

# Synthesis, crystal structure and charge distribution of $\text{Na}_7\text{As}_{11}\text{O}_{31}$ : An oxygen-deficient layered sodium arsenate

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## Abstract

A new sodium arsenate with layer structure has been synthesized and its crystal structure solved and refined by single-crystal X-ray diffraction. The crystal is trigonal, space group  $P\bar{3}m1$ ,  $a = 11.199(3)\text{Å}$ ,  $c = 5.411(2)\text{Å}$ ,  $V = 587.80(3)\text{Å}^3$ ,  $Z = 1$ ; the refinement converged to  $R = 0.0282$  and  $wR = 0.0751$  for 590 reflections with  $(I) > 2\sigma(I)$ . The structural model gives the formula  $\text{Na}_7\text{As}_{11}\text{O}_{32}$ , which would be non-neutral; besides, the structural model is not validated by the charge distribution (CD) analysis, which gives an unsatisfactory agreement on the computed charges of the cations. The CD analysis suggest incomplete (5/6) occupation of the O5 site, which leads to the deficiency of an oxygen atom per unit cell and to formula  $\text{Na}_7\text{As}_{11}\text{O}_{31}$ : this new structural model corresponds to a neutral compound, is validated by the CD analysis, and results in better displacement parameters for O5 than its non neutral counterpart. The (001) anionic layers are built up from corner and edge sharing of As1 and As2 distorted octahedra and As3 distorted tetrahedra, the sodium cations playing the role of interlayer cations. The effects of the oxygen deficiency on the crystal structure are discussed.

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## 1. Introduction

Layer compounds are the subject of intensive research due to the potential existence of ionic conduction pathways in the structure. Our research currently focuses on alkali arsenates, in particular on the seek for new compounds of potential technological interest in the binary  $\text{Na}_2\text{O}-\text{As}_2\text{O}_5$  system, as a function of several synthesis parameters, such as the chemical composition and the heating conditions. The condensed arsenates are obtained with lower O/As ratio corresponding to compositions in the acid zone ( $\text{Na}_2\text{O}/\text{As}_2\text{O}_5 < 1$ ), the lowest value obtained so far being for  $\text{Na}_2\text{As}_4\text{O}_{11}$  [1]. The condensation of the arsenate groups can result in layer or framework structures. Here, we report the synthesis and the crystal structure of the first oxygen-deficient arsenate with a layer octahedral–tetrahe-

dral framework. The structure is elucidated by combining X-ray diffraction data and charge distribution (CD) analysis.

Among various possible structural validation tools we have chosen the CD analysis [2–4], because of the insights into the structural details that it gives at the same time. The CD method is the most recent development of the classical theory of bond strength [5] and differs from the bond valence (BV) approach [6,7] in exploiting the experimental bond distances rather than employing empirical curves; it can then analyze equally well structures determined at ambient conditions and under extreme conditions. The CD method has been used to validate structures, elucidate the non-stoichiometry of  $\text{YbFeMnO}_4$  [8], investigate structural changes, e.g. as a function of composition, temperature and pressure [3,4], etc.

The CD method exploits the experimental bond distances to compute a non-integer coordination number (effective coordination number (ECoN)) and distributes

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the formal oxidation number ( $q$ ) of each atom among all its bonds as a function of ECoN. By labeling  $Q$  the computed charges, a  $q/Q$  ratio close to 1 for the cations indicates the correctness of the structure determination; the same ratio for the anions measures the degree of over/under bonding. The analysis of the structural details on the basis of the strength of each bond (called “bond valence” in the BV and “bond weight” in the CD) is meaningful only when the structure is correctly refined and the empirical method itself is applicable. The BV method does not contain any internal criterion for such an evaluation, while the CD method has in the  $q/Q$  ratio for the cations precisely this kind of criterion [3,4].

