

## Crystal Structure of the Sodium Ion Conductor $\alpha$ - $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ : Evidence for a Long-Range Ordering of the $\text{Na}^+$ Ions

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The new sodium iron(III) diphosphate,  $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ , exhibits a high-temperature form, “ $\beta$ ”, monoclinic, isotypic with  $\text{Na}_7\text{Fe}_3(\text{As}_2\text{O}_7)_4$  and a room-temperature form, “ $\alpha$ ”, which is a superstructure of  $\beta$ . The structure of the  $\alpha$ -form has been solved in two stages. First, the superstructure reflections were neglected and the average structure (cell constants:  $a = 9.506(3)$ ,  $b = 8.333(2)$ ,  $c = 27.732(5)$  Å,  $\beta = 93.33(3)^\circ$ ,  $V = 2193(2)$  Å<sup>3</sup>,  $Z = 4$ ) was solved in the space group  $C2/c$ . Final reliability factors are  $R = 0.030$  and  $R_w = 0.042$  for 3180 unique reflections with  $I \geq 3 \sigma(I)$ . The structure consists of  $\text{FeO}_6$  octahedra sharing their corners with  $\text{P}_2\text{O}_7$  groups to form a three-dimensional framework  $[\text{Fe}_3(\text{P}_2\text{O}_7)_4]_x$  into which the sodium ions are inserted. With the exception of Na(1), the sodium sites are partially occupied and lie in the vicinity of  $\pi$ -planes parallel to (001), which at high temperature play the role of diffusion planes for the  $\text{Na}^+$  ions. In a second stage, the superstructure (cell constants:  $a = 28.519(3)$ ,  $b = 8.333(2)$ ,  $c = 29.834(5)$  Å,  $\beta = 111.88(1)^\circ$ ,  $V = 6579(4)$  Å<sup>3</sup>,  $Z = 12$ ) was solved in the space group  $C2/c$  and refined to  $R = 0.039$  and  $R_w = 0.041$  for 4343 independent reflections with  $I \geq \sigma(I)$ . A distribution of vacancies and totally occupied sodium sites was found in the  $\pi$ -planes. The long-range ordering of the sodium ions is accompanied by slight atomic displacements in the  $[\text{Fe}_3(\text{P}_2\text{O}_7)_4]_x$  framework. © 1991 Academic Press, Inc.

### Introduction

A new sodium iron diphosphate,  $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ , has been recently synthesized. Differential thermal analysis and X-ray diffraction experiments at controlled temperatures (precession method) indicate a reversible transition  $\alpha \rightleftharpoons \beta$  between 165 and 190°C. X-ray and conductivity data suggest that the sodium ions are implicated in

an order–disorder type transformation ( $I$ ). The high temperature form  $\beta$  is isostructural with the diarsenate  $\text{Na}_7\text{Fe}_3(\text{As}_2\text{O}_7)_4$  (monoclinic, space group  $C2/c$ ) (2) in which the sodium ions are partially disordered. The low-temperature form  $\alpha$  is a superstructure of  $\beta$ . The unit-cell vectors of the  $\alpha$ -form ( $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$ ) are related to those of the  $\beta$ -form ( $\mathbf{a}_0$ ,  $\mathbf{b}_0$ ,  $\mathbf{c}_0$ ) by:  $\mathbf{a} = 3\mathbf{a}_0$ ,  $\mathbf{b} = \mathbf{b}_0$  and  $\mathbf{c} = -\mathbf{a}_0 + \mathbf{c}_0$  (Fig. 1). The crystal structure of  $\alpha$ - $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$  is reported here. It was solved in two stages:

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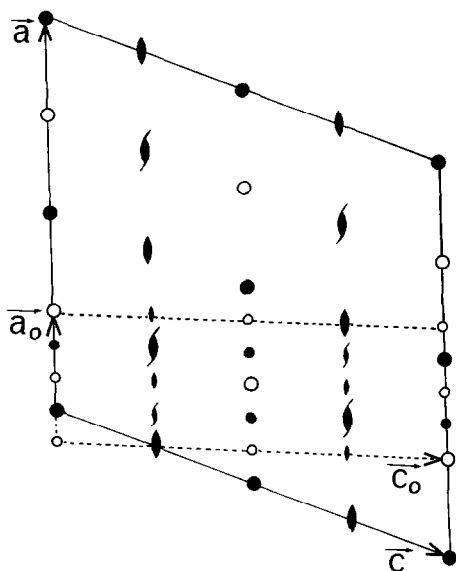


FIG. 1. Geometrical relationship between the average structure unit cell ( $\mathbf{a}_0, \mathbf{b}_0, \mathbf{c}_0$ ) and the superstructure unit cell ( $\mathbf{a}, \mathbf{b}, \mathbf{c}$ ). Space group  $C2/c$  for both structures. The small symbols refer to symmetry elements belonging to the average structure only. Open circles, inversion centers at  $y_0 = 0$  ( $y = \frac{1}{4}$  in the supercell). Solid circles, inversion centers at  $y_0 = \frac{1}{4}$  ( $y = 0$  in the supercell). The atomic coordinates for the asymmetric unit of the superstructure ( $x, y, z$ ) are related to those of the average structure ( $x_0, y_0, z_0$ ) by  $x_a = (x_0 + z_0)/3 - \frac{1}{2}$ ,  $x_b = x_a + \frac{1}{3}$ ,  $x_c = x_a + \frac{2}{3}$ ,  $y_a = y_0 + \frac{1}{4}$ ,  $y_b = y_a$ ,  $y_c = y_a$ ,  $z_a = z_0$ ,  $z_b = z_a$ ,  $z_c = z_a$ .

—First, the superstructure reflections were neglected and an average structure with partially occupied sodium sites was obtained.

—Second, the superstructure was determined from all the observed reflections. A long-range ordering of the sodium ions was evidenced.

### Experimental

Crystals of  $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$  were grown in a flux of sodium phosphates. A starting mixture  $\text{Fe}_2\text{O}_3 + 4 \text{Na}_4\text{P}_2\text{O}_7 + 12 \text{NaPO}_3$  was heated progressively and melted at  $720^\circ\text{C}$  and cooled down to  $500^\circ\text{C}$  at a rate of  $1^\circ\text{C} \cdot$

$\text{hr}^{-1}$  and then to room temperature ( $100^\circ\text{C} \cdot \text{hr}^{-1}$ ). The resulting product was washed with water in order to eliminate the sodium phosphates in excess. The selected crystal was elongated on  $[\bar{1}10]$  and delimited by  $\{\bar{1}11\}$  and  $\{001\}$  (the indices are relative to the average structure unit cell ( $\mathbf{a}_0, \mathbf{b}_0, \mathbf{c}_0$ )).

Intensities were collected on an Enraf-Nonius CAD4 diffractometer at 294 K. Crystal data and experimental conditions for intensity measurements and refinements are reported in Table I. The unit-cell constants listed in Table I were determined from 25 single-crystal reflections. They agree satisfactorily with those refined from powder diffraction patterns (1). The reflections were corrected for Lorentz and polarization effects. Absorption corrections were performed using the program ABSCOR (3). Atomic scattering factors were taken from "International Tables for X-Ray Crystallography" (4).

