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Structure of the Sodium Ion Conductor $\text{Na}_7\text{Fe}_3(\text{As}_2\text{O}_7)_4$

BY C. MASQUELIER AND F. D'YVOIRE

Laboratoire de Chimie des Solides, UA CNRS 446, Université Paris-Sud, 91405 Orsay CEDEX, France

AND N. RODIER

Laboratoire de Chimie Minérale, Faculté des Sciences pharmaceutiques et biologiques, 5 rue J.-B. Clément, 92296 Châtenay-Malabry CEDEX, France

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Abstract. Heptasodium triiron tetrakis(diarsenate), $\text{Na}_7\text{Fe}_3(\text{As}_2\text{O}_7)_4$, $M_r = 1375.83$, monoclinic, $C2/c$, $a = 9.940$ (1), $b = 8.5483$ (7), $c = 28.762$ (2) Å, $\beta = 93.683$ (8)°, $V = 2438.9$ (4) Å³, $Z = 4$, $D_x = 3.747$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 12.81$ mm⁻¹, $F(000) = 2572$, $T = 294$ (1) K, $R = 0.033$ for 2440 independent reflections. The structure consists of a three-dimensional framework of FeO_6 octahedra sharing corners with As_2O_7 groups and an interstitial space in which the Na ions are located. The framework can be described as a succession of layers of $\text{Fe}(\text{As}_2\text{O}_7)_2$ (*A*) and $\text{Fe}_2(\text{As}_2\text{O}_7)_2$ (*B*), parallel to (001). The presence of wide windows between the Na sites as well as the delocalization of some of the Na ions account for the fast cation-transport properties exhibited by the solid. The diffusion of Na ions seems to be easy parallel to (001) through the *A* layer while crossing the *B* layer requires passage through a rather narrow bottleneck.

Introduction. A new sodium iron diphosphate, $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$, and the isotopic diarsenate, $\text{Na}_7\text{Fe}_3(\text{As}_2\text{O}_7)_4$, have recently been synthesized. Both exhibit good cation-exchange properties and a rather high ionic conductivity (d'Yvoire, Masquelier, Bretey, Peytour & Berthet, 1990). The crystal structure of the arsenate is reported here.

Experimental. Crystals of $\text{Na}_7\text{Fe}_3(\text{As}_2\text{O}_7)_4$ were prepared in a flux of sodium arsenates. A mixture of composition $\text{Fe}_2\text{O}_3 + 3.7\text{As}_2\text{O}_5 + 5.1\text{Na}_4\text{As}_2\text{O}_7$ was melted at 1073 K, cooled at a rate of 100 K h⁻¹ down to room temperature and then washed with water in order to eliminate the excess of sodium arsenates. Small single crystals delimited by $\{\bar{1}11\}$ and $\{001\}$ were obtained. The selected crystal was elongated along [101] (0.16 × 0.11 × 0.09 mm). The unit-cell constants, measured from 25 independent reflections with $6.91 \leq \theta \leq 25.55^\circ$, are $a = 9.926$ (2), b

= 8.537 (2), $c = 28.725$ (5) Å, $\beta = 93.64$ (2)°. These values were used to calculate interatomic distances and angles. They agree satisfactorily with those determined from powder data (given in *Abstract*). Enraf-Nonius CAD-4 diffractometer, graphite monochromator. $0.039 \leq (\sin\theta)/\lambda \leq 0.704$ Å⁻¹. $0 \leq h \leq 13$, $0 \leq k \leq 12$, $-40 \leq l \leq 40$. Intensity controlled with $\bar{2}2\bar{5}$, $0\bar{2}7$ and 513 reflections with no significant variations. Scan mode: $\theta - 2\theta$ with $(0.75 + 0.35 \tan \theta)^\circ$ range. 3528 independent reflections among which 1088 were unobserved [$I \leq 3\sigma(I)$]. Absorption corrections performed using the program *ABSCOR* (Coppens, Leiserowitz & Rabinovich, 1965); min., max. transmission coefficients 0.272, 0.369. Direct methods, *MULTAN11/82* program (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Refinements on F^2 s based on full-matrix least-squares calculations. Scattering factors and f' , f'' from *International Tables for X-ray Crystallography* (1974). Refined parameters: x , y , z and thermal parameters of all atoms (anisotropic except for three Na sites). $R = 0.033$, $wR = 0.042$, $w = 1/\sigma^2(F)$, $S = 1.48$, $(\Delta/\sigma) \leq 0.01$, $|\Delta\rho|_{\max} = 1.6$ (3) e Å⁻³. The final atomic parameters are listed in Table 1.* Selected interatomic distances and angles are given in Table 2. Calculation programs from the *SDP* system (B. A. Frenz & Associates, Inc., 1982). Fig. 1 drawn with *ORTEPII* (Johnson, 1976). Computer used: DEC PDP-11/44.

