The OD structure of zorite

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It is shown that zorite (an alkaline titanosilicate) has an OD structure; the superposition structure is solved in a cell with the parameters $\hat{a} = 23.241(7)$ Å, $\hat{b} = 7.238(4)$ Å, $\hat{c} = 6.955(4)$ Å, with the Fedorov group *Cmmm* ($\mathbf{R}_{\hat{k}\hat{k}\hat{l}}$0.085). There is a rod-shaped fragment with the translation b_0 14.476 Å such that its disorderly arrangement in the structure destroys the periodicity along the *a* and *c* axes, and this is manifested in the form of diffuse reflections. The Fourier transform of the proposed model of the OD structure is derived and analysed. In solving the structure the authors establish the crystal-chemical formula of zorite, $Na_6[Ti(Ti_{0.9}Nb_{0.1})_4(Si_6O_{17})_2(O, OH)_5].11H_2O$. The zeolite framework of zorite is made up of xonotlite-like bands $[Si_6O_{17}]_\infty$ joined by Ti semioctahedra and octahedral $[(Ti, Nb)_2O_{10}]_\infty$ chains; it contains two types of channels with minimum cavity diameters of 4.3 and 4.6 Å. The framework is statistically filled with Na^+ cations and water molecules.

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The obscure chemical formula and large unit cell of the new zeolite-type alkali titanosilicate zorite, together with the rising interest in structures with mixed radicals, have attracted attention to the structure of this mineral, which was discovered by Mer'kov and Nedorezova[1] in the central natrolite region of the "Yubileinaya" pegmatoid vein of the Lovozero massif.

As a result of our x-ray diffraction investigation of specimens of zorite from the A. E. Fersman Mineralogical Museum of the Academy of Sciences of the USSR we have found diffraction effects which were not mentioned in the work of the first discoverers.[1] As well as the point reflections corresponding to an orthorhombic C-cell with the parameters $\hat{a} = 23.9$; $\hat{b} = 7.23$; $\hat{c}_0 = 14.24$ Å (Ref. 1), in Laue photographs, rotation photographs, and precession photographs we also found diffuse reflections doubling the $\hat{b}$ period and breaking the periodicity along the *a* and c axes. In the C-cell chosen by Mer'kov and Nedorezova,[1] on our diffraction patterns there is a clear pseudoperiod $\hat{c} = c_0/2$ broken by a few weak reflections. The diffuse reflections indicate that the structure of zorite is of the OD type, and their disk-like shape indicates that the structure contains rod-shaped fragments with period $b_0 = 2\hat{b}$ with polyvariant relative displacements. We were unable to find crystals without disorder, i.e., with diffraction patterns having point reflections instead of the diffuse ones. Difficulties in measuring the intensities of the diffuse reflections made it possible to solve only the superposition structure, information on which is contained in the point reflections, i.e., the reflections of the OD family.[1)]

The parameters of the superposition cell were refined in a "Syntex P$\bar{1}$" automatic diffractometer: $a = 23.241(7)$ $\hat{b} = 7.238(1)$; $\hat{c} = 6.955(2)$ Å; $\hat{V} = 1169.8$ Å^3. An experimental set of 660 independent nonzero reflections was registered on the same autodiffractometer in the independent region with $\sin\theta/\lambda \leq 0.7$ Å^{-1} by the θ:2θ method with a variable scanning rate of 4–24 deg/min (Mo Kα radiation, plane graphite monochromator). The systematic extinctions $\hat{h}\hat{k}\hat{l}$:$\hat{h} + \hat{k} = 2n$ confirmed the C-centering. Thirty weak reflections doubled the period $\hat{c}$. On the basis of a three-dimensional set of intensities we indexed the powder pattern of zorite (Table I).

The superposition structure of zorite was solved with

TABLE I. Interplanar Distances of Zorite *

d_{meas}	I	$\hat{h}\hat{k}\hat{l}$	d_{calc}	d_{meas}	I	$\hat{h}\hat{k}l$	d_{calc}
11.57	40	2 0 0	11.62	2,58	15	6 0 4	2.59
6.93	100	0 0 2	6.95	2,50	3	0 2 4	2.51
		1 1 0	6,91	2,45	3	2 2 4	2.45
5.95	2	2 0 2	5,97	2.43	5	9 1 0	2.43
5.81	3	4 0 0	5.81	2,27	3	4 2 4	2.30
5.26	15	3 1 0	5,29	2.23	1	8 0 4	2,23
4.44	10	4 0 2	4.46	2,18	1	3 3 2	2,19
3.60	20	0 2 0	3,62	2,15	5	4 0 6	2.15
3,44	20	0 0 4	3,48	2.13	5	5 3 0	2.14
		2 2 0	3,45	1,934	3	10 0 4	1,932
3,38	10	6 0 2	3,38	1.894	3	8 2 4	1.897
3.20	3	0 2 2	3.21	1.803	10	0 4 0	1,809
3,08	25	2 2 2	3,09	1.780	5	2 4 0	1.787
3,06	32	4 2 0	3.07	1.757	3	6 2 6	..743
2,98	15	4 0 4	2,98			9 3 0	1.762
2.90	10	3 1 4	2,91	1.738	15	0 0 8	1.739
2.76	3	7 1 2	2,77	1.723	3	2 0 8	1.720
2,64	10	6 2 0	2,64	1.702	5	10 2 4	1.704
				1.544	5	4 4 4	1,546

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*Diffractometer, Kα Fe radiation, Mn filter.