### The Average Structure

The average structure was determined first. The  $h, k, l$  indices of the collected reflections were transformed into  $h_0, k_0, l_0$  according to  $h_0 = 1/3 h$ ,  $k_0 = k$ ,  $l_0 = 1/3 h + l$  and the reflections with a fractional  $h_0$  index were rejected. The structure of the isotopic compound  $\beta\text{-Na}_7\text{Fe}_3(\text{As}_2\text{O}_7)_4$  (2) was taken as a starting model. The coordinates of all atoms, the occupancy factors of the sodium sites, and the anisotropic thermal motion coefficients (except for four sodium sites) were refined to  $R = 0.030$  and  $R_w = 0.042$ . Final atomic parameters are listed in Table II. Selected interatomic distances and angles are given in Table III.<sup>1</sup>

The structure can be described as a three-dimensional framework  $[\text{Fe}_3(\text{P}_2\text{O}_7)_4]_\infty$  in which the sodium ions are inserted (Fig. 2).

<sup>1</sup> Lists of structure factors and anisotropic thermal motion parameters are available on request to the authors.

TABLE I  
CRYSTAL DATA AND EXPERIMENTAL CONDITIONS FOR CRYSTALLOGRAPHIC ANALYSIS OF  $\alpha$ - $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$

	Crystal data	
	Average structure	Superstructure
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> (Å)	9.506(3)	28.519(3)
<i>b</i> (Å)	8.333(2)	8.333(2)
<i>c</i> (Å)	27.732(5)	29.834(5)
$\beta$ (°)	93.33(3)	111.88(1)
<i>V</i> (Å <sup>3</sup> )	2193(2)	6579(4)
<i>Z</i>	4	12
Formula mass (amu)		1024.24
Crystal size (mm)		0.21 × 0.15 × 0.09
<i>D<sub>x</sub></i> (g · cm <sup>-3</sup> )		3.092
	Intensity measurements (superstructure)	
Monochromator	Graphite	
$\lambda$ (MoK $\alpha$ ) (Å)	0.7107	
<i>T</i> (K)	294	
Scan technique	$\theta$ - $2\theta$	
Scan width	0.75 + 0.35 tan $\theta$	
Scan speed (°/min)	~1.5 to 7	
$\theta$ range (°)	1.59 ≤ $\theta$ ≤ 30	
Standard reflections	6 2 -17, 0 4 7, 15 -3 -5	
Data collected	-40 ≤ <i>h</i> ≤ 40, 0 ≤ <i>k</i> ≤ 11, 0 ≤ <i>l</i> ≤ 42	
	Refinements	
	Average structure	Superstructure
Number of unique reflections	3180 ( <i>I</i> ≥ 3 $\sigma$ ( <i>I</i> ))	3573 ( <i>I</i> ≥ 3 $\sigma$ ( <i>I</i> )) 4343 ( <i>I</i> ≥ 1 $\sigma$ ( <i>I</i> ))
Total number of reflections	3823	10181
Number of variables	129	624
<i>F</i> (000)	1996	5988
Agreement factors	<i>R</i> = 0.030 <i>R<sub>w</sub></i> = 0.042	<i>R</i> = 0.039 <sup>a</sup> <i>R<sub>w</sub></i> = 0.041 <sup>a</sup>
Weighting scheme		1/ $\sigma^2$ ( <i>F</i> )
Function minimized		$\Sigma w(F_o - F_c)^2$
Absorption coefficient (cm <sup>-1</sup> )		28.05
Transmission factors		min = 0.729 max = 0.856

<sup>a</sup> Value calculated for *I* ≥ 1 $\sigma$ (*I*)

The framework is made of FeO<sub>6</sub> octahedra sharing their corners with diphosphate P<sub>2</sub>O<sub>7</sub> groups. It consists of a succession of alternate layers A: Fe(1)[P(1)P(2)O<sub>7</sub>]<sub>2</sub> and B: [Fe(2)P(3)P(4)O<sub>7</sub>]<sub>2</sub>, parallel to (001) and connected via the O(7) atom. Figure 3 represents the arrangement of FeO<sub>6</sub> octahedra

and P<sub>2</sub>O<sub>7</sub> groups in the A-layer. The Fe(1) atom, which lies on the twofold axis, is chelated by two symmetrically equivalent P(1)P(2)O<sub>7</sub> groups. Such a configuration is similar to that recently reported by Wang and Hwu for the Ti(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub> structural unit in BaTi<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub> (5). The structure of the frame-

TABLE II  
OCCUPANCY FACTORS, ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS  
OF  $\alpha\text{-Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$  (AVERAGE STRUCTURE)

Atom	Occ.	x	y	z	$B_{\text{eq}}$ ( $\text{\AA}^2$ )
P(1)	1	0.29949(8)	0.27448(9)	0.24637(3)	0.57(1)
P(2)	1	0.22403(8)	0.14893(9)	0.33686(3)	0.54(1)
P(3)	1	0.50899(7)	0.66301(9)	0.44384(3)	0.42(1)
P(4)	1	0.41514(7)	0.79013(9)	0.53496(3)	0.39(1)
Fe(1)	1	0	0.09607(7)	$\frac{1}{4}$	0.51(1)
Fe(2)	1	0.31691(4)	0.97657(5)	0.43746(1)	0.41(1)
Na(1)	1	0.2663(2)	0.3841(2)	0.44268(5)	1.51(2)
Na(2)	0.33	0.5364(5)	0.3402(5)	0.3600(2)	1.36(7)
Na(2')	0.66	0.4923(3)	0.3647(3)	0.35329(8)	2.08(4)
Na(3)	0.36	$\frac{1}{2}$	0.0017(7)	$\frac{1}{4}$	1.70(9) <sup>a</sup>
Na(3')	0.47	0.5264(4)	0.9463(4)	0.3123(2)	3.32(8)
Na(3'')	0.17	0.489(1)	0.894(1)	0.3330(3)	2.1(2) <sup>a</sup>
Na(4)	0.33	0.2986(5)	0.5854(6)	0.3436(2)	2.18(8) <sup>a</sup>
Na(4')	0.37	0.3407(5)	0.7202(6)	0.3520(2)	2.24(8) <sup>a</sup>
O(1)	1	0.3731(2)	0.2076(3)	0.20465(8)	0.98(4)
O(2)	1	0.3591(2)	0.4323(3)	0.26661(8)	0.84(4)
O(3)	1	0.1387(2)	0.2815(3)	0.23709(8)	0.79(4)
O(4)	1	0.3214(2)	0.1480(3)	0.29086(7)	0.64(3)
O(5)	1	0.0732(2)	0.1080(3)	0.31805(8)	0.86(4)
O(6)	1	0.2365(3)	0.3107(3)	0.35933(8)	1.17(4)
O(7)	1	0.2846(2)	0.0089(3)	0.36660(8)	0.85(4)
O(8)	1	0.4806(2)	0.8337(3)	0.42564(8)	0.67(3)
O(9)	1	0.6669(2)	0.6354(3)	0.45349(8)	0.69(3)
O(10)	1	0.4360(2)	0.5371(3)	0.41364(8)	0.79(4)
O(11)	1	0.4462(2)	0.6551(3)	0.49645(7)	0.63(3)
O(12)	1	0.3466(2)	0.9312(3)	0.50809(7)	0.62(3)
O(13)	1	0.5543(2)	0.8338(3)	0.56108(8)	0.77(4)
O(14)	1	0.3192(2)	0.7110(3)	0.56981(8)	0.64(3)

Note.  $B_{\text{eq}} = \frac{1}{3} (\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab \cdot \cos \gamma + \beta_{13}ac \cdot \cos \beta + \beta_{23}bc \cdot \cos \alpha)$  ( $\text{\AA}^2$ ).  
<sup>a</sup> Refined isotropically.