Discussion. The structure consists of a three-dimensional framework $[\text{Fe}_3(\text{As}_2\text{O}_7)_4]$ in which the Na ions are inserted (Fig. 1). The framework is made of FeO_6 octahedra sharing their O atoms with diarsenate groups As_2O_7 . It can be described as a succession of layers *A* and *B* parallel to (001).

In the *A* layer, $\text{Fe}(1)[\text{As}(1)\text{As}(2)\text{O}_7]_2$, each Fe atom is chelated by two $\text{As}(1)\text{As}(2)\text{O}_7$ groups via O(3) and O(5) and singly connected with two other $\text{As}(1)\text{As}(2)\text{O}_7$ groups via O(2).

In the *B* layer, $[\text{Fe}(2)\text{As}(3)\text{As}(4)\text{O}_7]_2$, each Fe atom is chelated by one $\text{As}(3)\text{As}(4)\text{O}_7$ group via O(8) and O(12) and singly connected with three other $\text{As}(3)\text{As}(4)\text{O}_7$ groups via O(9), O(13) and O(14). In addition, Fe(2) is linked via O(7) to an $\text{As}(1)\text{As}(2)\text{O}_7$ group of the adjacent *A* layer. This connection between *A* and *B* layers maintains the three-dimensional character of the framework.

The O atoms O(1) and O(6) in the *A* layer and O(10) in the *B* layer belong to only one polyhedron of the framework (an AsO_4 tetrahedron).

* Lists of structure factors, anisotropic thermal parameters, bond angles and interatomic distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52848 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Occupancy factors, atomic coordinates and isotropic temperature factors for $\text{Na}_7\text{Fe}_3(\text{As}_2\text{O}_7)_4$*

$$B_{\text{eq}} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (abc\cos\gamma)\beta_{12} + (accos\beta)\beta_{13} + (bccos\alpha)\beta_{23}].$$