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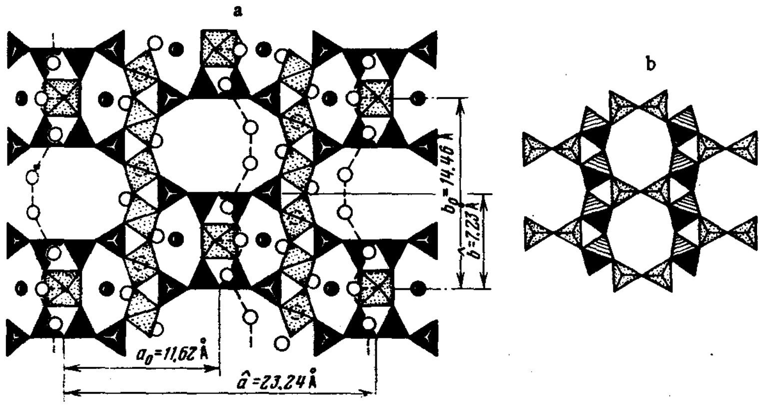

FIG. 1. Comparison between structures of zorite and nenadkevichite. a) Showing xy projection of ordered zorite structure with space group P112/m; b) showing side view of structure of nenadkevichite. Dashes denote hydrogen bonds.

the aid of a systematic analysis of the Patterson function $\hat{P}(uvw)$ as in Ref. 3. On the electron density synthesis $\hat{\rho}(xyz)$ constructed with allowance for the Ti_1 and Si_1 atoms found from $\hat{P}(uvw)$ ($R_{\hat{h}\hat{k}\hat{l}}$ = 38%) we located the atoms Si_2 and $Na_{1,2}$ and all the O atoms from the cation environment. There was an extra maximum which was initially identified with an Al atom. Refinement of the model by the method of least squares in the group Cmmm reduced $R_{\hat{h}\hat{k}\hat{l}}$ to 10.2%. In analyzing the superposition structure we elucidated some of its features.

1. The pair of Si_2 tetrahedra with a common face in the mirror plane m_y is filled with multiplicity one-half.

2. The distance Na_1-Aq_1 = 2.10 Å to the Aq_1 atom[1)] lying in the plane m_y is anomalously short.

3. The maximum initially identified with an Al atom is markedly elongated along the c axis. The character of the elongation can be judged from the anisotropic thermal factors calculated for Al: B_{11} and B_{22} are about 1.0 Å^2, but B_{33} = 13 Å^2.

4. B_j for Ti is negative, confirming that as usual it is partly replaced by the "heavier" niobium.[4]

5. B_j is very high for a number of O and Na atoms, indicating statistical filling of their positions in the superposition cell with symmetry Cmmm.

We interpreted these features as follows.

1. The common face of the Si_2 tetrahedra is removed when we go from the superposition structure to the OD structure with real period $b_0 = 2\hat{b}$ (Fig. 1). The lack of information on the reflections odd with respect to b_0 permitted only an indirect confirmation of this hypothesis – the correspondence between the observed diffraction pattern and the Fourier transformation derived for the model of the OD structure of zorite (see below). The facial joining of the Si_2 tetrahedra can be eliminated a priori by changing to the group Cm2m or to the cell proposed in Ref. 1 with symmetry C2cm. In our opinion, both the latter models are untenable – first, owing to crystal-chemical considerations (requirement of local balance of valence forces and unwarrantably large number (3) of free vertices of Ti_2 hemioctahedra); and secondly, owing to the higher value of the R index and the marked scatter of the interatomic distances in attempts to refine these models. The second version with glide reflection plane c_y is also refuted by the presence of reflections which violate the extinction $\hat{h}0l$ with $l = 2n$. But what is most important, neither model explains the appearance of strong diffuse lines doubling $\hat{b}$.

2. On the final synthesis $\hat{\rho}(xyz)$ there appeared a double peak indicating a shift of atom Aq_1 from the m_y mirror plane. The Na_1 atoms coordinated in the octahedra and joined in columns by the trans vertices of the Aq_1 with full multiplicity have very high values of B_j = 7 Å^2, and we therefore formed the hypothesis that these atoms occupy only half the octahedra in the column, alternating with empty ones. Then the distance from Aq_1 to the center of the filled octahedron is elongated, and that in an empty one is correspondingly shortened (Fig. 1). Refinement of this version by the method of least squares

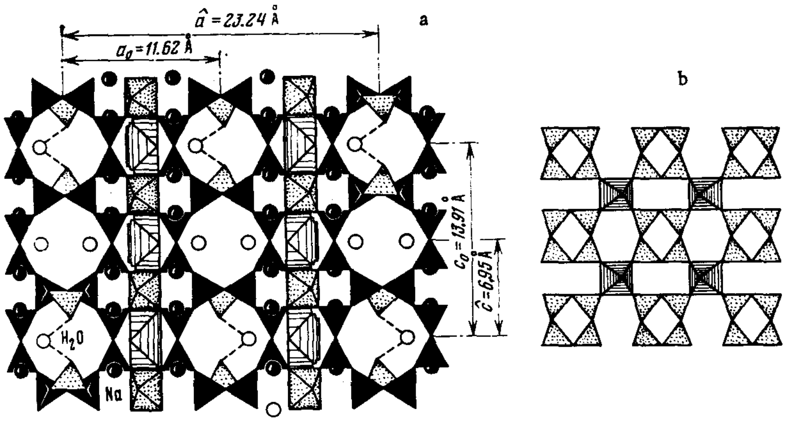

FIG. 2. Structures of zorite and nenadkevichite. a) Showing xy projection of OD structure of zorite (half of Na_1 octahedra is omitted; note the lack of periodicity along the *a* and *c* axes); b) plane of structure of nenadkevichite.[5]

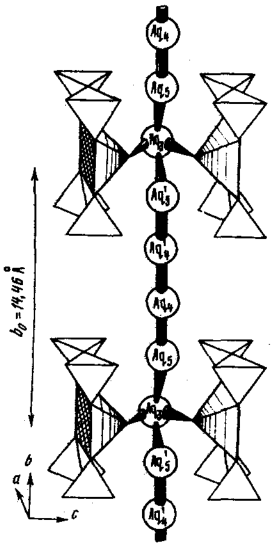

FIG. 3. Rod-like fragment of zorite structure and possible mechanism of its ordering along b axis.