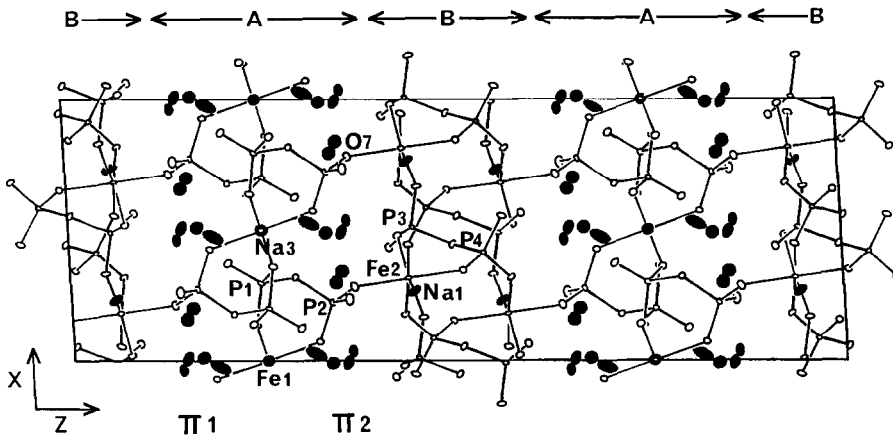


FIG. 2. Projection of the average structure of  $\alpha\text{-Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$  along [010]. The sodium ions are represented in black.

TABLE III  
SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN THE AVERAGE STRUCTURE  
OF  $\alpha$ - $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$

P(1)-O(1)	1.494(2)	P(2)-O(4)	1.619(2)	P(3)-O(8)	1.528(2)	P(4)-O(11)	1.591(2)
P(1)-O(2)	1.526(2)	P(2)-O(5)	1.535(2)	P(3)-O(9)	1.527(2)	P(4)-O(12)	1.519(2)
P(1)-O(3)	1.536(2)	P(2)-O(6)	1.487(2)	P(3)-O(10)	1.489(2)	P(4)-O(13)	1.515(2)
P(1)-O(4)	1.627(2)	P(2)-O(7)	1.522(2)	P(3)-O(11)	1.610(2)	P(4)-O(14)	1.518(2)
Fe(1)-O(2) x2	1.985(2)	Fe(2)-O(7) <sub>i</sub>	1.989(2)	Fe(2)-O(12)	1.999(2)		
Fe(1)-O(3) x2	2.076(2)	Fe(2)-O(8)	2.001(2)	Fe(2)-O(13) <sub>iii</sub>	1.998(2)		
Fe(1)-O(5) x2	1.975(2)	Fe(2)-O(9) <sub>ii</sub>	2.014(2)	Fe(2)-O(14) <sub>iv</sub>	2.031(2)		
Na(1)-O(10)	2.242(3)	Na(2)-O(10)	2.446(5)	Na(2')-O(10)	2.292(3)		
Na(1)-O(9) <sub>v</sub>	2.304(3)	Na(2)-O(1) <sub>vii</sub>	2.314(5)	Na(2')-O(5) <sub>ii</sub>	2.396(3)		
Na(1)-O(12) <sub>iv</sub>	2.356(3)	Na(2)-O(5) <sub>ii</sub>	2.550(5)	Na(2')-O(6)	2.488(4)		
Na(1)-O(6)	2.392(3)	Na(2)-O(14) <sub>vi</sub>	2.355(5)	Na(2')-O(2)	2.710(3)		
Na(1)-O(13) <sub>vi</sub>	2.498(3)	Na(2)-O(7) <sub>viii</sub>	2.743(5)	Na(2')-O(1) <sub>vii</sub>	2.485(3)		
Na(1)-O(8) <sub>v</sub>	2.761(2)	Na(2)-O(6)	2.860(5)	Na(2')-O(4)	2.927(3)		
Na(1)-O(9) <sub>vi</sub>	2.917(3)	Na(2)-O(13) <sub>vi</sub>	2.803(5)	Na(2')-O(13) <sub>vi</sub>	2.949(3)		
				Na(2')-O(14) <sub>vi</sub>	2.778(3)		
Na(3)-O(3)x2	2.300(5)	Na(3')-O(3) <sub>xi</sub>	2.444(4)	Na(3'')-O(4) <sub>ix</sub>	2.859(10)		
Na(3)-O(1)x2	2.409(5)	Na(3')-O(3) <sub>ii</sub>	2.763(5)	Na(3'')-O(6) <sub>ii</sub>	2.517(10)		
Na(3)-O(4)x2	2.424(4)	Na(3')-O(4) <sub>x</sub>	2.615(4)	Na(3'')-O(7) <sub>ix</sub>	2.405(10)		
		Na(3')-O(5) <sub>ii</sub>	2.857(4)	Na(3'')-O(8)	2.624(10)		
Na(4)-O(10)	2.312(5)	Na(3')-O(6) <sub>ii</sub>	2.581(4)	Na(3'')-O(3) <sub>xi</sub>	2.423(9)		
Na(4)-O(1) <sub>xi</sub>	2.289(5)	Na(3')-O(7) <sub>ix</sub>	2.868(5)	Na(3'')-O(5) <sub>ii</sub>	2.556(10)		
Na(4)-O(6)	2.411(6)	Na(3')-O(1) <sub>x</sub>	2.435(4)				
Na(4)-O(2)	2.581(6)			Na(4')-O(3) <sub>xi</sub>	2.542(5)		
Na(4)-O(5) <sub>ii</sub>	2.750(6)	Na(4')-O(10)	2.427(5)	Na(4')-O(5) <sub>ii</sub>	2.625(5)		
Na(4)-O(3) <sub>xi</sub>	2.862(6)	Na(4')-O(7) <sub>ix</sub>	2.502(5)	Na(4')-O(1) <sub>xi</sub>	2.498(5)		
		Na(4')-O(8)	2.552(5)	Na(4')-O(14) <sub>iv</sub>	2.778(5)		
O(3)-O(4)-O(5)	66.92(9)						
O(8)-O(11)-O(12)	67.90(9)	P(1)-O(4)-P(2)	122.7(1)	P(3)-O(11)-P(4)	132.3(1)		
Na(4)-Na(2')	2.605(6)	Na(4)-Na(4')	1.211(7)	Na(3)-Na(3')	1.792(5)		
Na(2')-Na(2)	0.493(5)	Na(4')-Na(3')	2.846(6)	Na(3')-Na(3'')	0.82(1)		
Na(2)-Na(4')	3.081(6)	Na(3')-Na(4)	2.922(6)	Na(3)-Na(3'')	2.48(1)		