	Occupancy	x	y	z	$B_{\text{eq}}/B_{\text{iso}}(\text{\AA}^2)$
As(1)	1	0.29984 (6)	0.29537 (7)	0.24664 (2)	0.664 (9)
As(2)	1	0.21985 (6)	0.16184 (7)	0.33893 (2)	0.654 (9)
As(3)	1	0.51105 (5)	0.66258 (7)	0.44285 (2)	0.512 (9)
As(4)	1	0.41229 (5)	0.79584 (7)	0.53617 (2)	0.475 (9)
Fe(1)	1	0	0.1202 (1)	$\frac{1}{2}$	0.58 (2)
Fe(2)	1	0.31751 (8)	0.9771 (1)	0.43648 (3)	0.53 (1)
Na(1)	1	0.2783 (3)	0.3808 (3)	0.4457 (1)	1.60 (5)
Na(2)	0.88	0.5211 (4)	0.3577 (4)	0.3561 (1)	2.80 (7)
Na(2')	0.16	0.475 (2)	0.384 (2)	0.3447 (7)	2.0 (3)*
Na(3)	0.60	$\frac{1}{2}$	0.0168 (8)	$\frac{1}{2}$	2.9 (2)
Na(3')	0.20	0.525 (2)	0.961 (2)	0.3094 (6)	2.4 (3)*
Na(4)	0.63	0.2957 (6)	0.6031 (8)	0.3461 (2)	3.9 (1)
Na(4')	0.31	0.339 (1)	0.719 (2)	0.3510 (5)	3.6 (2)*
O(1)	1	0.3742 (4)	0.2214 (6)	0.2019 (2)	1.28 (8)
O(2)	1	0.3623 (4)	0.4638 (5)	0.2685 (2)	1.11 (8)
O(3)	1	0.1313 (4)	0.2994 (5)	0.2385 (2)	0.95 (7)
O(4)	1	0.3294 (4)	0.1598 (5)	0.2926 (2)	0.91 (7)
O(5)	1	0.0632 (4)	0.1199 (5)	0.3172 (2)	1.16 (8)
O(6)	1	0.2371 (5)	0.3355 (6)	0.3626 (2)	1.66 (9)
O(7)	1	0.2751 (5)	0.0041 (5)	0.3690 (2)	1.25 (8)
O(8)	1	0.4772 (4)	0.8462 (5)	0.4254 (2)	1.01 (7)
O(9)	1	0.6768 (4)	0.6382 (5)	0.4532 (2)	0.82 (7)
O(10)	1	0.4353 (4)	0.5292 (5)	0.4100 (2)	1.01 (7)
O(11)	1	0.4463 (4)	0.6451 (5)	0.4982 (2)	0.89 (7)
O(12)	1	0.3425 (4)	0.9450 (5)	0.5056 (1)	0.79 (7)
O(13)	1	0.5593 (4)	0.8364 (5)	0.5642 (2)	0.96 (7)
O(14)	1	0.3086 (4)	0.7141 (5)	0.5722 (1)	0.82 (7)

* Refined isotropically.

In the $\text{As}(1)\text{As}(2)\text{O}_7$ group, the mean As—O distance is 1.769 Å for the bridging As—O bonds and 1.663 Å for the terminal ones. The corresponding values are 1.746 and 1.662 Å in the $\text{As}(3)\text{As}(4)\text{O}_7$ group. Similar differences between bridging and terminal bond lengths are observed in $\text{Na}_4\text{As}_2\text{O}_7$ (Leung & Calvo, 1973) and in diphosphates (see for instance Riou, Labbé & Goreaud, 1988). The As_2O_7 groups are in a nearly eclipsed configuration as shown by the values of the dihedral angles: 18.0 (2)° between the O(3)As(1)As(2) and O(5)As(1)As(2) planes; 17.1 (2)° between the O(8)As(3)As(4) and O(12)As(3)As(4) planes. The corresponding angles are 12° in NaFeP_2O_7 (Gabelica-Robert, Goreaud, Labbé & Raveau, 1982) and 13.4 (2)° in $\text{Na}_7(\text{FeP}_2\text{O}_7)_4\text{PO}_4$ (de la Rochère, Kahn, d'Yvoire & Bretey, 1985).*

The Na ions are distributed over seven sites. Each site is surrounded by five to seven O atoms with Na—O distances ranging from 2.30 to 3.00 Å (Table 2). The Na(1) site is fully occupied. The other sites form three pairs; for each pair, the two sites, $\text{Na}(i)$ and $\text{Na}(i')$, are too close to be simultaneously occupied (Table 2). Considering the asymmetric unit, the maximum number of Na ions in each of the $\text{Na}(2)$ – $\text{Na}(2')$ and $\text{Na}(4)$ – $\text{Na}(4')$ pairs is one. The effective

* The value given in this reference (8°) is incorrect.

