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β-$Zr_2(PO_4)_2SO_4$: A Zirconium Phosphato-sulfate with a $Sc_2(WO_4)_3$ Structure. A Comparison between Garnet, Nasicon, and $Sc_2(WO_4)_3$ Structure Types

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The single-phase compound β-$Zr_2(PO_4)_2SO_4$ has been prepared by refluxing zirconium phosphate gel in sulfuric acid at 200°C. It crystallizes in the orthorhombic system, space group *Pbcn* with a = 12.3742(9), b = 8.867(2), c = 8.951(1) Å, Z = 4. The structure was determined from 560 reflections collected on a Nonius CAD4 automatic diffractometer with $MoK_{\bar{\alpha}}$ radiation. The final R index and weighted R_w index are 0.049 and 0.062, respectively. The structure, built up from ZrO_6 octahedra and PO_4 and SO_4 tetrahedra linked by corners, is isotypic with that of $Sc_2(WO_4)_3$ and is closely related to that of garnet and nasicon. In these three structure types the arrangements of octahedral cations are very similar.

Introduction

In the past thirty years, there has been an increasing interest in the preparation and properties of many layered group (IV) and (V) phosphates and arsenates in the form of gels as well as in the form of crystalline materials, mainly due to the exciting new developments which have taken place in the areas of catalysis, electrochemistry, and fast-ion conductors (*1*).

Several attempts to prepare this type of material with sulfate groups, instead of PO_4 or AsO_4 groups, have already been reported (*2, 3*) and two zirconium phosphato-sulfates, α- and β-$Zr_2(PO_4)_2SO_4$, have been recently reported (*3*). In view of their powder patterns, these two phases have been assumed to be of the nasicon type, the β phase being the monoclinic distorted version of the α phase.

This paper presents the crystal structure of β-$Zr_2(PO_4)_2SO_4$, which is isotypic with that of $Sc_2(WO_4)_3$ (*4*). This latter type of structure is known to be closely related to the garnet one (*5*); however, a close relation with the nasicon structure exists as well and a comparison between garnet, $Sc_2(WO_4)_3$, and nasicon structure types is given.

Experimental

Single crystals of β-$Zr_2(PO_4)_2SO_4$ have been prepared by refluxing 5 g of zirconium phosphate gel in 40 ml of 98% sulfuric acid between 180 and 200°C for about 5 days. The zirconium phosphate gel was precipitated by adding 1 M H_3PO_4 to a mixture of

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TABLE I

UNIT CELL CONSTANTS

Crystal symmetry	Orthorhombic
a (Å)	12.3742(9)
b (Å)	8.867(2)
c (Å)	8.951(1)
V (Å^3)	982.2
D_{calc} (g cm^{-3})	3.168
Z	4
Space group	Pbcn
μ (cm^{-1}) for $\lambda\ K_{\bar{\alpha}} = 0.71069$ Å	26.7

0.1 M HNO_3 and 0.4 M $ZrO(NO_3)_2 \cdot 2H_2O$, the atomic P to Zr ratio being 2.5. The crystals are colorless, thin oval platelets with 0.3 mm in maximum dimension. Their analysis, conducted with an electron microprobe, confirms the formulation mentioned above. Single-crystal X-ray study indicates orthorhombic symmetry. The parameters (Table I) were least-squares refined from 25 reflections automatically centered on a Nonius CAD4 diffractometer using graphite-monochromated Mo$K_{\bar{\alpha}}$ radiation. Diffraction intensities were measured with the diffractometer operating in the conditions given in Table II. For β-$Zr_2(PO_4)_2SO_4$ the calculated linear absorption coefficient μ is 26.7 cm^{-1} and as the crystal was very small no absorption correction was applied. For the data reduction, structure solution, and refinement, the SDP-PLUS program chain (1982 version) of Enraf–Nonius, written by B. Frenz (*6*), was used.