Symmetry codes : i:  $x, 1+y, z$  ; ii:  $x-\frac{1}{2}, y+\frac{1}{2}, z$  ; iii:  $1-x, 2-y, 1-z$  ; iv :  $\frac{1}{2}-x, 3/2-y, 1-z$  ; v:  $x-\frac{1}{2}, y-\frac{1}{2}, z$  ; vi:  $1-x, 1-y, 1-z$  ; vii:  $1-x, y, \frac{1}{2}-z$  ; viii:  $x+\frac{1}{2}, y+\frac{1}{2}, z$  ; ix :  $x, 1+y, z$  ; x:  $1-x, 1+y, \frac{1}{2}-z$  ; xi:  $\frac{1}{2}-x, y+\frac{1}{2}, \frac{1}{2}-z$  .

work can be also regarded, as in  $\text{NaFeP}_2\text{O}_7$  (6), as an alternate stacking of octahedral ( $\text{FeO}_6$ ) layers and tetrahedral ( $\text{P}_2\text{O}_7$ ) layers parallel to (101). In the  $\text{P}_2\text{O}_7$  groups, the P-O bonds with a bridging oxygen atom (O(4) or O(11)) are longer than the other P-O bonds

as usually observed in diphosphates. The O(1), O(6), and O(10) oxygen atoms, which belong only to one polyhedron of the framework (a  $\text{PO}_4$  tetrahedron), correspond to the shortest P-O distances. The P(1)-O(4)-P(2) angle of  $122.7^\circ$  ranks among the lowest val-

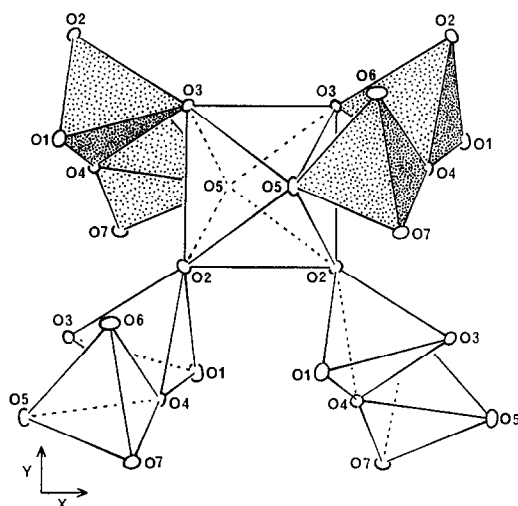


FIG. 3. Arrangement of  $\text{Fe}(1)\text{O}_6$  octahedra and  $\text{P}(1)\text{P}(2)\text{O}_7$  groups in the A-layer. Two diphosphate groups act as bidendate ligands to  $\text{Fe}(1)$ , via  $\text{O}(3)$  and  $\text{O}(5)$ . Projection along  $[001]^*$ .

ues of P–O–P angles reported in diphosphates (7).

The sodium ions are distributed over eight sites and are surrounded by six to eight oxygen atoms at distances ranging from 2.24 to 2.95 Å (Table III). The  $\text{Na}(1)$  site lies in the B-layer and is fully occupied. The other sites lie in the A-layer and form three sets:  $\text{Na}(2)\text{--Na}(2')$ ,  $\text{Na}(3)\text{--Na}(3')\text{--Na}(3'')$ , and  $\text{Na}(4)\text{--Na}(4')$ . In each set, the two or three sites are too close to be simultaneously occupied (Table III).

In order to determine the possible diffusion paths of the sodium ions in the crystal, the oxygen atom windows which separate the neighboring Na sites were examined. Those whose radius was found larger than about 2 Å were considered as possible passageways. The results are very similar to those obtained for  $\text{Na}_7\text{Fe}_3(\text{As}_2\text{O}_7)_4$  (2):

—Two neighboring  $\text{Na}(1)$  ions located on each side of the B-layer median plane are separated by a narrow window ( $R = 1.93$  Å) whose oxygen atoms display low-temperature factors. Thus, the diffusion of the  $\text{Na}^+$

ions through the B-layer seems to be rather difficult.

—The (2), (2'), (3'), (3''), (4), and (4') sodium sites are interconnected so as to form diffusion planes  $\pi_1$  and  $\pi_2$  parallel to (001) at  $z_1 \approx 0.15$  and  $z_2 \approx 0.35$ , respectively;  $\pi_1$  and  $\pi_2$  are equivalent by rotation around the twofold axis and are interconnected via the  $\text{Na}(3)$  site. In the  $\pi_2$  plane represented in Fig. 4, two diffusion paths can be distinguished:

“*i*”:  $\cdots \text{Na}(4) \cdots \text{Na}(2') \cdots \text{Na}(2)$   
 $\cdots \text{Na}(4') \cdots \text{Na}(4) \cdots$ ,  
 with  $\mathbf{a}_0 - \mathbf{b}_0$  as general direction;

“*j*”:  $\cdots \text{Na}(4) \cdots \text{Na}(4') \cdots \text{Na}(3'')$   
 $\cdots \text{Na}(3') \cdots \text{Na}(4) \cdots$ ,  
 with  $\mathbf{a}_0 + \mathbf{b}_0$  as general direction.

These paths have the  $\text{Na}(4)\text{--Na}(4')$  sequence in common and form a two-dimensional network. They skirt around the  $\text{P}(2)\text{O}_4$  tetrahedron, which is an obstacle in the diffusion plane.

The occupancy factors  $\tau$  of the sodium sites in  $\beta\text{-Na}_7\text{Fe}_3(\text{As}_2\text{O}_7)_4$  and  $\alpha\text{-Na}_7$

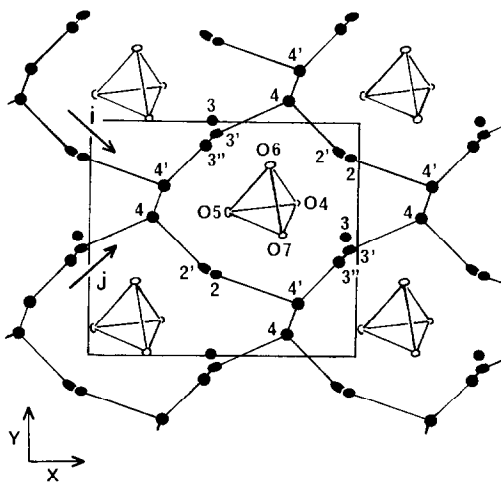


FIG. 4. Diffusion paths “*i*” and “*j*” in the  $\pi_2$  plane of the average structure. Projection along  $[001]^*$ . The numbers refer to Na sites.