Table 2. Selected interatomic distances (Å) and angles (°), distances between neighbouring sodium positions (Å), and radii *R* (Å) of the oxygen windows connecting these positions along the diffusion paths

As(1)—O(1)	1.647 (5)	As(2)—O(4)	1.771 (4)
As(1)—O(2)	1.672 (4)	As(2)—O(5)	1.677 (4)
As(1)—O(3)	1.675 (4)	As(2)—O(6)	1.636 (5)
As(1)—O(4)	1.766 (4)	As(2)—O(7)	1.673 (4)
As(3)—O(8)	1.674 (4)	As(4)—O(11)	1.733 (4)
As(3)—O(9)	1.666 (4)	As(4)—O(12)	1.671 (4)
As(3)—O(10)	1.631 (4)	As(4)—O(13)	1.659 (4)
As(3)—O(11)	1.760 (4)	As(4)—O(14)	1.660 (4)
As(1)—As(2)	3.0372 (8)	Fe(2)—O(7 ^h)	1.972 (4)
As(3)—As(4)	3.1265 (8)	Fe(2)—O(8)	1.981 (4)
Fe(1)—O(2) × 2	2.006 (4)	Fe(2)—O(9 ^h)	2.039 (4)
Fe(1)—O(3) × 2	2.050 (4)	Fe(2)—O(12)	2.005 (4)
Fe(1)—O(5) × 2	1.992 (4)	Fe(2)—O(13 ^h)	2.008 (4)
Na(1)—O(10)	2.300 (5)	Fe(2)—O(14 ^h)	2.063 (4)
Na(1)—O(9)	2.319 (5)	Na(2)—O(10)	2.331 (6)
Na(1)—O(12)	2.413 (5)	Na(2)—O(1)	2.331 (6)
Na(1)—O(6)	2.427 (6)	Na(2)—O(5)	2.548 (6)
Na(1)—O(13)	2.485 (5)	Na(2)—O(14)	2.650 (5)
Na(1)—O(9)	2.915 (5)	Na(2)—O(7)	2.817 (7)
Na(3)—O(1) × 2	2.510 (7)	Na(2)—O(6)	2.843 (7)
Na(3)—O(3) × 2	2.304 (7)	Na(2)—O(13)	2.974 (6)
Na(3)—O(4) × 2	2.474 (5)	Na(4)—O(10)	2.316 (7)
Na(2)—O(10)	2.30 (2)	Na(4)—O(1)	2.339 (8)
Na(2)—O(5)	2.35 (2)	Na(4)—O(6)	2.411 (8)
Na(2)—O(6)	2.48 (2)	Na(4)—O(2)	2.647 (8)
Na(2)—O(2)	2.49 (2)	Na(4)—O(5)	2.835 (8)
Na(2)—O(1)	2.50 (2)	Na(4)—O(10)	2.49 (1)
Na(2)—O(4)	2.78 (2)	Na(4)—O(7)	2.58 (1)
Na(3)—O(3)	2.44 (2)	Na(4)—O(5)	2.62 (1)
Na(3)—O(1)	2.47 (2)	Na(4)—O(1)	2.53 (1)
Na(3)—O(4)	2.60 (2)	Na(4)—O(8)	2.69 (1)
Na(3)—O(3)	2.73 (2)	Na(4)—O(3)	2.70 (1)
Na(3)—O(6)	2.74 (2)	Na(4)—O(14)	2.78 (1)
Na(3)—O(5)	2.95 (2)	O(3)—O(4)—O(5)	62.3 (2)
As(1)—O(4)—As(2)	118.3 (2)	O(8)—O(11)—O(12)	62.6 (2)
As(3)—O(11)—As(4)	127.1 (2)		
Diffusion paths			
α Na(4)—Na(2')	2.58 (2)	R[O(2),O(5),O(6),O(10)]	2.06
Na(2')—Na(2)	0.59 (2)	R[O(1),O(13),O(14)]	2.25
Na(2)—Na(4')	3.38 (1)		
β Na(4)—Na(4')	1.08 (1)	R[O(3),O(5),O(7)]	2.33
Na(4')—Na(3')	3.07 (2)	R[O(1),O(2),O(6)]	2.04
Na(3')—Na(4)	3.07 (2)	R[O(3),O(3),O(1)]	2.28
Na(3')—Na(3)	1.77 (2)	R[O(6),O(10),O(12)]	2.20
Na(4)—Na(1)	3.447 (2)	R[O(9),O(9),O(13)]	2.00
Na(1)—Na(1)	3.907 (4)		

Symmetry code: (i) $x, 1+y, z$; (ii) $x-\frac{1}{2}, y+\frac{1}{2}, z$; (iii) $1-x, 2-y, 1-z$; (iv) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$.

numbers of Na ions in these pairs (Table 1) are equal to the maximum value within the limits of error.

