the smallest axis, *c*, and the interlayer vector *b** is 94.24° as opposed to 90°

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Table 3. Average and Ranges for Bond Lengths (Å) and Bond Angles (deg) of $Zr_2(NaPO_4)_4{\cdot}6H_2O$[a]

atoms	dist range	av	atoms	dist range	av
Zr1–O	2.01(1)–2.11(1)	2.05	P2–O	1.52(1)–1.61(1)	1.56
Zr2–O	2.00(1)–2.13(1)	2.05	P3–O	1.51(1)–1.57(1)	1.56
P1–O	1.51(1)–1.58(1)	1.56	P4–O	1.53(2)–1.58(2)	1.56

atoms	angle range	av
O–Zr1–O (cis)	83(1)–97(1)	90
O–Zr1–O (trans)	174(1)–177(1)	176
O–Zr2–O (cis)	84(1)–95(1)	90
O–Zr2–O (trans)	175(1)–179(1)	177
O–P1–O	103(1)–115(1)	109
O–P2–O	107(1)–114(1)	109
O–P3–O	104(1)–114(1)	109
O–P4–O	105(1)–116(1)	109

atoms	angle range	av
Zr–O–P	138(1)–169(1)	155

atoms	dist	atoms	dist
Na1–O1	2.84(3)	Na3–O8	2.52(3)
Na1–O2^a	3.09(2)	Na3–O9^c	2.73(3)
Na1–O15	3.36(3)	Na3–O10^d	2.85(3)
Na1–O(W2)^b	2.83(4)	Na3–O12	2.50(3)
Na1–O(W2)	2.82(3)	Na3–O12^b	3.00(3)
Na1–O(W3)^b	2.43(4)	Na3–O(W1)^c	2.85(3)
Na1–O(W5)	2.69(4)		
Na2–O13	3.13(3)	Na4–O8	2.57(3)
Na2–O14	3.17(3)	Na4–O12	2.71(2)
Na2–O15	3.19(3)	Na4–O(W3)	2.52(5)
Na2–O16^b	2.78(3)	Na4–O(W6)	2.20(2)
Na2–O(W2)	2.27(3)		
Na2–O(W3)	2.78(4)		
Na2–O(W6)	2.25(2)		

atoms	dist	atoms	dist
O(W1)–O5	2.39(2)	O(W4)–O(W5)^d	2.33(4)
O(W1)–O6^e	2.72(4)	O(W4)–O(W6)	2.35(4)
O(W1)–O11	2.47(2)	O(W5)–O4^f	2.32(5)
O(W3)–O8^e	2.52(4)	O(W5)–O12^f	2.48(3)
O(W4)–O4	2.75(3)	O(W6)–O4	2.36(4)
O(W4)–O16	2.30(3)	O(W6)–O(W4)	2.35(4)

[a] Symmetry codes: (a) $x + 1, y, z - 1$; (b) $x, y, z - 1$; (c) $x - 1, y, z - 1$; (d) $x - 1, y, z$; (e) $x, y, z + 1$; (f) $x + 1, y, z$.

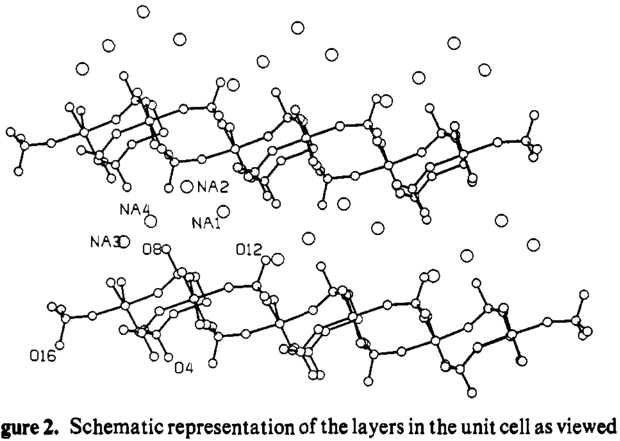

Figure 2. Schematic representation of the layers in the unit cell as viewed along the c axis. The a axis is horizontal. The sodium ions and P–O-type oxygens are labeled. The water molecules are not included.