Refinement of the Structure

Refinement was carried out by the full-matrix least-squares method. The starting positional parameters for Zr, S, and P atoms were taken by analogy with those of Sc, W(1), and W(2), respectively, in the structure of $Sc_2(WO_4)_3$ (*4*). In the first stage

TABLE II

DATA COLLECTION AND REFINEMENT CONDITIONS

Data collection	
Equipment	Nonius CAD4 diffractometer
Radiation (Å)	Mo$K_{\bar{\alpha}}$, $\lambda = 0.71069$
Scan mode	$\omega - 2\theta$
Scan angle (°)	$\Delta\omega = 1.0 + 0.35 \tan\theta$
Recording angular range (θ°)	1.5–35.0
Number of independent data observed with $\sigma(I)/I < 0.33$ (used in refinements)	560
Refinement	
Number of variables (isotropic temperature factors)	36
$R = \Sigma\,(\lvert\,\lvert F_o\rvert - \lvert F_c\rvert\,\rvert)/\Sigma\lvert F_o\rvert$	0.063
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w F_o^2]^{1/2}$ with $w = 1/(1 + [(F_{obs} - F_{av})/F]^2_{max})$	0.075
Number of variables (anisotropic temperature factors)	79
$R =$	0.049
$R_w =$ with same w scheme as above	0.062
Extinction parameter refined $g =$	$0.44(5) \times 10^{-6}$

TABLE III

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	Position	x	y	z	B_{eq} (Å^2)[a]
Zr	8d	0.3839(1)	0.2497(3)	0.4639(1)	1.42(2)
M(1)[b]	4c	0	0.4646(5)	0.25	0.59(7)
M(2)[b]	8d	0.3538(3)	0.3920(4)	0.1094(4)	0.68(4)
O(1)	8d	0.1478(9)	0.060 (1)	0.092 (1)	1.9 (2)
O(2)	8d	0.063 (1)	0.367 (1)	0.146 (1)	2.3 (2)
O(3)	8d	0.2708(9)	0.325 (1)	0.010 (1)	2.0 (2)
O(4)	8d	0.4213(9)	0.060 (1)	0.334 (1)	2.1 (2)
O(5)	8d	0.4634(8)	0.332 (1)	0.070 (1)	1.7 (2)
O(6)	8d	0.3316(9)	0.355 (1)	0.270 (1)	1.8 (2)

Atom	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zr	0.00265(6)	0.00434(9)	0.00392(8)	0.0004(3)	0.0009(2)	0.0014(5)
M(1)[b]	0.0014 (3)	0.0017 (4)	0.0012 (3)	0	−0.0002(6)	0
M(2)[b]	0.0006 (2)	0.0028 (3)	0.0024 (3)	−0.0003(4)	0.0002(4)	0.0028(6)
O(1)	0.0037 (7)	0.003 (1)	0.007 (1)	0.001 (2)	−0.004 (2)	0.003 (2)
O(2)	0.0040 (8)	0.010 (2)	0.004 (1)	0.006 (2)	0.000 (2)	−0.008 (2)
O(3)	0.0026 (7)	0.008 (1)	0.006 (1)	−0.007 (2)	−0.004 (1)	−0.001 (2)
O(4)	0.0036 (7)	0.005 (1)	0.008 (1)	0.001 (2)	0.003 (2)	−0.006 (2)
O(5)	0.0014 (6)	0.005 (1)	0.008 (1)	0.002 (1)	0.003 (2)	0.000 (2)
O(6)	0.0027 (7)	0.008 (1)	0.004 (1)	0.004 (2)	−0.001 (2)	0.005 (2)

[a] $B_{eq} = \frac{4}{3}\Sigma_i \Sigma_j \beta_{ij} \mathbf{a}_i\mathbf{a}_j$.

[b] $M(1)$ and $M(2) = (\frac{1}{3}S + \frac{2}{3}P)$.

[c] Expressions for anisotropic temperature factors are $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

of refinement the positional parameters and isotropic temperature factors of these atoms were refined. With use of these data, a Fourier difference map was computed which revealed the position of the oxygen atoms. In the subsequent stage the positional parameters and isotropic temperature factors of the nine unique atoms were refined to $R = 0.063$ and $R_w = 0.075$. Then anisotropic temperature factors were assigned to all atoms. Refinement converged with $R = 0.049$ and $R_w = 0.062$. At this stage S–O and P–O distances were calculated. They were found to be very similar with $\langle S\text{–}O\rangle = \langle P\text{–}O\rangle = 1.495$ Å. Then, a refinement which accounts for a disordered distribution of S and P atoms over the two tetrahedral sites was undertaken. It led to R, R_w, and atomic coordinate values which are the same as those obtained for the ordered situation (changes are less than the standard deviations). From the refinement itself, it is not possible to decide strictly whether the distribution of S and P atoms is ordered or not. Nevertheless, the distances calculated for the SO_4 and PO_4 tetrahedra indicate that the disorder is more likely. Details of the different stages of refinement are given in Table II. Table III presents the final atomic coordinates and thermal parameters (the structure factor table will be sent upon request). In Table IV are reported the calculated interplanar distances of the reflection planes along with the intensities calculated from the Lazy–Pulverix program (7) in the case of a Guinier–Hagg camera with a quartz crystal monochromator.