## 2. Experimental

### 2.1. Synthesis

Plate-shaped crystals of the title compound were obtained hydrothermally in a glass tube. Starting materials were from analytical grade. A mixture of  $\text{NaH}_2\text{AsO}_4$  (20 mmol) and  $\text{As}_2\text{O}_5$  (5.7 mmol) with the atomic ratio Na/As = 7/11 was first heated at 573 K. After grinding, the tube was quarter-filled with the mixture and heated to 723 K for 4 days under autogenous pressure. The title compound can also be obtained by a solid-state reaction: the mixture described above was dried and heated to 923 K for 3 h, the mixture then cooled to 723 K/12 h and finally slowly cooled down to room temperature. Colorless crystals of hexagonal section, same as those synthesized previously (identical X-ray data) but of worse quality, were obtained.

The semi-quantitative energy dispersive spectroscopy (EDS) analysis of some crystals on a JEOL-JSM 5400 scanning electron microscope revealed the presence of only Na, As, and O elements. The formula of the title compound,  $\text{Na}_7\text{As}_{11}\text{O}_{31}$ , has been established as a result of crystal structure and CD investigations.

### 2.2. Structure determination

A single crystal with dimensions  $0.07 \times 0.1 \times 0.1 \text{ mm}^3$  was chosen for the structure determination and refinement. The data were collected on an Enraf-Nonius CAD-4 diffractometer using the  $\text{MoK}\alpha$  radiation at room temperature [9]. The cell parameters were determined and refined using a least-squares method based upon 25 reflections in the range  $10.95\text{--}14.98^\circ$ .

The reflections were corrected for Lorentz and polarization effects; absorption correction was obtained via a psi-scan [10] and secondary extinction correction was applied too [11]. The structure was solved and refined against  $F^2$  in the centrosymmetric space-group type  $P\bar{3}m1$  using the SHELXL97 [11] computer program included in the WINGX software package [12]. The CD computations and structural figures have been obtained with the

Table 1

Summary of crystal data, intensity measurements and structure refinement parameters for  $\text{Na}_7\text{As}_{11}\text{O}_{31}$

<i>Crystal data</i>	
Formula	$\text{Na}_7\text{As}_{11}\text{O}_{31}$
Formula weight ( $\text{g mol}^{-1}$ )	1481.05
Crystal system; space-group type	Trigonal; $P\bar{3}m1$
$a$ ; $c$ ( $\text{\AA}$ )	11.199(3); 5.412(2)
$V$ ( $\text{\AA}^3$ ); $Z$	587.8(3); 1
$\rho_{\text{calc}}$ . ( $\text{g cm}^{-3}$ ); $\mu$ ( $\text{mm}^{-1}$ )	4.184; 15.693
Crystal shape, color	Parallelepiped; colorless
Crystal size (mm)	$0.07 \times 0.10 \times 0.10$
<i>Data collection</i>	
Radiation ( $\text{\AA}$ )	$\text{MoK}\alpha$ ( $\lambda = 0.71073$ )
Theta range (deg)	$2.10 \leq \theta \leq 29.93$
$hkl$ range	$-15 \leq h \leq 14$ ; $-1 \leq k \leq 15$ ; $-1 \leq l \leq 7$
Total and unique data	2546; 662
Observed data [ $I > 2\sigma(I)$ ]; $R(\text{int})$	590; 0.031
Absorption correction	Psi-scan [10]
$T_{\text{min}}$ ; $T_{\text{max}}$	0.108; 0.333
Standards; frequency (min); decay (%)	2; 120; 0
<i>Refinement</i>	
Parameters; restraints	55; 1
$R[I > 2\sigma(I)]$ /all; $wR(I)$ /all; S	0.0282/0.0332; 0.0751/0.0730; 1.133
Extinction coefficient	0.0039(6)
Min./max. residual density. ( $\text{e \AA}^{-3}$ )	-1.18/1.55

CHARDI-IT [13] and Diamond 2.0 [14] programs, respectively.

The details of the structure refinement, final agreement factors and crystallographic data are given in Tables 1 and 2. For geometrical parameters see Table 3.