TABLE IV  
OCCUPANCY FACTORS  $\tau$  OF THE SODIUM SITES IN  $\beta$ - $\text{Na}_7\text{Fe}_3(\text{As}_2\text{O}_7)_4$  AND  $\alpha$ - $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$

$\beta$ - $\text{Na}_7\text{Fe}_3(\text{As}_2\text{O}_7)_4$				$\alpha$ - $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$				$\alpha$ - $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$		
$C2/c, Z = 4$				Average structure $C2/c, Z = 4$				Superstructure $C2/c, Z = 12$		
Site	Position	$\tau$	$n^a$	Site	Position	$\tau$	$n^a$	Site	Position	$\tau$
Na(1)	8f	1	2	Na(1)	8f	1	2	Na(1a)	8f	1
Na(2)	8f	0.88	} 2.08	Na(2)	8f	0.33	0.66	Na(1b)	8f	1
Na(2')	8f	0.16		Na(2')	8f	0.66	1.32	Na(1c)	8f	1
Na(3)	4e	0.60	} 1	Na(3)	4e	0.36	0.36	Na(2a)	8f	1
Na(3')	8f	0.20		Na(3')	8f	0.47	0.94	Na(2b)	8f	0
Na(3'')	8f	0	} 1.64	Na(3'')	8f	0.17	0.34	Na(2c)	8f	0
Na(4)	8f	0.63		Na(4)	8f	0.33	0.66	Na(2'a)	8f	0
Na(4)'	8f	0.31	} 1.88	Na(4')	8f	0.37	0.74	Na(2'b)	8f	1
				Na(3'a)	8f			Na(2'c)	8f	1
								Na(3a)	8f	0
								Na(3b)	4e	1
								Na(3c)	8f	0
								Na(3'b)	8f	0
								Na(3'c)	8f	0.5 <sup>b</sup>
								Na(3''a)	8f	0
								Na(3''b)	8f	0
								Na(3''c)	8f	0.5 <sup>b</sup>
								Na(4a)	8f	1
								Na(4b)	8f	0
								Na(4c)	8f	0
								Na(4'a)	8f	0
								Na(4'b)	8f	1
								Na(4'c)	8f	0
$\Sigma n = 6.96$				$\Sigma n = 7.02$						

<sup>a</sup>  $n$  represents the number of sodium ions on a given site per formula unit.

<sup>b</sup> In the finally adopted description of the superstructure (Table V), the half-occupied Na(3'c) and Na(3''c) sites were transformed in a unique, totally occupied site, Na(3'''c), located halfway between Na(3'c) and Na(3''c).

$\text{Fe}_3(\text{P}_2\text{O}_7)_4$  are reported in Table IV. Their comparison leads to the following remarks:

—Na(1) is fully occupied in both structures.

—Na(3) and Na(4) have higher occupancy factors in the disordered form  $\beta$ - $\text{Na}_7\text{Fe}_3(\text{As}_2\text{O}_7)_4$ .

—The occupancy factors in  $\alpha$ - $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$  are approximately equal to multi-

ples of  $\frac{1}{3}$  except for the Na(3') and Na(3'') sites ( $\tau \approx \frac{1}{2}$  and  $\frac{1}{6}$ , respectively).

### The Superstructure

The determination of the superstructure was started in the space group  $Cc$  with initial atomic parameters deduced from those of the average structure. The atomic coordi-

nates and isotropic temperature factors of the Na(3a), Na(3b), and Na(3c) sites (issued from the Na(3) site) were refined first. Abnormally high values of the temperature factors were found for Na(3a) and Na(3c). Subsequently, both of these sites were considered vacant while Na(3b) was considered totally occupied. This agreed with the value of the occupancy factor close to  $\frac{1}{3}$  for Na(3) in the average structure. Similar operations were applied to the other sodium sites. A distribution of vacancies and totally occupied sodium sites which exhibited a pseudo- $C2/c$  symmetry was found. Consequently, the superstructure was refined in the space group  $C2/c$ .

Since the occupancy factor values for the Na(3') and Na(3'') sites in the average structure are close to  $\frac{1}{2}$  and  $\frac{1}{3}$ , respectively, some of the corresponding sodium sites of the superstructure were expected to be only partially occupied in the space group  $C2/c$ . A first solution of the superstructure was obtained (Table IV) with the following occupancy factors:

Na site:	3'a	3'b	3'c	3''a	3''b	3''c
$\tau$ :	1	0	0.5	0	0	0.5

The short distance (0.54 Å) between the Na(3'c) and Na(3''c) sites suggested a second solution in which these two sites would be replaced by a unique and totally occupied site, Na(3'''). Subsequent refinements converged to final reliability factors  $R = 0.039$  and  $R_w = 0.041$ . This solution, with a rather large temperature factor for Na(3'''), was adopted although the first one is virtually equivalent. Final atomic parameters are listed in Table V and selected distances and angles in Table VI.<sup>1</sup>

*Sodium distribution.* The superstructure of  $\alpha\text{-Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$  is characterized by a long-range ordering of the sodium ions. In the adopted description, these ions occupy 11 of the 22 sites derived from the average structure (Table IV). The distribution of totally occupied sodium sites and vacancies in the  $\pi_2$  plane is shown in Fig. 5. Along the  $i$  and  $j$  pathways defined above, the sodium ions form the following sequences:

“ $i$ ”:  $\cdots \text{Na}(4'b) \cdots \text{Na}(2'b) \cdots \text{Na}(4a) \cdots$   
 $\text{Na}(2a) \cdots \text{Na}(2'c) \cdots \text{Na}(4'b) \cdots$

“ $j$ ”:  $\cdots \text{Na}(4'b) \cdots \text{Na}(4a) \cdots \text{Na}(3'a) \cdots$   
 $\text{Na}(3''c) \cdots \text{Na}(4'b) \cdots$

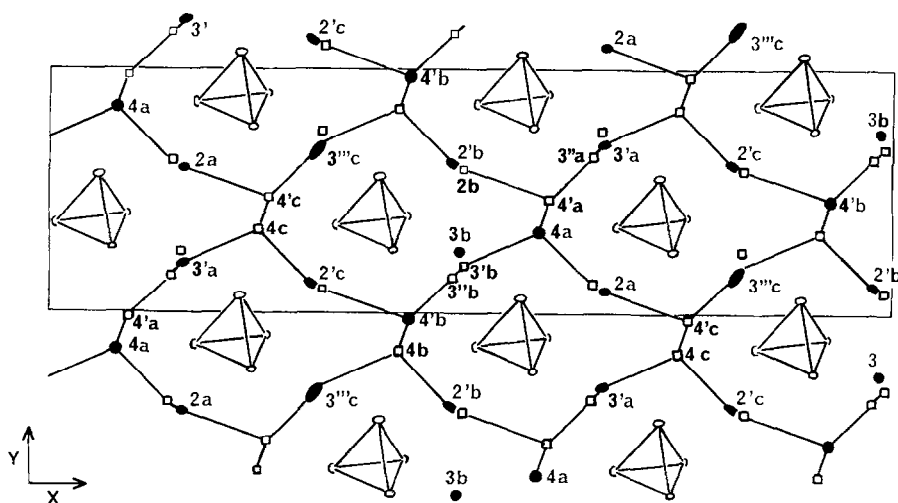


FIG. 5. Distribution of sodium sites (●) and vacancies (□) in the  $\pi_2$  plane of the superstructure. Projection along  $[001]^*$ .