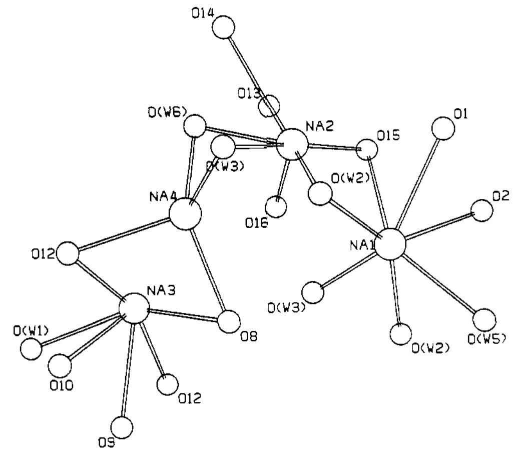

Figure 3. Arrangement of sodium ions in the interlayer space with their respective coordination spheres. The sodium ions are bridged by water or phosphate oxygens showing their connectivity.

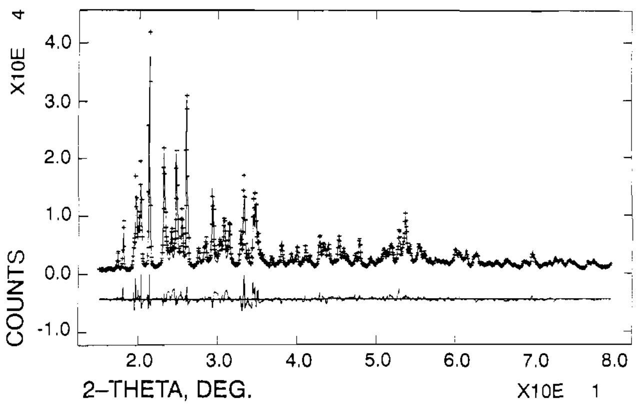

Figure 4. Observed (+) and calculated (—) profiles (X-ray intensity versus 2θ) for the Rietveld refinement of $Zr_2(NaPO_4)_4{\cdot}6H_2O$. The bottom curve is the difference plot on the same intensity scale.

in α-ZrP. Thus the symmetry is reduced to triclinic, in which it is possible to choose the origin at a Zr atom. Therefore, within the layer, the zirconium atoms are at (0, 0, 0) and roughly ($^1/_2$, $^1/_2$, 0.08) whereas in α-ZrP they are approximately at ($^1/_4$, $^1/_4$, 0.014) and ($^3/_4$, $^3/_4$, –0.014). The zirconium atoms in the latter structure are about 0.3 Å alternately above and below the mean plane of the layer. Similarly, in the present sodium ion structure, we can choose a mean plane with the Zr1 atom at the origin ~0.4 Å below the plane and Zr2 would then be ~0.4 Å above this mean plane. Phosphorus atoms P2 and P3 are 1.5 Å above the mean plane, and P1 and P4 are roughly the same distance below the mean plane. Three oxygen atoms of each phosphate group bridge across three different Zr atoms as they do in α-ZrP, and the fourth oxygen points away from the layer and is involved either in bonding to Na^+ or in hydrogen bonding to water oxygens. In the case of α-ZrP, these oxygens, labeled O7 and O10 are bonded to the protons that in the present structure are exchanged for Na^+ ions. Among the four such oxygens (P1–O4, P2–O8, P3–O12, P4–O16), O4 is involved only in hydrogen bonding to water molecules.