#### 2.2.1. Monovalent cations positions

The refinement of atomic coordinates and anisotropic thermal parameters of all atoms led to the reliability factors  $R = 0.032$  and  $R_w = 0.084$ . Two sodium positions were localized with normal values of the equivalent isotropic thermal factors. Moreover, a residual peak of  $5.25 \text{ e \AA}^{-3}$  was found on the difference Fourier map at  $0.98 \text{ \AA}$  from Na1. This led us to consider that the Na1 is probably split into two independent Na11 and Na12 positions. The refinement of the fractional occupancies was performed with the constraint to have the same thermal parameters (EADP option in the SHELX program [11]) leading to 72% and 28% for the Na11 and Na12 sites, respectively, and to an improvement of the agreement factors:  $R = 0.027$  and  $R_w = 0.073$ ; the two positions are  $0.928 \text{ \AA}$  apart. A third residual peak near the Na1 positions was tentatively refined as a further position for this cation but the refinement did not converge. Whether this third position is real or an artifact in the residual electron density, the particular environment of Na1 ions is confirmed: instead of occupying only the polyhedron center at the crystallographic inversion center, the cation is partly off-centered above and below this position.

Table 2  
Atomic coordinates, fractional occupancies and equivalent isotropic thermal factors in Na<sub>7</sub>As<sub>11</sub>O<sub>31</sub>

Atom	Position	x	y	Z	Occupancy	U <sub>eq</sub> (Å <sup>2</sup> )
As1	6h	0.25343(5)	0	0.5	1	0.01364(18)
As2	3f	0.5	0	0.5	1	0.00723(18)
As3	2d	0.3333	−0.3333	0.47972(14)	1	0.0054(2)
Na11	1a	0	0	0	0.716(16)	0.0222(18)
Na12	2c	0	0	0.172(6)	0.142(8)	0.0222(18)
Na2	6i	0.22720(12)	−0.22720(12)	−0.0043(4)	1	0.0190(5)
O1	6i	0.1546(2)	−0.1546(2)	0.3205(7)	1	0.0129(7)
O2	12j	0.5938(2)	−0.0543(3)	0.6984(5)	1	0.0114(5)
O3	6i	0.1755(3)	−0.41226(17)	0.3365(6)	1	0.0089(6)
O4	2d	0.3333	−0.3333	0.7843(10)	1	0.0092(11)
O5	6i	0.0956(2)	−0.0956(2)	0.6974(8)	0.83	0.0085(8)

Table 3  
Analysis of the coordination polyhedra for Na<sub>7</sub>As<sub>11</sub>O<sub>31</sub>: main interatomic distances (Å), classical coordination numbers (CN) and effective coordination numbers (ECoN) [2]

As1 octahedron	CN/ECoN: 6/5.94	Na11 polyhedron	CN/ECoN: 6/6.02
As(1)–O(1) <sup>#1</sup>	1.803(2)	Na(11)–O(5) <sup>#1</sup>	2.475(4)
As(1)–O(1)	1.803(2)	Na(11)–O(5) <sup>#8</sup>	2.475(4)
As(1)–O(2) <sup>#2</sup>	1.846(3)	Na(11)–O(5) <sup>#9</sup>	2.475(4)
As(1)–O(2) <sup>#3</sup>	1.846(3)	Na(11)–O(5) <sup>#10</sup>	2.475(4)
As(1)–O(5)	1.875(3)	Na(11)–O(5) <sup>#11</sup>	2.475(4)
As(1)–O(5) <sup>#1</sup>	1.875(3)	Na(11)–O(5) <sup>#12</sup>	2.475(4)
As2 octahedron:	CN/ECoN: 6/5.83	Na12 polyhedron:	CN/ECoN: 3/3.00
As(2)–O(2)	1.807(3)	Na(12)–O(5) <sup>#1</sup>	1.984(11)
As(2)–O(2) <sup>#3</sup>	1.807(3)	Na(12)–O(5) <sup>#9</sup>	1.984(11)
As(2)–O(2) <sup>#2</sup>	1.807(3)	Na(12)–O(5) <sup>#11</sup>	1.984(11)
As(2)–O(2) <sup>#4</sup>	1.807(3)		
As(2)–O(3) <sup>#5</sup>	1.918(3)	Na2 polyhedron:	CN/ECoN: 7/5.24
As(2)–O(3) <sup>#6</sup>	1.918(3)	Na(2)–O(1)	2.251(4)
As3 tetrahedron:	CN/ECoN: 4/3.95	Na(2)–O(4)	2.355(4)
As(3)–O(4)	1.648(6)	Na(2)–O(2) <sup>#12</sup>	2.363(3)
As(3)–O(3)	1.716(3)	Na(2)–O(2) <sup>#14</sup>	2.363(3)
As(3)–O(3) <sup>#6</sup>	1.716(3)	Na(2)–O(3) <sup>#15</sup>	2.614(3)
As(3)–O(3) <sup>#7</sup>	1.716(3)	Na(2)–O(3) <sup>#6</sup>	2.614(3)
		Na(2)–O(5)	3.020(5)
		Na(12)–Na(12) <sup>#12</sup>	1.87(6)
		Na(11)–Na(12) <sup>#13</sup>	0.93(3)