TABLE IV

CALCULATED X-RAY POWDER PATTERN

h	*k*	*l*	d_{calc} (Å)	I/I_0	*h*	*k*	*l*	d_{calc} (Å)	I/I_0
1	1	0	7.207	0.2	1	3	2	2.419	0.2
2	0	0	6.187	6.7	3	3	0	2.402	0.0
1	1	1	5.614	20.9	5	1	0	2.384	0.1
0	0	2	4.476	25.0	3	1	3	2.332	1.3
0	2	0	4.433	19.3	3	3	1	2.320	0.7
2	1	1	4.414	100.0	5	1	1	2.303	0.5
1	0	2	4.209	1.4	2	2	3	2.298	0.2
0	2	1	3.973	16.0	2	3	2	2.291	0.0
1	1	2	3.802	14.6	0	0	4	2.238	0.9
1	2	1	3.783	13.4	0	4	0	2.217	0.7
3	1	0	3.740	26.7	4	2	2	2.207	5.8
2	0	2	3.626	1.7	1	0	4	2.202	0.2
2	2	0	3.604	0.6	5	0	2	2.166	0.0
3	1	1	3.451	12.1	0	4	1	2.152	0.3
2	1	2	3.357	15.4	1	1	4	2.137	0.7
2	2	1	3.343	0.1	3	2	3	2.123	2.9
0	2	2	3.150	40.3	1	4	1	2.120	0.5
4	0	0	3.093	17.3	3	3	2	2.117	0.0
1	2	2	3.052	7.2	2	0	4	2.104	0.0
3	0	2	3.033	0.2	5	1	2	2.104	0.2
1	3	0	2.875	3.8	5	2	1	2.101	0.7
3	1	2	2.870	2.0	4	1	3	2.087	0.0
3	2	1	2.861	1.6	2	4	0	2.087	0.6
2	2	2	2.807	3.6	4	3	1	2.079	0.0
4	1	1	2.777	4.5	1	3	3	2.070	1.9
1	1	3	2.757	15.6	6	0	0	2.062	0.0
1	3	1	2.737	0.7	2	1	4	2.048	0.8
2	1	3	2.572	12.1	2	4	1	2.032	0.0
2	3	1	2.556	27.6	0	2	4	1.998	4.2
4	0	2	2.545	11.1	2	3	3	1.988	10.4
4	2	0	2.537	9.5	0	4	2	1.986	4.7
3	2	2	2.503	2.1	1	2	4	1.972	5.2
0	2	3	2.475	0.4	3	0	4	1.967	1.3
4	1	2	2.446	0.4	1	4	2	1.961	4.7
4	2	1	2.441	0.0	6	1	1	1.960	14.0
1	2	3	2.427	0.0	5	2	2	1.946	4.0

Description of the Structure: A Comparison between Garnet, $Sc_2(WO_4)_3$, and Nasicon Structure Types

The crystal structure of β-$Zr_2(PO_4)_2SO_4$ consists of a framework of corner-linked ZrO_6 octahedra and tetrahedra (PO_4 and SO_4) such that each oxygen atom is bonded to one Zr atom and one S or P atom, i.e., each ZrO_6 octahedron is connected to six tetrahedra, while each tetrahedron is linked to four octahedra. A list of bond distances and bond angles for these different polyhedra is given in Table V. The basic unit of the network, which is represented in Fig. 1, consists of two octahedra joined by three tetrahedra. These ($Zr_2P_2SO_{18}$) units are linked together via vertices in such a fashion that they may be considered to form layers in the *b–c* plane (Fig. 2). In the *a* direction, adjacent layers are related to each other by a *b*-glide plane (Fig. 3).