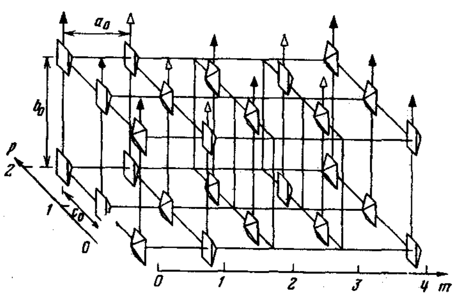

FIG. 4. Schematic axonometric representation of relative positioning of rod-like components with symmetry P(2)m(m) in OD structure of zorite. Black arrows indicate rods with shifts of 0 or $^1/_2$ of the b_0 translation; white arrows indicate shifts of $^1/_4$ or $^3/_4$ of the b_0 translation.

(with half multiplicity of Na_1 and Aq_1 atom shifted away from m_y) led to a reduction in the R index and the thermal factors of both atoms, and what is more important, to a normal distance $Na_1-O(Aq) = 2.43$ Å.

3. The very elongated peak of the Al atom was evidence of a shift of this atom away from the center of its coordination octahedron with the formation of a five-vertex figure (Figs. 2 and 3). The high value of B_j made it necessary to liquidate the more remote vertex and to shift the nearer one away from the mirror plane, because the maximum corresponding to atom O_7 was double. Moreover, from crystal-chemical considerations – namely, the improbability of an $[Al(H_2O)_5]$ hemioctahedron "hanging" in the Si, Ti framework – it followed that the multiplicity for Al is one, and this is to some extent confirmed by the chemical analysis in Ref. 1. Refinement of this version led to a further reduction in $R_{\hat{h}\hat{k}\hat{l}}$ and to positive location of the atom O_7 (B_j was reduced from 8.4 to 2.2 Å^2). One $Al-O_7$ distance was shortened to 1.67 Å, and B_j for Al was reduced to −0.40 Å^2. This supported the hypothesis that the hemioctahedron is filled not by an Al but by a Ti atom, for which such a configuration with characteristic shortening of the "titanyl" Ti–O bond averaging 1.68 Å is not uncommon.[5] Replacement of aluminum by titanium led to a normal thermal factor for this position and much improved the local valence balance. Moreover, the fivefold coordination of Ti_2 enables us to explain the doubling of the period c by the necessity of valence compensation of the free vertices of Ti hemioctahedra, which, as we shall show, forces them to turn with their free vertices pointing toward one another.

4. The question of the filling of the Ti_1 positions was solved by taking mixed f curves of (Ti + Nb) in steps of 2% Ti and refining B_j for all the independent atoms at each step. The best discrepancy index of 9.3% corresponds to filling of the positions with 90% Ti and 10% Nb.

5. As a result of these "modifications" we succeeded in reducing the B_j of all the atoms in question.

6. In the distribution $\hat{\rho}$ (xyz) we found weak but sharp maxima identified with O atoms from water molecules. An attempt to refine them was unsuccessful owing to their small contribution to the structure amplitude and to the zeolite character of this water.

The model obtained for the structure of zorite corresponds to the following formula for the superposition cell: $Na_6[Ti(Ti_{0.9}Nb_{0.1})_4(Si_6O_{17})_2(O, OH)_5] \cdot 11H_2O$ ($\rho_{calc} = 2.23$ g/cm^3, $\rho_{meas} = 2.27$–2.40 g/cm^3).

This formula differs from that calculated from the chemical analysis in Ref. 1 in having a lower percentage content of Na_2O and alumina, but a higher content of TiO_2. This discrepancy seems to result from contamination of the analytical sample of zorite by a small amount of pink natrolite, which is very similar to zorite and occurs in close proximity to it.

The final coordinates corresponding to a discrepancy index of $R_{\hat{h}\hat{k}\hat{l}} = 8.5\%$ for 630 reflections for a superposi-

TABLE II. Coordinates of Basis Atoms (×10^4) with Isotropic Thermal Factors in Structure of Zorite*

Atom	multiplicity	$x/\hat{a}$	$y/\hat{b}$	$z/\hat{c}$	B_{iso}, Å^2	Atom	multiplicity	$x/\hat{a}$	$y/\hat{b}$	$z/\hat{c}$	B_{iso}, Å^2
$(Ti, Nb)_1$	4	2500	2500	0	0.71	O_4	4	2208	5000	0	1.1
Ti_2	1	0	5000	457	1.53	O_5	2	0	0	0	1.0
Si_1	8	1618	0	2697	0.68	O_6	4	602	3197	0	2.3
Si_2	4	639	943	0	0.82	O_7	1	112	5000	2826	2.2
Na_1	2	2500	2500	5000	2.2	Aq_1	4	2949	537	5000	4.0
Na_2	4	3654	0	2182	3.9	Aq_2	2	811	3824	5000	6.1
O_1	4	1545	0	5000	1.7	Aq_3	0.5	720	5000	5000	—
O_2	8	952	0	1878	1.6	Aq_4	2	1000	3000	5000	—
O_3	16	1940	1853	2036	1.7	Aq_5	2	300	900	5000	—

*Coordinates of oxygen atoms of water molecules, Aq_3, Aq_4, Aq_5, obtained from synthesis ρ(xyz).