Symmetry transformations used to generate equivalent atoms: #1:  $x-y, x, -z+1$ ; #2:  $-x+y+1, y, z$ ; #3:  $-x+1, -y, -z+1$ ; #4:  $x-y, -y, -z+1$ ; #5:  $y+1, x, -z+1$ ; #6:  $-y, -x, z$ ; #7:  $-y, x-y-1, z$ ; #8:  $-x+y, -x, z-1$ ; #9:  $-x, -y, -z+1$ ; #10:  $-y, x-y, z-1$ ; #11:  $y, -x+y, -z+1$ ; #12:  $x, y, z-1$ ; #13:  $-x, -y, -z$ ; #14:  $-y, x-y-1, z-1$ ; #15:  $-x+y+1, y, z-1$ .

### 2.2.2. A vacancy-bearing oxygen network

At this stage of the study, the deduced chemical formula is Na<sub>7</sub>As<sub>11</sub>O<sub>32</sub>, which is not neutral. Two hypothesis are possible: the existence of two hydrogen atoms, which would give the missing cation charge: hydrogen atoms are however difficult to locate precisely by conventional X-ray diffraction in a structure containing relatively heavy atoms like arsenic; or some vacancies at the oxygen positions. The first possibility was excluded because it would be in contrast with the fact that this compound can be prepared by a solid-state reaction.

To check the second possibility, the occupancy factors of all atoms were refined. The refinement of the fractional occupancies and the ADPs of oxygen atoms is hardly

reliable because of the presence of heavy atoms (As), but a statistically significant deviation from full occupation is nevertheless considered a meaningful indication. Deviations were observed only for O5, whose occupancy refined at 95.8%, giving a small improvement of the reliability factors; this is however not sufficient to make the compound formula neutral and is therefore taken only as a qualitative indication of incomplete occupancy at the O5 site. To estimate the likely amount of oxygen deficiency the CD analysis (Table 4) was applied.

Table 4a shows the results of the CD analysis of the compound with complete occupancy. The structural model does not validate, as shown by the rather high (14%) data dispersion on the cations. The deviation from the formal

Table 4

Charge distribution analysis for the arsenate under investigation for two different models of O5 occupancy: complete occupancy (a) and 16.7% vacancy (b). The result of the BV computation according to the empirical Brown–Altermatt  $R$ - $s$  curve is also given for comparison (c)

Cation	$q(i).sof(i)$	$Q(i)$	$q(i)/Q(i)$	Anion	$q(r).sof(r)$	$Q(r)$	$q(r)/Q(r)$
(a)							
As1	5.00	5.20	0.96	O1	-2.00	-2.12	0.94
As2	5.00	5.12	0.98	O2	-2.00	-1.95	1.03
As3	5.00	5.00	1.00	O3	-2.00	-1.98	1.01
Na11	0.72	0.87	0.83	O4	-2.00	-2.06	0.97
Na12	0.14	0.17	0.83	O5	-2.00	-1.66	1.21
Na2	1.00	0.99	1.01				
	$\sigma = 0.14$				$\sigma = 0.19$		
(b)							
As1	5.00	4.94	1.01	O1	-2.00	-2.12	0.94
As2	5.00	5.12	0.98	O2	-2.00	-1.95	1.03
As3	5.00	5.00	1.00	O3	-2.00	-1.98	1.01
Na11	0.72	0.72	0.99	O4	-2.00	-2.06	0.97
Na12	0.14	0.14	0.99	O5	-1.67	-1.66	1.01
Na2	1.00	0.99	1.01				
	$\sigma = 0.06$				$\sigma = 0.075$		
(c)							
Cation	$Q(i)$	$q(i)/Q(i)$	Anion	$Q(r)$	$q(r)/Q(r)$		
As1	4.92	1.02	O1	-2.11	0.94		
As2	4.92	1.02	O2	-1.93	1.04		
As3	4.82	1.04	O3	-2.04	0.98		
Na11	0.70	1.02	O4	-2.04	0.98		
Na12	0.30	0.47	O5	-1.74	1.15		
Na2	1.21	0.82		$\sigma = 0.15$			
	$\sigma = 0.15$						