The nasicon structure (*8*, *9*) (Fig. 4) is built up from the same type of unit as represented in Fig. 1. The hexagonal cell ($R\bar{3}c$) of nasicon can also be indexed as a monoclinic cell ($C2/c$) with

$$\mathbf{a}_m = 2\mathbf{a}_h + \mathbf{b}_h$$
$$\mathbf{b}_m = \mathbf{b}_h$$
$$\mathbf{c}_m = (-2\mathbf{a}_h - \mathbf{b}_h + \mathbf{c}_h)/3.$$

In the b_m–c_m plane of nasicon the ($Zr_2P_3O_{18}$) units are linked together exactly in the same way as the ($Zr_2P_2SO_{18}$) units in the *b–c* plane of β-$Zr_2(PO_4)_2SO_4$ (Fig. 2). Then, these two types of structures are built up from the same type of layers. However, adjacent layers in the $[100]_m^*$ direction of nasicon are related to each other by an inversion center, i.e., without any translation, and this is the main difference between the two structures.

The prototype of this β-$Zr_2(PO_4)_2SO_4$ structure is the orthorhombic tungstate $Sc_2(WO_4)_3$ (*4*). A monoclinic distortion of this structure has been observed in compounds such as β-$Fe_2(SO_4)_3$ (*10*) or $Fe_2(MoO_4)_3$ (*11*, *12*), and for this latter com-

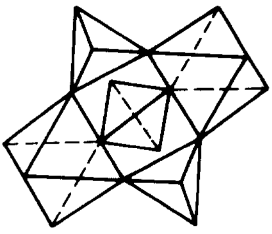

FIG. 1. ($Zr_2P_2SO_{18}$) unit from β-$Zr_2(PO_4)_2SO_4$.

TABLE V

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR THE COORDINATION POLYHEDRA

Zr-O(1)	2.079(9)	O(1)-Zr-O(2)	91.6(4)		
-O(2)	2.041(9)	O(1)-Zr-O(3)	88.5(4)		
-O(3)	2.06(1)	O(1)-Zr-O(4)	178.1(5)		
-O(4)	2.09(1)	O(1)-Zr-O(5)	88.1(4)		
-O(5)	2.047(9)	O(1)-Zr-O(6)	92.2(4)		
-O(6)	2.078(9)	O(2)-Zr-O(3)	88.8(4)		
		O(2)-Zr-O(4)	88.1(4)		
		O(2)-Zr-O(5)	89.9(5)		
		O(2)-Zr-O(6)	176.1(5)		
		O(3)-Zr-O(4)	93.4(4)		
		O(3)-Zr-O(5)	176.4(4)		
		O(3)-Zr-O(6)	91.0(4)		
		O(4)-Zr-O(5)	90.0(4)		
		O(4)-Zr-O(6)	88.0(4)		
		O(5)-Zr-O(6)	90.5(4)		
O(1)-O(2)	2.96(1)	O(1)-O(3)	2.89(1)	O(1)-O(5)	2.87(1)
O(1)-O(6)	3.00(1)	O(2)-O(3)	2.87(1)	O(2)-O(4)	2.87(1)
O(2)-O(5)	2.89(1)	O(3)-O(4)	3.02(1)	O(3)-O(6)	2.95(1)
O(4)-O(5)	2.93(1)	O(4)-O(6)	2.90(1)	O(5)-O(6)	2.93(1)
M(1)-O(2) (×2)	1.49(1)	O(2)-*M*(1)-O(2)	108.6(9)		
-O(4) (×2)	1.50(1)	O(2)-*M*(1)-O(4) (×2)	110.9(6)		
		O(2)-*M*(1)-O(4) (×2)	107.8(6)		
		O(4)-*M*(1)-O(4)	110.9(9)		
O(2)-O(2)	2.42(2)	O(2)-O(4) (×2)	2.46(1)	O(2)-O(4) (×2)	2.41(1)
O(4)-O(4)	2.47(2)				
M(2)-O(1)	1.497(9)	O(1)-*M*(2)-O(3)	109.3(6)		
-O(3)	1.49(1)	O(1)-*M*(2)-O(5)	110.0(6)		
-O(5)	1.50(1)	O(1)-*M*(2)-O(6)	108.3(6)		
-O(6)	1.499(9)	O(3)-*M*(2)-O(5)	109.8(6)		
		O(3)-*M*(2)-O(6)	110.9(6)		
		O(5)-*M*(2)-O(6)	108.5(6)		
O(1)-O(3)	2.43(1)	O(1)-O(5)	2.45(1)	O(1)-O(6)	2.43(1)
O(3)-O(5)	2.44(1)	O(3)-O(6)	2.46(1)	O(5)-O(6)	2.44(1)