The arrangement of sodium ions in the lattice is particularly interesting. The empirical formula of the compound is $Zr(NaPO_4)_2{\cdot}3H_2O$, but there are four independent sodium ions. This fact requires us to double the formula to $Zr_2(NaPO_4)_4{\cdot}6H_2O$. Na1 and Na2 occur in one cavity, and Na3 and Na4, in an adjacent cavity. We note in Figure 2 that the phosphate groups are tilted away from the perpendicular to the layers. That is, if we consider the 3-fold axis through P3–O12, it points to the right of the perpendicular while P2–O8 points to the left. A similar situation exists for P1–O4 and P4–O16. The phosphate groups pointing away from each other create a broadened cavity while the adjacent cavities become constricted. This tilting arises from the large separation, in the b direction (~0.8 Å) of neighboring zirconium atoms across which the phosphate must bridge. A similar situation is present in $Zr(NaPO_4)(HPO_4){\cdot}H_2O$[7] but not in $Zr(NH_4PO_4){\cdot}H_2O$.[13]

The sodium atoms Na1 and Na2 are bridged by O15 and a water molecule, O(W2), Na2 is bridged to Na4 by waters O(W3) and O(W6), and Na4 in turn is linked to Na3 through two bridging atoms O8 and O12. This bridging leads to a chain of four sodium ions in the form of a boat. The distances between these ions are Na1–Na2 = 3.1 Å, Na2–Na4 = 2.82 Å, and Na4–Na3 = 3.01

Å. This arrangement of sodium ions produce a zigzag chain (Figure 2) in the interlayer space running along the *a* direction of the crystal in which the translated Na3 atom is 4.2 Å from Na1. Sodium atoms Na1 and Na3 have *z* parameters close to zero while these parameters for Na2 and Na4 are slightly less than $^1/_2$. As a result, there are close contacts (Na2---Na1′ = 3.87 Å and Na3---Na4′ = 4.0 Å) between the boatlike chain of four sodiums in one unit cell with those of another chain in the adjacent unit cell in the *c* direction. These translated chains are connected by water molecules and phosphate oxygen atoms. Na1 is bridged not only to Na2 in the same unit cell through O(W2) but also to Na1 one unit cell away in the *c* direction. Similarly, O(W3) bridges Na2 and Na4 in the same unit cell but then connects to Na1 in the adjacent unit cell in the *c* direction. Finally, O12 bonds to Na3 in the same unit cell (Na–O = 2.50 Å) and connects to Na3′ along the *c* direction 3.00 Å away. Thus, an intricate network of P–O$^-$ groups and water molecules binds the chains of four sodium ions together in the *c* direction but not in the *a* direction.

The coordination of each of the sodium ions is shown in Figure 3. As expected, these coordination polyhedra are highly distorted because the oxygen atoms of the layers are constrained by their bonding to the layer atoms. Na1 is seven-coordinate but with one long contact, Na1–O15, at 3.36 Å. Interestingly, this sodium is not near any of the P–O$^-$ groups but is held in the lattice by water molecules and phosphate oxygens. Na2 is also seven-coordinate but is bonded to a P–O16 oxygen as well as water and phosphate oxygens. Na4 is four-coordinate in a somewhat distorted tetrahedral arrangement, two of the four bonds being of the P–O$^-$ type. Na3 is six-coordinate and bonded to three P–O$^-$ oxygens, one water molecule, O(W1), and two framework oxygens. The P–O4 oxygen is not bonded to any of the sodium atoms but rather is close to three water molecules (O(W4), O(W5), and O(W6)) at reasonable bond distances. O(W2) has close contacts with three sodium ions, Na1, Na1′, and Na2, while O(W3) also has three sodium ion contacts (Na1, Na2, and Na4) and one lattice oxygen, O8. All the other water molecules have four close contacts and form an extensive system of hydrogen bonds.

The only other fully exchanged α-ZrP compound whose structure is known is that of the ammonium ion phase, $Zr(NH_4PO_4)_2\cdot H_2O$.[13] This structure is much more regular. Each NH_4^+ ion is bonded to four PO$^-$ type oxygens and the water molecule which bridges two NH_4^+ ions. Each PO$^-$ oxygen is surrounded by four ammonium ions. Thus the ammonium ions are not associated with individual PO$^-$ sites. Rather an ionic type coordination occurs where each ammonium ion is coordinated to four negative ions and each negative site is surrounded by four positive ions, forming a regular network throughout the interlamellar space.