$\sigma$  measures the deviation of the computed charges ( $Q$ ) with respect to the formal oxidation numbers ( $q$ ) and is defined as  $\sigma = \left[ \sum_{i=1}^N (q_i - Q_i) / N - 1 \right]^{1/2}$ .

charge on the anions suggests that the reason is most likely in the full occupancy assumed for O5: in fact, the computed charge for this oxygen atom is quite far from the expected value (-1.66 instead of -2.00). The difference in the anionic computed charges in this case cannot be interpreted simply as an over-under bonding (OUB) effect as it is the case when the charges computed for the cations are sufficiently close to the expected values to validate the structure.

A second model was thus submitted to the CD analysis, where the site occupancy factor (s.o.f.) of O5 was taken to coincide with the value necessary to have a neutral compound, namely 0.833 (Table 4b). This time, not only the agreement on the charges of the cations is satisfactory, validating the structural model, but also the computed anion charges match the expected ones, with the exception of a slight overbonding effect on the O1 site.

The structure was thus finally refined keeping the s.o.f(O5) fixed to 0.833: the final agreement factors did not change significantly ( $R = 0.028$ ;  $wR = 0.075$ ), as one could expect from the minimal effect of having removed only one oxygen atom from the unit formula; nevertheless, significant improvements were observed in the displacement and thermal parameters for O5. We conclude, by associating the results of the crystal structure refinement and of the CD analysis, that the arsenate under investigation is an oxygen-deficient one, the corresponding formula

being  $\text{Na}_7\text{As}_{11}\text{O}_{31}$ , where 1/32 of the total oxygen sites are vacant. The effect of this defect on the crystal structure is discussed below.

### 3. Structure description and discussion

The structure of  $\text{Na}_7\text{As}_{11}\text{O}_{31}$  is depicted in Fig. 1. The structure consists of  $(\text{As}_{11}\text{O}_{31}\square)_n^{7n-}$  (001) layers (where  $\square$  indicates a vacancy) stacked along the crystallographic  $c$  direction and connected through  $\text{Na}^+$  cations. These layers are built up of corner and edge-sharing of arsenic polyhedra (Fig. 2). There are three independent arsenic atoms in the asymmetric unit; two of them are coordinated by six oxygen atoms in a distorted octahedral coordination, the third forms a distorted tetrahedron.

The As1 polyhedron, which we will indicate by  $\text{As}(1)\text{O}_{5+5/6}\square_{1/6}$  to express the absence of one oxygen atom (O5) per six As1 equivalents polyhedra, forms three pairs of bonds of slightly different length with three crystallographic different oxygen atoms, resulting in a coordination which one may indicate as a  $2+2+2$ . The overall degree of distortion with respect to an octahedron is however limited, as shown by the value of the ECoN, 5.94.

The As2 polyhedron is actually a tetragonal bipyramid with a  $4+2$  ( $4 \times \text{As2-O2} + 2 \times \text{As2-O3}$ ) coordination. ECoN is 5.84, showing that this polyhedron is somewhat