pound a detailed comparison of its structure with the garnet framework was conducted by Plyasova *et al.* (*5*). The removal of the M' (eight-coordinated) atoms in the garnet structure type $M'_3M''_2(M'''O_4)_3$ results in a three-dimensional framework built of $M''O_6$ octahedra and $M'''O_4$ tetrahedra in which each octahedron is joined via vertex-sharing to six tetrahedra. It was pointed out by Wells (*13*) that the garnet framework (without M' atoms) exists, in a much distorted form, in the structure of $Al_2(WO_4)_3$ (*14, 15*) isotypic with that of $Sc_2(WO_4)_3$. In fact, this assertion is not true since, for example, a ($M''_2M'''_3$ O_{18}) unit similar to that represented in Fig. 1 does not exist in the garnet framework. As indicated by Plyasova *et al.* (*5*), it is only the arrangement of the octahedra which is the same in these two structures. It will be shown now that

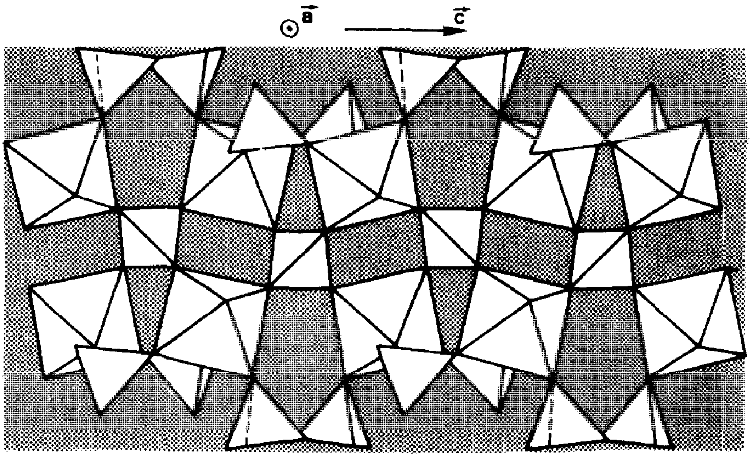

FIG. 2. Fragment of the β-$Zr_2(PO_4)_2SO_4$ structure in the b–c plane.

this arrangement exists as well in the nasicon framework and this is the basis of the comparison between the three structure types of garnet, $Sc_2(WO_4)_3$, and nasicon.

In the garnet framework the octahedral cations are situated on the 16a position of the $Ia\bar{3}d$ space group, i.e., on the threefold nonintersecting axes. Then each M'' atom is located at the center of a cube formed by eight neighboring M'' atoms (at a distance of $(a\sqrt{3})/4$), two of these being situated on the threefold axis which goes through the

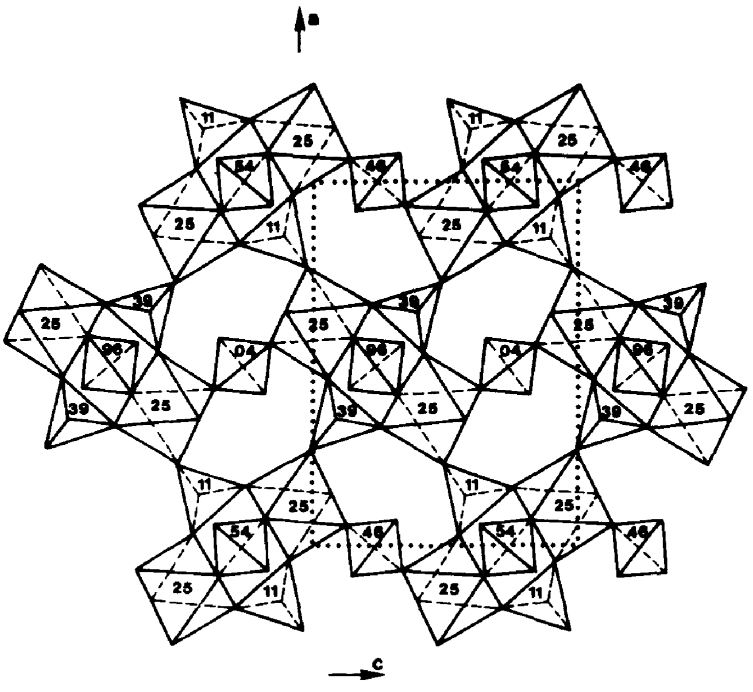

FIG. 3. Projection of half the unit cell along [010] in β-$Zr_2(PO_4)_2SO_4$.