TABLE V  
 ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS ( $\text{\AA}^2$ ) IN THE SUPERSTRUCTURE  
 OF  $\alpha\text{-Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$

	x	y	z	Beq.		x	y	z	Beq.
Fe(1a)	0	.3512 (1)	1/4	0.40 (2)	0(7a)	.1348 (1)	.2622 (5)	.3655 (1)	0.92 (8)
Fe(1b)	.33278(3)	.34345(8)	.25160(3)	0.43 (1)	0(7b)	.4667 (1)	.2575 (5)	.3671 (1)	0.87 (8)
Fe(2a)	.16774(3)	.2255 (1)	.43589(2)	0.33 (1)	0(7c)	.7997 (1)	.2572 (5)	.3671 (1)	0.72 (7)
Fe(2b)	.50136(3)	.2290 (1)	.43838(3)	0.40 (1)	0(8a)	.2188 (1)	.0838 (5)	.4249 (1)	0.75 (8)
Fe(2c)	.83526(3)	.2251 (1)	.43809(3)	0.38 (1)	0(8b)	.5516 (1)	.0839 (4)	.4259 (1)	0.66 (7)
P(1a)	.09886(5)	.5243 (2)	.24510(5)	0.41 (2)	0(8c)	.8858 (1)	.0834 (4)	.4261 (1)	0.59 (6)
P(1b)	.43115(5)	.5315 (2)	.24738(5)	0.48 (2)	0(9a)	.2903 (1)	.8858 (5)	.4532 (1)	0.71 (7)
P(1c)	.76584(5)	.5179 (2)	.24663(5)	0.49 (2)	0(9b)	.6230 (1)	.8845 (5)	.4524 (1)	0.78 (7)
P(2a)	.10480(5)	.4038 (2)	.33639(5)	0.53 (2)	0(9c)	.9572 (1)	.8857 (5)	.4548 (1)	0.56 (7)
P(2b)	.43736(5)	.3991 (2)	.33770(5)	0.43 (2)	0(10a)	.2000 (1)	.7860 (5)	.4125 (1)	0.78 (8)
P(2c)	.76880(5)	.3938 (2)	.33651(5)	0.46 (2)	0(10b)	.5323 (1)	.7902 (5)	.4131 (1)	0.78 (7)
P(3a)	.90077(5)	.9124 (2)	.44445(5)	0.44 (2)	0(10c)	.8673 (1)	.7851 (5)	.4151 (1)	0.73 (7)
P(3b)	.23441(5)	.9136 (2)	.44291(5)	0.44 (2)	0(11a)	.2305 (1)	.9044 (4)	.4951 (1)	0.57 (7)
P(3c)	.56762(5)	.9130 (2)	.44411(5)	0.33 (2)	0(11b)	.5652 (1)	.9049 (5)	.4971 (1)	0.66 (7)
P(4a)	.23268(5)	.0403 (2)	.53351(5)	0.36 (2)	0(11c)	.8970 (1)	.9061 (5)	.4971 (1)	0.59 (7)
P(4b)	.56710(5)	.0394 (2)	.53564(5)	0.33 (2)	0(12a)	.2007 (1)	.1808 (5)	.5064 (1)	0.74 (7)
P(4c)	.90031(5)	.0408 (2)	.53573(5)	0.38 (2)	0(12b)	.5353 (1)	.1790 (5)	.5086 (1)	0.46 (7)
O(1a)	.1083 (1)	.4610 (5)	.2023 (1)	0.80 (8)	0(12c)	.8686 (1)	.1834 (5)	.5093 (1)	0.53 (7)
O(1b)	.4426 (1)	.4609 (5)	.2063 (1)	0.95 (8)	0(13a)	.2875 (1)	.0841 (5)	.5603 (1)	0.78 (8)
O(1c)	.7768 (1)	.4506 (5)	.2054 (1)	0.85 (8)	0(13b)	.6221 (1)	.0838 (4)	.5619 (1)	0.54 (7)
O(2a)	.1242 (1)	.6847 (5)	.2654 (1)	0.76 (8)	0(13c)	.9555 (1)	.0839 (5)	.5610 (1)	0.99 (7)
O(2b)	.4586 (1)	.6876 (5)	.2670 (1)	0.69 (7)	0(14a)	.2121 (1)	.9602 (5)	.5679 (1)	0.69 (7)
O(2c)	.7929 (1)	.6745 (5)	.2674 (1)	0.79 (8)	0(14b)	.5462 (1)	.9594 (5)	.5701 (1)	0.57 (7)
O(3a)	.0418 (1)	.5308 (5)	.2355 (1)	0.58 (7)	0(14c)	.8804 (1)	.9625 (5)	.5712 (1)	0.54 (7)
O(3b)	.3748 (1)	.5346 (5)	.2375 (1)	0.89 (8)	Na(1a)	.15575(9)	.6303 (3)	.44497(8)	1.43 (5)
O(3c)	.7092 (1)	.5291 (5)	.2382 (1)	0.76 (8)	Na(1b)	.48657(8)	.6329 (3)	.44315(8)	1.15 (5)
O(4a)	.1206 (1)	.3991 (5)	.2895 (1)	0.57 (7)	Na(1c)	.81635(9)	.6398 (3)	.43968(8)	1.47 (5)
O(4b)	.4544 (1)	.4035 (5)	.2916 (1)	0.53 (7)	Na(2a)	.21536(9)	.5893 (3)	.35965(8)	1.51 (5)
O(4c)	.7873 (1)	.3911 (5)	.2915 (1)	0.59 (7)	Na(2' b)	.53623(9)	.6072 (3)	.35491(8)	1.62 (5)
O(5a)	.0483 (1)	.3647 (5)	.3186 (1)	0.68 (7)	Na(2' c)	.86107(9)	.6232 (3)	.35227(9)	1.75 (5)
O(5b)	.3806 (1)	.3611 (5)	.3185 (1)	0.69 (7)	Na(3' a)	.1972 (1)	.1995 (4)	.3088 (1)	2.63 (7)
O(5c)	.7123 (1)	.3480 (5)	.3170 (1)	0.84 (8)	Na(3b)	1/2	.2512 (4)	1/4	1.50 (7)
O(6a)	.1192 (1)	.5637 (5)	.3594 (1)	0.95 (8)	Na(3'''c)	.8591(1)	.1648 (5)	.3274 (1)	5.3 (1)
O(6b)	.4486 (1)	.5602 (5)	.3607 (1)	0.89 (8)	Na(4a)	.1308 (1)	.8362 (4)	.3438 (1)	2.40 (6)
O(6c)	.7781 (1)	.5579 (5)	.3577 (1)	0.99 (8)	Na(4' b)	.4805 (1)	.9705 (4)	.35204(9)	2.07 (6)

$$B_{\text{eq}} = 4/3 ( B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{12}ab.\cos\gamma + B_{13}ac.\cos\beta + B_{23}bc.\cos\alpha ) (\text{\AA}^2).$$

TABLE VI  
SELECTED INTERATOMIC DISTANCES AND ANGLES IN THE SUPERSTRUCTURE OF  $\alpha$ -Na<sub>7</sub>Fe<sub>3</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>4</sub>