TABLE III. Interatomic Distances in angstroms) and Valence Angles (in degrees) in OD Structure of Zorite

Si_1-tetrahedron		Si_2-tetrahedron		(Ti, Nb)- octahedron	
Si_1-O_1	1.61	Si_2-2O_2	1.64	$(Ti, Nb)-4O_3$	1.98
O_2	1.65	O_5	1.64	$2O_4$	1.93
$2O_3$	1.60	O_6	1.63	Mean	1.96
Mean	1.62	Mean	1.64		
O_1-O_2	2.57	O_2-O_2'	2.62	O_3-2O_3'	2.77
$2O_3$	2.63	$2O_5$	2.57	$2O_3''$	2.83
O_2-2O_3	2.66	$2O_6$	2.78	$4O_4$	2.75
O_3-O_3'	2.68	O_5-O_6	2.70	$4O_4'$	2.78
Mean	2.64	Mean	2.67	Mean	2.78
$O_1-Si_1-O_2$	104.1	$O_2-Si_2-O_2$	105.7	$O_3-(Ti, Nb)-O_3'\times2$	88.7
$O_3\times2$	109.6	$-O_5\times2$	108.2	$-O_3''\times2$	91.4
$O_2-Si_1-O_3\times2$	109.8	$-O_6\times2$	116.0	$-O_4\times4$	89.5
O_3-Si-O_3'	113.6	$O_5-Si_2-O_6$	114.4	$-O_4''\times4$	90.5
Mean	109.4	Mean	109.3	Mean	90.0
Ti-pyramid		Na_1-environment		Na_2- environment	
$Ti-O_6\times4$	1.94	$Na_1-Aq_1\times2$	2.43	Na_2-O_4	2.52
O_7	1.67	$O_3\times4$	2.48	$O_3\times2$	2.67
Mean	1.89	Mean	2.47	$O_6\times2$	2.65
		Na_2-environment		Aq_3	2.45
$O_6-O_6'\times2$	2.61	Na_2-O_4	2.52	Aq_1	2.58
$O_6''\times2$	2.80	$O_3\times2$	2.67	Mean	2.60
$O_7\times2$	2.62	$O_6\times2$	2.65		
$O_7'\times2$	2.89	O_7	2.90	Na_2-O_4	2.52
Mean	2.73	Aq_1	2.58	$O_3\times2$	2.67
		Mean	2.66	$O_6\times2$	2.65
$O_6-Ti-O_6'\times2$	84.6			Aq_2	2.47
$-O_6''\times2$	92.4			Aq_1	2.58
$-O_7\times2$	92.8			Mean	2.60
$-O_7'\times2$	105.9				
Mean	93.9				

Titanium niobium silicate framework

(Ti, Nb)	$-O_4-(Ti, Nb)$	139.0	Si_1	$-O_1-Si_1'$	167.5	Si_2 $-O_5-Si_2'$	130.5
	$-O_3-Si_1$	135.3		$-O_2-Si_2$	133.6	$-O_6-Ti$	135.2

tion cell with symmetry Cmmm are listed in Table II. The interatomic distances for a possible model of the OD structure are listed in Table III. The local valence balance is listed in Table IV.

The disorder of the zorite structure is due to a haphazard arrangement of rod-like fragments of the structure $P_{m,p}$ relative to some initial $P_{0,0}$. From an analysis of the superposition structure it follows that a rod with translation vector $\mathbf{b}_0$ is formed from only part of the atoms in the structure: Ti_2, Si_2, $Na_{1,2}$, and $O_{5-7}Aq_{1-5}$ (Fig. 3).

Adjacent rods along the mutually perpendicular x and z axes are spaced apart by distances which can be represented by the vectors $\mathbf{a}_0$ and $\mathbf{c}_0$, respectively. The remaining atoms Ti_1, Si_1, O_{1-4} form a sublattice with translation vectors $\hat{\mathbf{a}} = 2\mathbf{a}_0$, $\hat{\mathbf{b}} = \mathbf{b}_0/2$, $\hat{\mathbf{c}} = \mathbf{c}_0/2$ and satisfy the symmetry Cmmm. The symmetry of the rod is represented by the group P(2)m(m). Adjacent rods can be related by several possible combinations of σ operations of the τ and ρ types (Fig. 4). The aggregate of partial symmetry operations of the rod and of the operations relating adjacent rods is represented by the OD groupoid. Since the problem of the notation of the OD groupoid for rod-like OD structures has not yet been worked out in detail, and the symbolism in Ref. 6 does not seem to us to be very convenient, we shall suggest our own method of writing the symbol of the OD groupoid for rod-type structures. The symbol must contain the necessary and sufficient information to obtain all possible combinations of neighboring rods. For this purpose it is necessary and sufficient to list, as well as the symmetry groups of the rod, all possible combinations of σ-partial operations relating neighboring rods in pairs along two chosen coordinate axes lying in a plane perpendicular to the rod axis. The number of combinations of σ operations is determined by the number of types of pairs, which in general can exceed two and violate the third condition of adjacency formulated in Ref. 2. We shall call the set of OD structures violating this condition the "OD family". Before giving the symbol for the OD groupoid of zorite, let us consider the necessary indication of the partial operations. In front of the symbol for the operation which converts rod $P_{m,p}$ to rod $P_{m',p'}$, we shall put the symbol for the corresponding pair of rods, m, p/m', p'. After the symbol for the set of σ operations we shall put the symbol for the direction of the corresponding pair of rods (x, y, or z), and not the symbols of the pairs. The latter would cause many complications and cumbersomeness in the notation for the symbol of the OD groupoid. Then the OD groupoid of zorite takes the following form:

$$\begin{array}{ll} \multicolumn{2}{c}{P(2)m(m)} \\ \{(2_2)a_2(n_{2,r})\}_x & \{(2)c_2(b_{1/2-s})\}_z \\ \{(2_2)n_{2,1}(n_{2,r})\}_x & \{(n_{1/2-s,2})2_{1/2-s}(2_2)\}_z \\ \{(b_r)2_r(2)\}_x & \\ \{(n_{r,1})2_r(2_1)\}_x, & \end{array}$$

where r and s are equal to either +1/2 or −1/2.