The greater distortion in the sodium versus the ammonium ion structure may arise from the way that they are formed. The half-exchanged sodium ion phase contains 5 mol of water, and the interlayer spacing increases from 7.6 Å in α-ZrP to 11.8 Å in the pentahydrate.[5] The second sodium enters the interlamellar space in which the layers are relatively far apart and ejects two water molecules while pulling the layers down to a separation of 9.88 Å. This complex rearrangement lends itself to disorder. In contrast, the exchange of ammonium ions is in actuality intercalation of NH_3.[16] Exchange does not occur until the pH is above 5.6,[17] a condition at which the ammonium ion is in equilibrium with ammonia molecules. No half-exchanged phase forms, but instead 2 moles of NH_3 is incorporated in a single step accompanied by interlayer expansion to 9.36 Å. Although some disorder occurs, as shown by streaking on Weissenberg photographs, it was still possible to solve the structure from single-crystal data. However, the sodium ion phase exhibited such large disorder that the Weissenberg photographs of single crystals were uninterpretable.

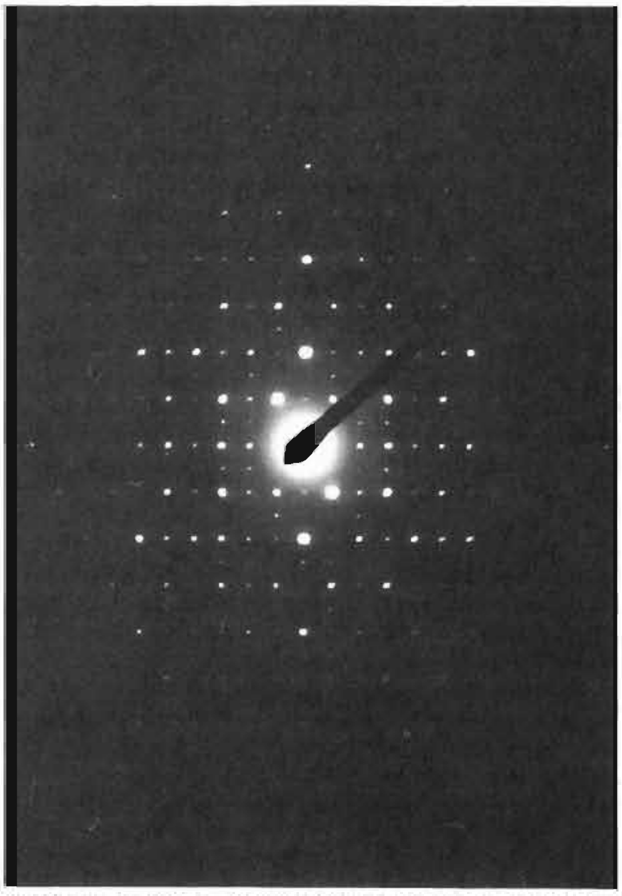

Figure 5. Electron diffraction pattern of a thin crystal of the title compound showing the doubling of the *c* (5.4 Å) axis (vertical).

One type of disorder is manifested in the electron diffraction pattern shown in Figure 5. Earlier, Vliers *et al.*[18] obtained highly disordered single crystals of the disodium phase by ion-exchanging α-ZrP with Na^+. From Weissenberg photographs they showed that the crystals are monoclinic and that the smallest axis (5.4 Å) is doubled. Although their unit cell dimensions and the symmetry are incorrect, their observation of doubling of one of the axes is consistent with our electron diffraction results. We have used thin crystals of the title compound for electron diffraction. In most cases, we obtained the diffraction pattern along the *b* axis (of the present case). The doubling of the axis, as observed by Vliers *et al.*, is very prominent in this pattern (Figure 5). The a^* and c^* dimensions obtained from this electron diffraction pattern are very close to the values obtained by Rietveld refinement; the included angle was very close to 90° (the refined value is 90.16°). Additionally, the intensity distribution in this case is strikingly different from that obtained for α-ZrP. This feature clearly indicated that the layers are distorted when α-ZrP is fully exchanged with Na^+ ions. However, we did not attempt a solution in the larger unit cell because the number of parameters to refine would have been too large for the amount of data available.

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