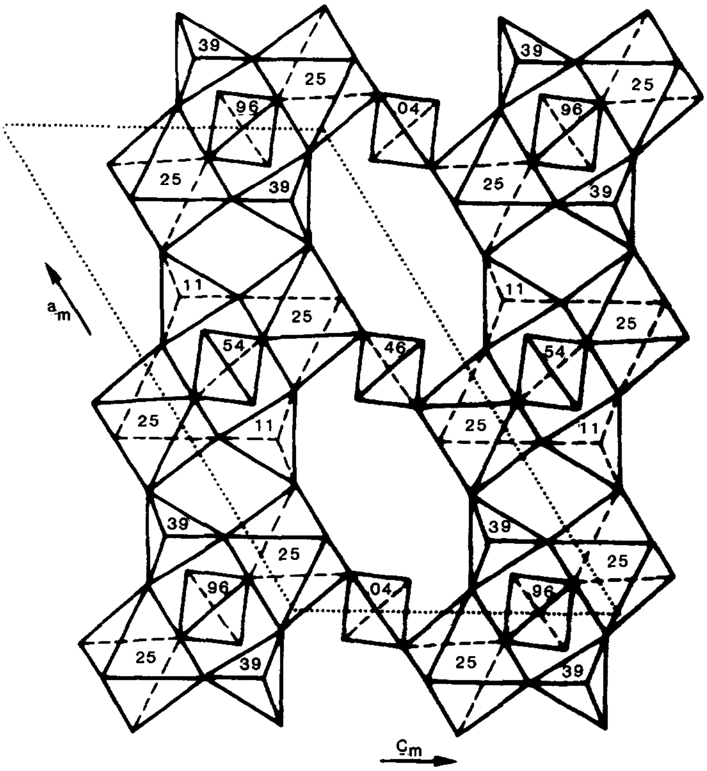

FIG. 4. Projection of half the unit cell along $[010]_m$ in nasicon.

center of this cube (Figs. 5a and b). The next nearest M'' cations, located at a larger distance $a/2$, are the six centers of the next nearest cubes. The different octahedra are linked to each other via O–O bonds which are edges of tetrahedra and hereafter called T-bonds. In garnet, as well as in the two other structures, each octahedron is linked to six tetrahedra via vertex-sharing so that there are 18 T-bonds between this octahedron and its neighboring and next nearest neighboring octahedra. How are they distributed in the three structure types?

In the garnet framework, a given $M''O_6$ octahedron is linked to each of six nearest neighbors via two T-bonds and to each of the six next nearest neighbors via one T-bond. Consequently there is not any T-bond with two of the nearest neighbors; more precisely, there is not any T-bond between octahedra which are located on the same threefold axis. These octahedra are linked together by the $M'O_8$ polyedra.

In the case of β-$Zr_2(PO_4)_2SO_4$ ($Sc_2(WO_4)_3$ type), the cubic arrangement is slightly distorted, as indicated by distances and angles given in Table VI and shown in Figs. 5c and d. A given ZrO_6 octahedron is linked to its 14 neighbors in the following way:

—One T-bond with five of the nearest neighbors.

—Two T-bonds with two of the nearest neighbors.

—Three T-bonds with one of the nearest neighbors, leading to the ($Zr_2P_2SO_{18}$) unit represented in Fig. 1.

—As in garnet, there is one T-bond with each of the six next nearest neighbors.