The equivalent points for a single rod, starting from its symmetry group, are written as

$$[\mathbf{P}_{0,0}]=[x;\ \pm y;\ \pm z]. \tag{1}$$

For the succeeding rods,

TABLE IV. Local Balance of Valence Forces (× 100) in OD Structure of Zorite, According to Yu. A. Pyatenko[5]*

	(Ti, Nb)Ti		Si_1	Si_2	Na_1	Na_2'	Na_2''	Na_2'''	H	Σ
O_1	–	–	2×102	–	–	–	–	–	–	204
O_2	–	–	88	98	–	–	–	–	–	186
O_3	66	–	105	–	160	14	–	–	(17)	201 (202)
	66	–	105	–	160	14	13	–	(17)	200 (201)
	66	–	105	–	160	–	–	13	(17)	200 (201)
O_4	2×72	–	–	–	–	16	–	15	–	175
	2×72	–	–	–	–	–	15	15	–	174
	2×72	–	–	–	–	–	–	–	?	144?
O_5	–	–	–	2×101	–	–	–	–	–	202
O_6	–	65	–	102	–	14	–	14	–	195
	–	65	–	102	–	–	14	14	–	195
O_7	–	138	–	–	–	2×11	–	–	31	191
Aq_1	–	–	–	–	20	2×14(0)	–	–	? (167)	215 (187)
Aq_2	–	–	–	–	–	–	–	2×16	?	32?
Aq_3	–	–	–	–	–	–	2×16	–	138+16	186
Aq_4	–	–	–	–	–	–	–	–	194	194
Aq_5	–	–	–	–	–	–	–	–	184+6	190
Sum **	412	400	400	400	99	99	100	100		

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*In parentheses are contributions and sums for O_3 and Aq_1 from empty "Na_1" octahedron; question marks denote unknown contribution from H atoms.

**Sum calculated with allowance for multiplicity.

$$\begin{aligned}
[\mathbf{P}_{1,0}]&=\left[1+\varepsilon_{1,0}x;\ \frac{\alpha_1}{4}\pm y;\ \frac{1+\gamma_1}{4}\pm z\right],\\
[\mathbf{P}_{2,0}]&=\left[2+\varepsilon_{2,0}x;\ \frac{\alpha_1+\alpha_2}{4}\pm y;\ \frac{2+(\gamma_1+\gamma_2)}{4}\pm z\right],\\
[\mathbf{P}_{0,1}]&=\left[\varepsilon_{0,1}x;\ \frac{\beta_1}{2}\pm y;\ 1\pm z\right],\\
[\mathbf{P}_{0,2}]&=\left[\varepsilon_{0,2}x;\ \frac{\beta_1+\beta_2}{2}\pm y;\ 2\pm z\right],\\
[\mathbf{P}_{m,p}]&=\left[m+\varepsilon_{m,p}x;\ {}^1/_4\sum_m\alpha_m+{}^1/_2\sum_p\beta_p\pm y,\ p+\frac{m+\sum\limits_m\gamma_m}{4}\pm z\right],
\end{aligned}\tag{2}$$

where α_m, β_m, γ_m, and $\varepsilon_{m,p}=\pm1$ according to the shift of the rod $\mathbf{P}_{m,p}$ to the right, to the left, downward, or upward relative to the original $\mathbf{P}_{0,0}$ and according to the type of σ operation (τ or ρ).

By (2), the Fourier transform $F_{m,p}(\xi k \zeta)$ of rod $\mathbf{P}_{m,p}$ takes the form

$$\begin{aligned}
F_{m,p}(\xi k\zeta)&=\sum_j f_j\exp\left\{2\pi i\left[\xi m+k\left({}^1/_4\sum_m\alpha_m+{}^1/_2\sum_p\beta_p\right)\right.\right.\\
&\left.\left.+\zeta\left(p+\frac{m+\sum\limits_m\gamma_m}{4}\right)\right]\right\}\times\{\exp[2\pi i(\xi\varepsilon_{m,p}x_j+ky_j+\zeta z_j)]\\
&+\exp[2\pi i(\xi\varepsilon_{m,p}x_j-ky_j+\zeta z_j)]+\exp[2\pi i(\xi\varepsilon_{m,p}x_j\\
&+ky_j-\zeta z_j)]+\exp[2\pi i(\xi\varepsilon_{m,p}x_j-ky_j-\zeta z_j)]\}\\
&=4\sum_j f_j\exp\left\{2\pi i\left[\xi m+k\left({}^1/_4\sum_m\alpha_m+{}^1/_2\sum_p\beta_p\right)\right.\right.\\
&\left.\left.+\zeta\left(p+\frac{m+\sum\limits_m\gamma_m}{4}\right)\right]\right\}\times\cos 2\pi ky_j\cos 2\pi\zeta z_j\exp(2\pi i\xi\varepsilon_{m,p}x_j).
\end{aligned}\tag{3}$$