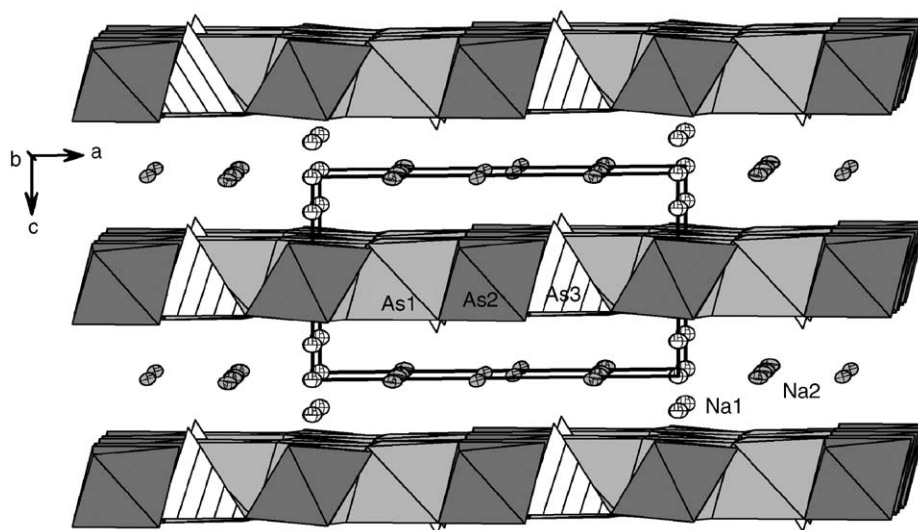


Fig. 1. Perspective view of the structure of  $\text{Na}_7\text{As}_{11}\text{O}_{31}$ . Both partially and fully occupied Na sites are shown. (Thermal ellipsoids drawn at the 50% probability level.)

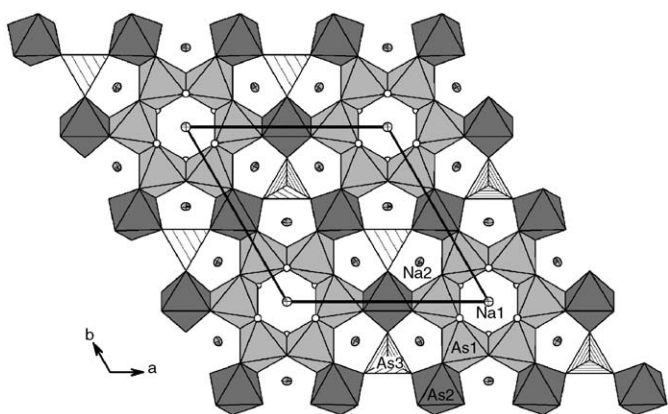


Fig. 2. The structure of  $\text{Na}_7\text{As}_{11}\text{O}_{31}$  viewed along [001]. White circles represent O5 atoms.

more distorted than  $\text{As}(1)\text{O}_{5+5/6}\square_{1/6}$ , despite its more symmetric shape. This comes from the fact that the  $\text{As}2\text{--O}3$  bonds are the longest among the  $\text{As}\text{--O}$  polyhedra in this compound. The difference in the two As polyhedra is evidently related to the different environment in which they are located: the  $\text{As}(1)\text{O}_{5+5/6}\square_{1/6}$  polyhedron shares three edges with three octahedral neighbors, where  $\text{As}(2)\text{O}_6$  shares two edges and two corners with two  $\text{As}(1)\text{O}_{5+5/6}\square_{1/6}$  polyhedra and two  $\text{As}3$  distorted tetrahedra, respectively.

The  $\text{As}3$  polyhedron is a slightly distorted tetrahedron, and more precisely a trigonal pyramid. The ECoN of 3.95 shows that the overall degree of distortion with respect to its regular counterpart is limited. The  $\text{As}3$  polyhedra share their three basal oxygen atoms with three  $\text{As}(2)\text{O}_6$  polyhedra; the apical oxygen pointing into the interlayer region.

The oxygen-deficient polyhedra form six-member  $[\text{As}(1)\text{O}_{5+5/6}\square_{1/6}]_6$  rings, bridged by the  $\text{As}(2)\text{O}_6$  polyhedra which share with them two of their edges. Each six-member