Sodium ion transport. The partial occupation of the Na(2) to Na(4') sites is a favourable factor for fast diffusion of the Na ions. This diffusion requires yet another condition: it is usually assumed that the radius *R* of the windows which separate the neighbouring Na sites must be at least equal to the sum $r(\text{Na}^+) + r(\text{O}^{2-}) = 2.35 \text{ \AA}$. Nevertheless, in some ionic conductors the windows have a much smaller

radius. For instance, $R = 1.90 \text{ \AA}$ in $\text{II-Na}_3\text{Fe}_2(\text{AsO}_4)_3$ (d'Yvoire, Bretey & Collin, 1988). (In this compound, the O atoms that form the windows belong to only one polyhedron of the framework and have a high equivalent isotropic temperature factor, 1.8 \AA^2 ; their thermal motion may facilitate the migration of the Na ions through the narrow window.) For the crystal under study, the windows were systematically examined: those whose radius is larger than about 2 \AA were considered as possible passageways for the Na ions. The main results are presented in Table 2. Their examination leads us to the following conclusions:

(i) Inside the *A* layer (Fig. 1), the Na(2), Na(2'), Na(3'), Na(4) and Na(4') sites are interconnected so as to form two diffusion planes π_1 and π_2 parallel to (001) at $z_1 = 0.15$ and $z_2 = 0.35$ respectively. Fig. 2 represents the most probable diffusion paths in the π_2 plane. Two paths can be distinguished:

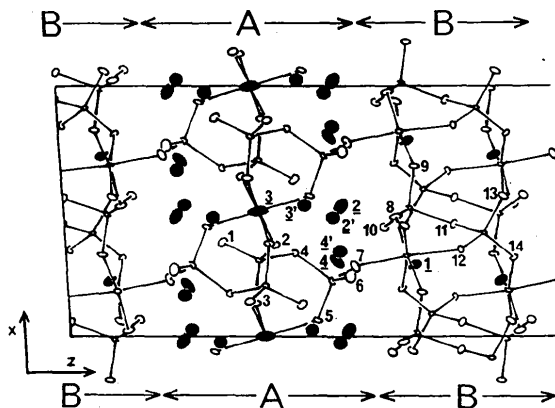


Fig. 1. Partial view of the structure along [010]. Na sites in black. The underlined numbers refer to Na sites; other numbers refer to O sites.

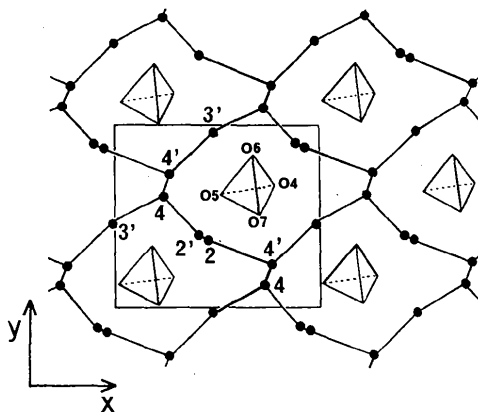
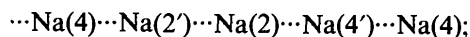
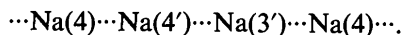


Fig. 2. Diffusion paths in the π_2 plane. Projection along [001]*. The numbers refer to Na-atom positions.

α with $\mathbf{a} - \mathbf{b}$ as general direction



β with $\mathbf{a} + \mathbf{b}$ as general direction



These paths form a two-dimensional network. They have the Na(4) \cdots Na(4') sequence in common and skirt round the As(2)O₄ tetrahedron which is an obstacle in the diffusion plane.