Introducing the relations ${}^1/_4\sum\limits_m\alpha_m=\frac{m+2d_m}{4}$, ${}^1/_2\sum\limits_p\beta_p=\frac{p+e_p}{2}$ and $\frac{m+\sum\limits_m\gamma_m}{4}=\frac{m+f_m}{2}$, where d_m, e_p and f_m are the whole values dependent on m and p and the variables for various members of the OD structure of zorite, we obtain for the Fourier-transform of all rods of the structure $F(\xi k\zeta)$:

$$\begin{aligned}
F(\xi k\zeta)&=\frac{4}{mp}\sum_m\sum_p\sum_j f_j\exp\left\{2\pi i\left[\xi m+k\left(\frac{m+2d_m}{4}\right.\right.\right.\\
&\left.\left.\left.+\frac{p+e_p}{2}\right)+\zeta\left(p+\frac{m+f_m}{2}\right)\right]\right\}\times\cos 2\pi ky_i\cos 2\pi\zeta z_j\exp(2\pi i\xi\varepsilon_{m,p}x_j).
\end{aligned}\tag{4}$$

We divide each sum in (4) into two parts such that one of them would contain all components with $\varepsilon_{m,p}=+1$, the other is $\varepsilon_{m,p}=-1$, and we introduce $F_0(\xi k\zeta)=\sum\limits_j f_j 4\cos 2\pi ky_j\cos 2\pi\zeta z_j\exp(2\pi i\xi x_j)$;

$$\begin{aligned}
S_0(\xi k\zeta)&=\frac{1}{4mp}\sum_m\sum_p(-1)^{(d_m+e_p)k+f_m\xi}\\
&\times\exp\left\{2\pi i\left[\left(\xi+\frac{k}{4}+\zeta/2\right)m+\left(\frac{k}{2}+\zeta\right)p\right]\right\};\\
S_1(\xi k\zeta)&=\frac{1}{4mp}\sum_m\sum_p\varepsilon_{m,p}(-1)^{(d_m+e_p)k+f_m\xi}\\
&\times\exp\{2\pi i[(\xi+k/4+\zeta/2)m+(k/2+\zeta)p]\}.
\end{aligned}\tag{5}$$

Then the Fourier-transform $F(\xi k\zeta)$ will assume the form

$$\begin{aligned}
F(\xi k\zeta)&=[S_0(\xi k\zeta)F_0(\xi k\zeta)+S_0(\xi k\zeta)F_0(\xi k\zeta)]\\
&+[S_1(\xi k\zeta)F_0(\xi k\zeta)-S_1(\xi k\zeta)F_0(\xi k\zeta)].
\end{aligned}\tag{6}$$

The structural amplitudes of $F(\xi k\zeta)$ for various members of the OD structure will have known identical values only for $S_0(\xi k\zeta)$, independent of d_m, e_p, and f_m – that is, for $k=2\hat{k}$ and $\zeta=2\hat{l}$, and for the simultaneous equation to zero of the second part of (Eq. 6). This is possible only for $F_0(\xi k\zeta)=F_0(\bar{\xi}k\zeta)$ and $S_1(\xi k\zeta)=S_1(\bar{\xi}k\zeta)$, that is, for reflexes $0k\zeta$. Then we obtain for the reflexes of the structure of zorite

$$S_0(0\hat{k}\hat{l})=\frac{1}{4mp}\sum_m\sum_p\exp\left\{2\pi i\left[\left(\frac{\hat{k}}{2}+\hat{l}\right)m+(\hat{k}+2\hat{l})p\right]\right\}.\tag{7}$$

Considering that the number mp of rods is large, $S_0(0k\hat{l})=1$ only for $\hat{k}/2+\hat{l}=n$ or $\hat{k}=2n$.

However, point reflections which can be identified with reflections of the zorite family are observed not only when $\xi = 0$ but also for certain integral values of ξ. This phenomenon can be explained by assuming an average statistical symmetry of the rods P(m)m(m). Let us assume that σ-partial operations of the τ and ρ types are equally probable; then the second part of expression (6) vanishes and we can write

$$\begin{aligned} F(\xi k\zeta) &= S_0(\xi k\zeta)F_0(\xi k\zeta)+S_0(\bar{\xi}k\zeta)F_0(\bar{\xi}k\zeta) \\ &= F(\bar{\xi}k\zeta)=\hat{S}_0(\xi k\zeta)\hat{F}_0(\xi k\zeta), \end{aligned} \tag{8}$$

where

$$\hat{F}_0(\xi k\zeta)=8\sum_j f_j \cos 2\pi\xi x_j \cos 2\pi k y_i \cos 2\pi\zeta z_j; \quad \hat{S}_0(\xi k\zeta)=2S_0(\xi k\zeta). \tag{9}$$

From (9) it follows that in this case the statistical symmetry of the rod can be represented as P(m)m(m). Then reflections of the family $[S_0(\xi k\zeta)=1=\mathrm{const}]$ arise on the condition that

$$k=2\hat{k},\ \zeta=2\hat{l}\ \text{and}\ \hat{h}+\hat{k}=2n, \tag{10}$$

where $\hat{h} = 2\xi$, $\hat{k}$, and $\hat{l}$ are any integers.

The observed point reflections satisfy conditions (10) and (9), i.e., they obey the symmetry mmm and have extinctions corresponding to a c-cell with the parameters $\hat{\mathbf{a}} = 2\mathbf{a}_0$, $\hat{\mathbf{b}} = \mathbf{b}_0/2$ and $\hat{\mathbf{c}} = \mathbf{c}_0/2$.