For nasicon, the cubic arrangement of

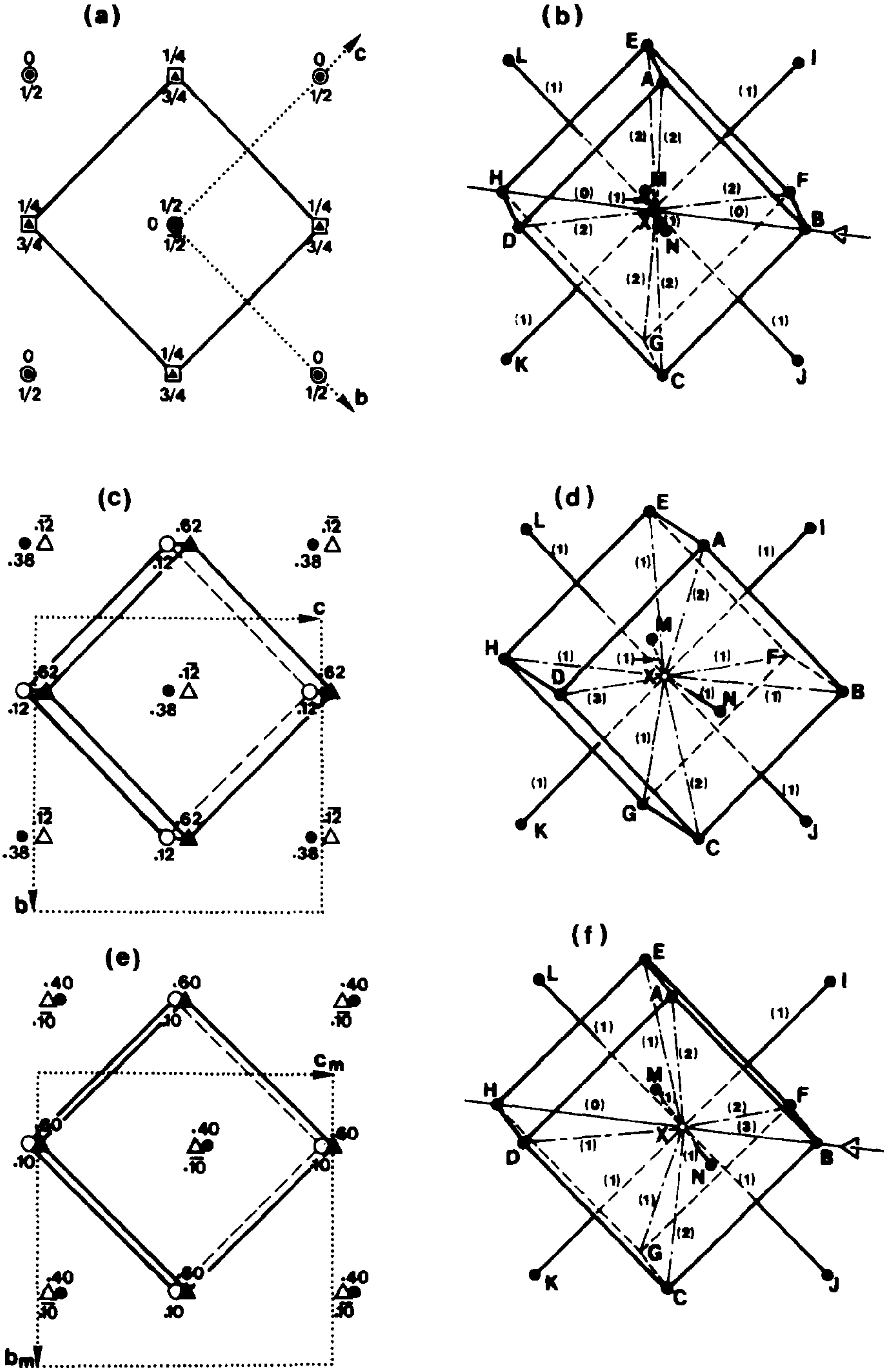

FIG. 5. Projection of the octahedral cations along (a) [100] in garnet, (c) [100] in β-$Zr_2(PO_4)_2SO_4$, and (e) $[100]_m^*$ in nasicon. (b), (d), and (f) are the perspective views corresponding to (a), (c), and (e), respectively. Figures between brackets indicate the number of T-bonds between the "central" atom *X* and its neighbors (*A*, *B*, . . . , *N*).