(ii) The Na(3') \cdots Na(3) \cdots Na(3') sequence ensures the connection between the π_1 and π_2 path networks.

(iii) The Na(1) and Na(4) sites are connected by a wide window ($R = 2.20 \text{ \AA}$). By contrast, two neighbouring Na(1) positions located on each side of the *B*-layer median plane are separated by a narrow window ($R = 2.00 \text{ \AA}$) whose O atoms display low temperature factors. Thus, the diffusion of the Na ions through the *B* layer seems to be rather difficult. The low temperature factor of the Na(1) ion is another indication in favour of this conclusion.

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Die Struktur der eindimensional fehlgeordneten Blei-Vanadiumbronze, $\beta\text{-Pb}_{0,333}\text{V}_2\text{O}_5$

VON KATSUO KATO UND KOUSUKE KOSUDA

Mukizaishitsu Kenkyusho, † 1-1 Namiki, Tsukuba-shi, Ibaraki-ken 305, Japan

UND TETSUYA KOGA UND HIROSHI NAGASAWA ‡

Institute of Physics, University of Tsukuba, Tsukuba-shi, Ibaraki-ken 305, Japan

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Abstract. β -Lead divanadate, $M_r = 250.88$, monoclinic, $C2/m$, $a = 15.463 (14)$, $b = 3.6477 (5)$, $c = 10.116 (9) \text{ \AA}$, $\beta = 109.20 (4)^\circ$, $V = 538.9 (7) \text{ \AA}^3$, $Z = 6$, $D_x = 4.639 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha_{1,2}) = 0.709300$, 0.713590 \AA , $\mu = 20.6 \text{ mm}^{-1}$, $F(000) = 679.8$, $T = 296 \text{ K}$, final $R = 0.054$ for 1926 unique observed reflections. The structure is isotypic with that of $\beta\text{-Na}_x\text{V}_2\text{O}_5$ [Darriet, Von der Mühl & Galy (1969). *Bull. Soc. Fr. Minéral. Crystallogr.* 92, 17–24; Wadsley (1955). *Acta Cryst.* 8, 695–701]. On account of the one-dimensional disorder of the staggered chains of Pb ions running along [010], superlattice reflections appearing at $h/2$, $k + 1/2$, l are tied by lines of diffuse scattering parallel to \mathbf{a}^* . The disorder can be characterized by four probability parameters.

* Staatliches Institut für Anorganische Materialforschung.

‡ Gast-Mitarbeiter des obigen Instituts.

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Einleitung. Um PbVO₃ herzustellen, erhitzte man ein Gemisch von PbO und VO₂ in einer evakuierten Quarzglasampulle. Dabei wurde die Ampulle stark von dem Gemisch geätzt und barst schließlich.

In der zum Teil oxydierten Reaktionsmasse wurden die Kristalle von $\beta\text{-Pb}_x\text{V}_2\text{O}_5$ gefunden, welche diffuse Überstrukturreflexe aufwiesen. Aus drei Analysen mit der Elektronenmikrosonde EMX-SM7 der Firma Shimadzu ergaben sich die Werte: V 39,1 bis 40,7, Pb 27,6 bis 28,6 Gew.-%. Die Kristalle wurden somit als $\text{Pb}_{0,333}\text{V}_2\text{O}_5$ (V 40,6, Pb 27,5 Gew.-%) betrachtet.

$\beta\text{-Pb}_x\text{V}_2\text{O}_5$, isotyp mit $\beta\text{-Na}_x\text{V}_2\text{O}_5$ (Wadsley, 1955), ist bereits von Darriet, Von der Mühl & Galy (1969) eingehend untersucht worden. Verzerrte VO₆-Oktaeder und VO₅-Pyramiden sind über gemeinsame Kanten miteinander verknüpft und bilden Schichten parallel (100). Die Schichten sind durch