In general, for odd values of k, $\hat{S}_0(\xi k \zeta)$ can be nonzero at any points in reciprocal space. This is manifested by the presence of disk-shaped diffuse reflections for odd values of k. If k is even and l odd, diffuse reflections elongated along a^* may also be found. However, when $l = 2n + 1$ and $k = 2n$, we observe very weak maxima with integral $\hat{h}$. These are evidence of the preferential importance of certain pairs of rods in the zorite structure. Since these maxima are present only when $\hat{h} + \hat{k} = 2n$, we can conclude that σ operations not containing the translation $\mathbf{c}_0/2$, i.e., $\{(2_2)a_2(n_{2,r})\}_X$ and $\{(b_r)2_r(2)\}_X$, occur more often.

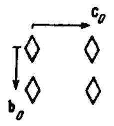
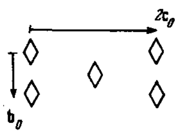
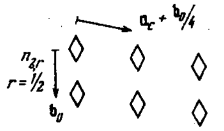
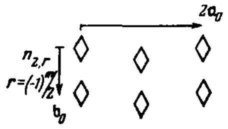
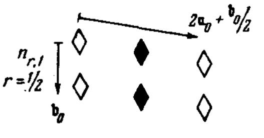
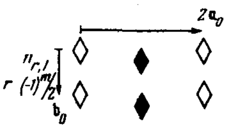
It is important to derive the possible ordered structures of the OD family of zorite. We can imagine a fairly large number of these structures; therefore, we shall limit ourselves to cases with not more than two rods per repeat period along the x and z axes, and statistical symmetry P(m)m(m) of the rods. The possible cases are listed in Table V.

The structural investigation confirmed that zorite is a zeolite, as shown by the presence of a peculiar titanium silicate framework with channels along the y and z axes. The channels along the y axis have octagonal, nearly circular cross sections with the longitudinal cavities 4.3 Å in diameter; the channels along the c axis are made up of dodecagonal, nearly elliptical rings with cavities 4.6 Å in minimum diameter and 7.6 Å in maximum diameter (Figs. 1 and 2). The latter channels can pass right through the specimen only in an ordered zorite structure in which neighboring rods along the z axis are not translated relative to one another by half a translation along b_0. Otherwise the channels are interrupted. The mixed zeolite framework of zorite is composed of three types of polyhedron: silicate tetrahedra $[SiO_4]$, $[(Ti, Nb)O_6]$ octahedra, and $[TiO_5]$ four-sided pyramids (hemioctahedra). As we see from Table III, the bonds in the Si_2 tetrahedron are on average somewhat longer than those in the Si_1 tetrahedron; this may be due to partial replacement of Si_2 atoms by Al atoms. Both the independent $[SiO_4]$ tetrahedra are distorted with scatter of the O–Si–O angles of 103-116°; their means, however, remain close to the ideal value of 109.5° (Table III). The mirror-symmetrical pairs of Si_1 and Si_2 tetrahedra from mutually perpendicular diortho groups composing xonotlite-like bands $[Si_6 \cdot O_{17}]_\infty$ (Figs. 1 and 2). Note that the two types of diortho groups are not crystal-chemically equivalent, since the diortho groups of Si_2 tetrahedra are closed on the edges of a small Ti_2 hemioctahedron, but those of Si_1 tetrahedra are closed on the edges of a large octahedron, filled with Na_1 atoms or empty. This nonequivalence of the diortho groups is clearly expressed in the values of their valence angles Si–O–Si, which are minimal (130.5°) for the former but maximal (167.5°) for the latter. A zorite band extending along the c axis can be thought of as a pair of wollastonite chains condensed by a mirror plane (Fig. 3), in contrast with the actual xonotlite band – a condensate of wollastonite chains due to the dyad axis.[7] A complicated silicon–oxygen radical derived from the xonotlite radical is found in tinaxite.[8] But whereas in tinaxite and xonotlite the relation between the silicate radicals is based on the similarity between the cation bases of the structures, zorite cannot be assigned to the group of minerals structurally derived from wollastonite, if for no other reason, because the titanium in zorite (unlike that in tinaxite) clearly performs its acidic function – there is no edge linkage of Ti polyhedra, and the titanyl bonds of the Ti hemioctahedron are clearly covalent. This hemioctahedron is distorted (Table III) on account of a displacement of the O atom nearest to the Ti_2 from the position mm2 to a position m, caused by the requirements of local valence balance (see below). In the $[(Ti, Nb)O_6]$ octahedra, linked via trans-vertices into rocking columns $[(Ti, Nb)_2O_{10}]_\infty$, the bonds between (Ti, Nb) and the bridging O atoms are shortened; this can be attributed to marked valence unsaturation of the latter, if we take account only of the contributions made by the Ti, Si, and Na ions.

The senior relative of zorite in the structural plan is nenadkevichite, $(Na, K)_{2-x}[(Nb, Ti)_2(Si_4O_{12})(O, OH)_2] \cdot 4H_2O$ (Ref. 9 and Figs. 1 and 2). The $\{Na_2(Nb, Ti)_2 \cdot (Si_2O_{7-2/2})_2(O, OH)_2 4H_2O\}^\infty_\infty$ layers from which the nenadkevichite structure is built up are also an important component in the structure of zorite. The rods in the nenadkevichite layer are $[(Ti, Nb)_2O_{10}]_\infty$ columns linked by $[Si_2O_7]$ diortho groups. Between the (Ti, Nb) columns there are large alkali cations. In nenadkevichite the layers are linked directly together, forming a mixed titanium–niobium silicate framework. In zorite these layers are linked via $\{Na_2Ti(Si_2O_{7-4/2})_2O\}$ groups composed of $[TiO_5]$ hemioctahedra incrusted with $[Si_2O_7]$ diortho groups and Na^+ cations adjoining the free vertices of the latter (see Figs. 1, 2, and 3). These groups are formally equivalent to narsarsukite $Na_2[Ti(Si_4O_{11})]$, and thus the structure of zorite can be thought of as a hydrated product of the reaction between nenadkevichite and narsarsukite:

$$\begin{aligned} 2\{Na_2[(Ti, Nb)_2(Si_2O_{7-2/2})_2(O, OH)_2]4H_2O\}^\infty_\infty+\{Na_2[Ti(Si_2O_{7-4/2})_2O\}_\infty \\ +3H_2O=Na_6[Ti(Ti, Nb)_4(Si_6O_{17})_2(O, OH)_5]11H_2O. \end{aligned}$$