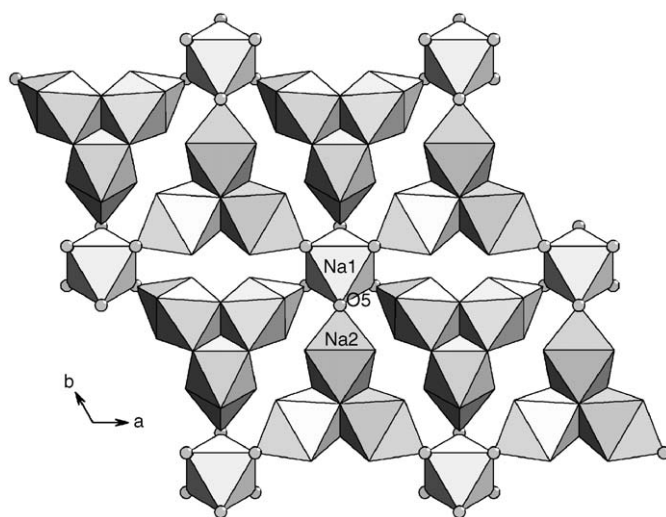


Fig. 3. Connection of the sodium polyhedra in the  $ab$  plane.

ring is circumscribed by six five-member rings, each formed by two  $\text{As}1$ , two  $\text{As}2$  and one  $\text{As}3$  polyhedron.

The arithmetic and weighted [4] average interatomic distances in the octahedra are  $\langle \text{As}1\text{--O} \rangle = 1.841 \text{ \AA}$  and  $\langle \text{As}2\text{--O} \rangle = 1.844 \text{ \AA}$  and  $\langle \text{As}1\text{--O} \rangle = 1.839 \text{ \AA}$  and  $\langle \text{As}2\text{--O} \rangle = 1.835 \text{ \AA}$ , respectively. The deficiency of an oxygen atom O5 per ring of six  $\text{As}1$  “octahedra” does not have a visible effect on these averages within the limit of the results precision.

The bond lengths in the  $\text{As}1\text{--O}2\text{--As}2$  bridges are similar; the distances in the  $\text{As}2\text{--O}3\text{--As}3$  bridges are different due to the different coordination numbers between two arsenic atoms: the strong connection established in the tetrahedron weakens that with the octahedral arsenic.

The average  $\text{As}3\text{--O}$  distances (arithmetic  $1.699 \text{ \AA}$ , weighted  $1.696 \text{ \AA}$ ) agree with data in the literature; the  $\text{As}3\text{--O}$  distance of  $1.65 \text{ \AA}$  for the terminal O4 oxygen is

somewhat longer than the typical values (e.g. 1.614 Å in Na<sub>2</sub>As<sub>4</sub>O<sub>11</sub> [1]) due the interaction between O4 and three equivalent Na2 cations with short distances of 2.35 Å.

The sodium cations play the role of interlayer cations. The average thickness of the interlayer region is 3.26 Å.

The Na1 site is split between two positions. Na11 (s.o.f. 72%) is located at the inversion center and occupies a regular octahedron (six bonds at 2.47 Å) defined by two six-member As rings, one on each side. The three closest O5 atoms on each side define the octahedron around Na1; due to the oxygen vacancy, however, only 5/6 of each corner is occupied by an oxygen atom. Na12 (28%) is split at  $\pm z$  and only the three closest O5 atoms (1.98 Å) are coordinated.

The Na2 site has a more irregular coordination, as often occurs with alkali cations. The Na2 cations are at 4.39 Å from Na11 and are linked to seven oxygen atoms with Na2–O distances ranging from 2.25 to 3.02 Å. The longest distance is established with the deficient O5 atom, the short Na2–O1 bond length of 2.25 Å is reflected in the calculated charge of the oxygen atom in the CD: a weak over-bonding effect appears for O1 with a  $q/Q$  ratio of 0.94 (see Table 4). ECoN is as low as 5.24, showing that the coordination polyhedron is quite irregular. The Na2 cations are associated in three-polyhedral units by sharing edges; the six O(5)<sub>5</sub>□ corners are common between the Na1 octahedron and six neighbors polyhedral Na2 units (Fig. 3).

In conclusion, this is the first time, to our knowledge, that such an oxygen-deficient arsenate with a layered structure has been isolated. This study shows an original anion (As<sub>11</sub>O<sub>31</sub>□)<sub>n</sub><sup>7n-</sup> with a vacant oxygen framework.

The result is based on crystal structure and CD calculations. The main crystallographic characteristics related to the existence of the oxygen deficiency are discussed.

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