TABLE VI

DISTANCES (Å) AND ANGLES (°) FOR THE CUBIC ARRANGEMENT OF OCTAHEDRAL CATIONS IN (a) GARNET, (b) β-$Zr_2(PO_4)_2SO_4$, AND (c) NASICON

(a) ($ABCDEFGH$) is a cube[a]

$$\left.\begin{array}{l} X\text{–}(A, B, \ldots, H) = (a\sqrt{3})/4 \\ X\text{–}(I, J, \ldots, N) = (a/2) \end{array}\right\} \text{ with } a = \text{lattice parameter of garnet} \quad a \simeq 12.5\ \text{Å}$$

(b) ($ABCDEFGH$) is a pseudocube

$XA = 5.314$, $XB = 5.873$, $XC = 5.330$, $XD = 4.786$

$XH = XF = 5.570$, $XE = XG = 5.536$

$XM = XN = AE = BF = CG = DH = 6.221$

$XI = XL = AB = AD = GF = GH = 6.293$

$XJ = XK = CB = CD = EF = EH = 6.307$

$\widehat{CBF} = \widehat{EHD} = \widehat{DCG} = \widehat{AEF} = \widehat{JXN} = \widehat{JXM} = 85.70$

$\widehat{BFG} = \widehat{ADH} = \widehat{CGH} = \widehat{BAE} = \widehat{LXN} = \widehat{LXM} = 94.70$

$\widehat{BCG} = \widehat{AEH} = \widehat{CDH} = \widehat{BFE} = \widehat{KXN} = \widehat{KXM} = 94.17$

$\widehat{CGF} = \widehat{DAE} = \widehat{DHG} = \widehat{ABF} = \widehat{IXN} = \widehat{IXM} = 85.83$

$\widehat{EFG} = \widehat{EHG} = \widehat{ADC} = \widehat{ABC} = \widehat{IXJ} = \widehat{KXL} = 89.45$

$\widehat{FGH} = \widehat{BAD} = \widehat{IXL} = 90.67$

$\widehat{FEH} = \widehat{BCD} = \widehat{JXK} = 90.42$

(c) ($ABCDEFGH$) is a rhombohedron with $a = 6.346$ Å
and $\alpha = 88°$ ($\widehat{ABC}$)

$XB = 4.746$, $XH = 6.627$

$XA = XC = XF = 5.178$

$XE = XD = XG = 5.826$

X–($I, J, \ldots, N$) $= a = 6.346$

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[a] $A, B, \ldots, N$ are the 14 octahedral cations which are represented in Figs. 5b, d, and f around the "central" X cation.

ZrO_6 octahedra is more distorted than in β-$Zr_2(PO_4)_2SO_4$ (Table VI). The "central" zirconium atom is displaced in such a way that it is farther from one of the apices of the cube than from the previously called "next nearest" neighbors. Nevertheless, the similarity with the garnet arrangement still exists, as can be seen in Figs. 5e and f. Each ZrO_6 octahedron is linked to its neighbors in the following way:

—One T-bond with three of the nearest neighbors.

—Two T-bonds with three of the nearest neighbors.

—Three T-bonds with one of the nearest neighbors as in β-$Zr_2(PO_4)_2SO_4$.

—As in garnet and β-$Zr_2(PO_4)_2SO_4$, there is one T-bond with each of the six next nearest neighbors.

In nasicon, one of the main diagonals of the pseudocube coincides with a threefold axis (Fig. 5f) and the distances between zirconium atoms along this axis are alternatively short (4.75 Å) and long (6.83 Å). They correspond respectively to ZrO_6 octahedra linked by three T-bonds and no T-bonds. The empty space between two ZrO_6 octahedra which are not linked together by

T-bonds is occupied by a sodium atom located on the threefold axis, halfway between the two Zr atoms.

The langbeinite ($K_2Mg_2(SO_4)_3$) framework (*16*) is also built of octahedra (MgO_6) and tetrahedra (SO_4) linked together via vertex-sharing in such a way that each octahedron is linked to six tetrahedra. Furthermore, the arrangement of octahedra and tetrahedra leads to ($Mg_2S_3O_{18}$) units similar to that represented in Fig. 1. The 18 T-bonds link each octahedron to 13 neighboring octahedra as in nasicon (three T-bonds with one octahedron, two T-bonds with three, and one T-bond with nine). Nevertheless, it is not possible to go further in the comparison of the langbeinite framework with the structure types which have been described above since the arrangement of octahedra is very different, and by no means a pseudocubic centered one.

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