<b>Na(2a)</b>		<b>Na(4'b)</b>		<b>Na(2'c)</b>		<b>Na(3b)</b>			
O(1c)	2.340(5)	O(10b)	2.399(4)	O(10c)	2.262(5)	O(3a)	2.315(5) x2		
O(14a)	2.407(4)	O(1a)	2.449(4)	O(5b)	2.383(5)	O(1b)	2.417(5) x2		
O(10a)	2.424(5)	O(7b)	2.491(5)	O(6c)	2.491(5)	O(4b)	2.457(5) x2		
O(5c)	2.488(5)	O(3a)	2.498(5)	O(1a)	2.510(5)				
O(7c)	2.718(5)	O(8b)	2.554(4)	O(2c)	2.590(4)				
O(6a)	2.749(5)	O(5a)	2.635(5)	O(4c)	2.935(4)				
O(13a)	2.819(5)			O(14b)	2.876(4)				
				O(13b)	2.974(4)				
<b>Na(3'a)</b>		<b>Na(3''c)</b>		<b>Na(4a)</b>		<b>Na(2'b)</b>			
O(1c)	2.312(5)	O(3c)	2.461(5)	O(10a)	2.293(4)	O(10b)	2.345(5)		
O(3b)	2.429(4)	O(7c)	2.523(6)	O(1b)	2.316(4)	O(1b)	2.451(5)		
O(6c)	2.518(4)	O(6b)	2.527(5)	O(6a)	2.365(5)	O(5a)	2.485(5)		
O(4a)	2.632(5)	O(5b)	2.641(6)	O(2a)	2.601(5)	O(6b)	2.597(5)		
O(3c)	2.668(5)	O(4c)	2.694(5)	O(5c)	2.727(5)	O(14c)	2.634(4)		
O(7a)	2.923(6)	O(8c)	2.837(4)	O(3b)	2.890(5)	O(2b)	2.810(4)		
O(5c)	2.958(5)	O(1a)	2.891(6)			O(13c)	2.906(5)		
						O(4b)	2.934(4)		
<b>P1a</b>	<b>O(1a)</b>	<b>O(2a)</b>	<b>O(3a)</b>	<b>O(4a)</b>	<b>P1b</b>	<b>O(1b)</b>	<b>O(2b)</b>	<b>O(3b)</b>	<b>O(4b)</b>
<b>01a</b>	<u>1.495(4)</u>	2.567(6)	2.514(6)	2.544(5)	<b>01b</b>	<u>1.501(5)</u>	2.539(6)	2.514(6)	2.485(6)
<b>02a</b>	115.9(3)	<u>1.533(4)</u>	2.531(5)	2.498(6)	<b>02b</b>	114.4(2)	<u>1.520(4)</u>	2.559(5)	2.494(6)
<b>03a</b>	111.6(2)	110.6(2)	<u>1.546(4)</u>	2.481(5)	<b>03b</b>	112.6(2)	114.6(2)	<u>1.522(4)</u>	2.495(5)
<b>04a</b>	109.6(2)	104.9(2)	103.3(2)	<u>1.617(4)</u>	<b>04b</b>	104.9(2)	104.6(2)	104.5(2)	<u>1.632(4)</u>
<b>P1c</b>	<b>O(1c)</b>	<b>O(2c)</b>	<b>O(3c)</b>	<b>O(4c)</b>	<b>P2a</b>	<b>O(4a)</b>	<b>O(5a)</b>	<b>O(6a)</b>	<b>O(7a)</b>
<b>01c</b>	<u>1.487(4)</u>	2.545(6)	2.550(6)	2.524(5)	<b>04a</b>	<u>1.622(4)</u>	2.534(6)	2.508(6)	2.434(5)
<b>02c</b>	115.3(2)	<u>1.526(4)</u>	2.525(5)	2.492(6)	<b>05a</b>	106.8(2)	<u>1.532(4)</u>	2.546(5)	2.490(5)
<b>03c</b>	114.7(2)	110.8(2)	<u>1.541(4)</u>	2.484(5)	<b>06a</b>	107.6(2)	115.1(2)	<u>1.484(4)</u>	2.546(6)
<b>04c</b>	107.7(2)	104.0(2)	102.8(2)	<u>1.635(4)</u>	<b>07a</b>	101.3(2)	109.1(2)	115.6(2)	<u>1.524(4)</u>
<b>P2b</b>	<b>O(4b)</b>	<b>O(5b)</b>	<b>O(6b)</b>	<b>O(7b)</b>	<b>P2c</b>	<b>O(4c)</b>	<b>O(5c)</b>	<b>O(6c)</b>	<b>O(7c)</b>
<b>04b</b>	<u>1.622(4)</u>	2.541(6)	2.497(6)	2.467(5)	<b>04c</b>	<u>1.614(4)</u>	2.547(6)	2.507(6)	2.421(5)
<b>05b</b>	107.2(2)	<u>1.534(4)</u>	2.505(5)	2.494(5)	<b>05c</b>	107.5(2)	<u>1.543(4)</u>	2.522(5)	2.498(5)
<b>06b</b>	106.8(2)	112.1(2)	<u>1.486(4)</u>	2.567(6)	<b>06c</b>	107.7(2)	112.5(2)	<u>1.489(4)</u>	2.570(6)
<b>07b</b>	103.4(2)	109.4(2)	117.2(2)	<u>1.521(4)</u>	<b>08c</b>	101.2(2)	109.4(2)	117.4(2)	<u>1.518(4)</u>
<b>P3a</b>	<b>O(8a)</b>	<b>O(9a)</b>	<b>O(10a)</b>	<b>O(11a)</b>	<b>P3b</b>	<b>O(8b)</b>	<b>O(9b)</b>	<b>O(10b)</b>	<b>O(11b)</b>
<b>08a</b>	<u>1.523(4)</u>	2.512(5)	2.536(6)	2.491(5)	<b>08b</b>	<u>1.533(4)</u>	2.517(5)	2.507(5)	2.506(5)
<b>09a</b>	111.0(2)	<u>1.524(4)</u>	2.542(5)	2.467(6)	<b>09b</b>	110.9(2)	<u>1.524(4)</u>	2.535(5)	2.483(6)
<b>010a</b>	114.0(2)	114.4(2)	<u>1.500(4)</u>	2.492(5)	<b>010b</b>	112.0(2)	114.4(2)	<u>1.491(4)</u>	2.513(5)
<b>011a</b>	105.6(2)	104.1(2)	106.7(1)	<u>1.604(4)</u>	<b>011b</b>	105.8(2)	104.8(2)	108.3(1)	<u>1.609(4)</u>
<b>P3c</b>	<b>O(8c)</b>	<b>O(9c)</b>	<b>O(10c)</b>	<b>O(11c)</b>	<b>P4a</b>	<b>O(11a)</b>	<b>O(12a)</b>	<b>O(13a)</b>	<b>O(14a)</b>
<b>08c</b>	<u>1.530(4)</u>	2.510(5)	2.537(5)	2.504(5)	<b>011a</b>	<u>1.595(4)</u>	2.520(5)	2.512(5)	2.460(6)
<b>09c</b>	109.8(2)	<u>1.537(4)</u>	2.533(5)	2.486(6)	<b>012a</b>	108.1(2)	<u>1.519(4)</u>	2.528(5)	2.529(6)
<b>010c</b>	115.1(2)	114.4(2)	<u>1.476(4)</u>	2.485(5)	<b>013a</b>	107.9(2)	113.1(2)	<u>1.511(4)</u>	2.470(6)
<b>011c</b>	105.5(2)	104.1(2)	106.9(1)	<u>1.615(4)</u>	<b>014a</b>	104.6(2)	113.1(2)	109.6(2)	<u>1.512(4)</u>
<b>P4b</b>	<b>O(11b)</b>	<b>O(12b)</b>	<b>O(13b)</b>	<b>O(14b)</b>	<b>P4c</b>	<b>O(11c)</b>	<b>O(12c)</b>	<b>O(13c)</b>	<b>O(14c)</b>
<b>011b</b>	<u>1.592(4)</u>	2.506(5)	2.502(4)	2.475(6)	<b>011c</b>	<u>1.586(4)</u>	2.519(6)	2.499(5)	2.472(6)
<b>012b</b>	107.7(2)	<u>1.510(4)</u>	2.521(4)	2.528(5)	<b>012c</b>	108.2(2)	<u>1.523(4)</u>	2.522(4)	2.540(5)
<b>013b</b>	107.2(2)	112.8(2)	<u>1.516(3)</u>	2.494(5)	<b>013c</b>	107.4(2)	112.3(2)	<u>1.514(3)</u>	2.488(6)
<b>014b</b>	105.3(2)	113.0(2)	110.4(1)	<u>1.521(4)</u>	<b>014c</b>	105.4(2)	113.1(2)	110.1(2)	<u>1.521(4)</u>

Note. The P–O distances are underlined. The O–O distances are given above the diagonal, the O–P–O angles below.

TABLE VII

Na-Na DISTANCES AND RADII,  $R$ , OF THE OXYGEN WINDOWS ( $\text{\AA}$ ) IN THE  $i$  AND  $j$  CONDUCTION PATHWAYS

Sodium sites	Distance	Oxygen windows	$R$ ( $\text{\AA}$ )
<i>i</i>			
Na(4'b)-Na(2'b)	3.405(4)	O(2b),O(5a),O(6b),O(10b)	2.085
Na(2'b)-Na(4a)	3.626(4)	O(1b),O(13c),O(14c)	2.251
Na(4a)-Na(2a)	3.070(4)	O(2a),O(5c),O(6a),O(10a)	2.096
Na(2a)-□(4'c)		O(1c),O(13a),O(14a)	2.236
□(4c)-Na(2'c)		O(2c),O(5b),O(6c),O(10c)	2.114
Na(2'c)-Na(4'b)	3.640(4)	O(1a),O(13b),O(14b)	2.187
<i>j</i>			
Na(4'b)-□(3''b)		O(3a),O(5a),O(7b)	2.277
□(3'b)-Na(4a)		O(1b),O(2a),O(6a)	2.014
Na(4a)-Na(3'a)	3.914(5)	O(3b),O(5c),O(7a)	2.307
Na(3'a)-□(4c)		O(1c),O(2c),O(6c)	1.989
□(4'c)-Na(3''c)		O(3c),O(5b),O(7c)	2.282
Na(3''c)-Na(4'b)	4.138(5)	O(1a),O(2b),O(6b)	2.014

They are distributed over the available sites so that two proximate sites are not occupied simultaneously. This probably minimizes the electrostatic repulsions between the  $\text{Na}^+$  ions. In some cases, two or even three neighboring sodium sites are vacant: (4c)-(4'c), (3'b)-(3''b), (2b)-(4'a)-(3''a). The sodium-sodium distances (Table VII) range from 3.07 to 4.138  $\text{\AA}$  and are shorter in the  $i$  pathway than in the  $j$  one.

*Influence of the superstructure on the framework.* The sodium ion ordering is associated with small shifts in the Fe, P, and O positions. These shifts were calculated for each atom  $A(n)$  ( $A = \text{Fe}, \text{P}, \text{O}$ ) as follows: The  $x$  coordinates of  $A(nb)$  and  $A(nc)$  were first reduced by  $\frac{1}{3}$  and  $\frac{2}{3}$  respectively, then the  $A(nb)$ - $A(na)$ ,  $A(nc)$ - $A(na)$ , and  $A(nc)$ - $A(nb)$  interatomic distances were calculated. For the Fe and P atoms the maximum shifts were observed in the A-layer: 0.08 and 0.13  $\text{\AA}$ , respectively. For the oxygen atoms, the shifts do not exceed 0.13  $\text{\AA}$  in the A-layer, except for O(5a)-O(5c) (0.16  $\text{\AA}$ ) and O(6a)-O(6c) (0.21  $\text{\AA}$ ). In the B-layer, they are even lower (max. value: 0.08  $\text{\AA}$ ). It is interesting to examine the effects of these low oxygen shifts on the sodium coordina-

tion polyhedra: considering the  $\text{Na}(na)$ ,  $\text{Na}(nb)$ , and  $\text{Na}(nc)$  sites derived from a particular  $\text{Na}(n)$  site of the average structure, one notes that the coordination polyhedra do not greatly differ in shape and size whether the site is occupied or not. Nevertheless, when the sodium coordination polyhedron shares an edge with a  $\text{PO}_4$  tetrahedron, the occupation of the sodium site is associated with a significant shortening of the shared edge and with a reduction of the corresponding O-P-O angle so that the electrostatic repulsion between phosphorus and sodium is lowered (Table VIII).

*Oxygen windows.* The radius  $R$  of the oxygen windows which separate neighboring Na sites are given in Table VII. Most of them are slightly shorter than those reported for  $\beta\text{-Na}_7\text{Fe}_3(\text{As}_2\text{O}_7)_4$ . There is no evidence for a preferential conduction pathway in the  $\pi$ -plane.

*Possibility of nonstoichiometry.* A close examination of the sodium ion distribution suggests a possibility of nonstoichiometry. This would result from the introduction of additional sodium ions on sites which are normally vacant in the stoichiometric material. Taking into account the necessity for

TABLE VIII  
O—O DISTANCES AND O—P—O ANGLES FOR EDGES SHARED BY A PO<sub>4</sub> TETRAHEDRON AND A Na SITE  
COORDINATION POLYHEDRON

P atom	Shared edge	Neighboring sodium site or vacancy	O—O distance (Å)	O—P—O angle (°)
P(1b)	O(1b)—O(3b)	Na(4a)	2.514(6)	112.6(2)
P(1a)	O(1a)—O(3a)	Na(4'b)	2.514(6)	111.6(2)
P(1c)	O(1c)—O(3c)	□(4c)	2.550(6)	114.7(2)
P(1b)	O(1b)—O(4b)	Na(3b)	2.485(6)	104.9(2)
P(1c)	O(1c)—O(4c)	□(3a)	2.524(5)	107.7(2)
P(1a)	O(1a)—O(4a)	□(3a)	2.544(5)	109.6(2)
P(2c)	O(4c)—O(7c)	Na(3''c)	2.421(5)	101.2(2)
P(2a)	O(4a)—O(7a)	□(3''a)	2.434(5)	101.3(2)
P(2b)	O(4b)—O(7b)	□(3''b)	2.467(5)	103.4(2)

a sodium ion to be located at a minimum distance—say about 3 Å—from any other sodium ion, it appears that the (4c) or (4'c) vacant sites could be occupied. The occupation of the (3'b) or (3''b) vacancy with a concomitant emptying of the (3b) site is another possibility to be considered. These two modifications would bring about per se additional contents of  $\frac{2}{3}$  and  $\frac{1}{3}$  Na, respectively, per formula unit. Obviously they should be accompanied by changes in the framework composition for charge compensation. In fact, among the arsenates isotypic with the title compound, two cases of nonstoichiometry have been encountered. Their study is now in progress.

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