TABLE V. Schematic Representation, Unit Cell Parameters, and Symmetry of Possible Ordered Structural Varieties of Zorite with Statistical Symmetry P(m)m(m) of Rod-like Components*

σ operations having continuation → ↓ $m,\ p/m+1,\ p \leftrightarrow m',\ p'/m'+1,\ p'$	$m,\ p/m,\ p+1 \leftrightarrow m',\ p'/m',\ p'+1$	
		
	$a = a_0 + b_0/4$ $b = b_0$ $c = c_0$ *P112/m*	$a = a_0 + b_0/4$ $b = b_0$ $c = 2c_0$ *A112/m*
	$a = 2a_0$ $b = b_0$ $c = c_0$ *Pmam*	$a = 2a_0$ $b = b_0$ $c = 2c_0$ *Amam*
	$a = 2a_0 + b_0/2$ $b = b_0$ $c = c_0$ *B112/m*	$a = 4a_0$ $b = b_0$ $c = 2c_0$ *Fd2d*
	$a = 2a_0$ $b = b_0$ $c = c_0$ *Pmnm*	$a = 2a_0$ $b = b_0$ $c = 2c_0$ *A2/m11*

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*The signs ◇ and ◆ correspond to the systems of points [±x, ±y, ±z] and [±x, ±y, $^1/_2$±z].

The isolated $Na_2TiSi_4O_{11}$ groups, which are polar on account of the polarity of the [TiO_5] pyramid, are a component of the rod fragment (Fig. 3), and introduce an element of disorder into the structure, because these groups can link nenadkevichite layers at several different levels along the y axis – 0, 1/4, 1/2, or 3/4. It is quite clear that the true **b** period can only be a multiple of b_0 = 14.46 Å, because there cannot be common faces between the Si tetrahedra. A priori we can suppose that there is arbitrary rotation of these polar groups relative to the (001) plane. However, this variant does not actually occur, owing to the sharp periodicity of the zorite structure along the b axis. The question arises: What is the mechanism which causes these isolated groups to form periodic rods? From our viewpoint the mechanism is the local balance of valence forces. In fact, the free O_7 vertices of the Ti_2 pyramids have marked valence unsaturation, even if we take account of the shortening of the titanyl bond to 1.67 Å. This unsaturation of the O_7 anions is the cause of their displacement from the m mirror plane toward one of the right-hand or left-hand pairs of Na_2 cations with partial compensation of their negative charge. Nevertheless, 0.5 v.u. is insufficient for complete saturation of O_7, and their further neutralization proceeds as follows. The Ti pyramids which link pairs of diortho groups adjacent along the c axis are rotated toward one another, and the protons from the water molecule Aq_3 are brought closer to O_7 (by 2.45 Å), yielding 0.3 v.u., and increase their sum at O_7 to an acceptable 1.91 v.u. But then the oxygen of Aq_3 itself becomes unsaturated by −0.6 v.u. (admittedly the Na_2^+ ions partly neutralize it, contributing 0.3 v.u.) and is forced to form a hydrogen bond in the capacity of an acceptor, where the donor is Aq_5 at a distance of about 3.1 Å. This causes slight discompensation of Aq_5, which is again removed by a weak H bond with Aq_4, about 3.2 Å long. The Aq_4 atoms also take part in a mutual H bond ($Aq_4 - Aq_4'$ = 2.8 Å). Then this chain of hydrogen bonds is continued (Fig. 3), and thus causes a periodicity in the rotation of the Ti pyramids in the rod. In other words, the formation of a periodic rod can be thought of as a threading of titanium silicate rings on a chain of H_2O molecules linked by H bonds.

The zeolite framework of zorite is filled not only with H_2O molecules but also by large Na cations. The Na_1 cations, as already observed, each occupy one gap in the zigzag octahedral chains squeezed between the $[(Ti, Nb)_2 \cdot O_{10}]_\infty$ chains (Figs. 1 and 2). If we take account of the lengths of the H bonds,[10] the local balance of valence forces again supports our hypothesis of alternation of empty and full Na octahedra in the chain, since owing to the absence of positive cationic nuclei, unsaturation of the O_3 anions arises in the former. However, if we allow the existence of H bonds between O_3 and the water molecules Aq_1, which are displaced away from the mirror plane owing to separation of the Aq_1 by the Na_1 atoms and thus brought 2.80 Å closer to O_3, then the contribution from the protons to the acceptor O_3 is equal to 0.165 v.u. (according to Lippincot and Schroeder[10]), i.e., it exactly agrees with the contribution made by Na_1 in the filled octahedron. The positions of the Na_2 cations are not so clear, because, whereas half of them (Na$_2'$ and Na$_2''$) must, from considerations of local balance, occupy positions within the rod, the other half can occupy several possible positions in the framework, and this distribution is apparently statistical. At the sites of Na$_2$ vacancies there is marked undersaturation of the O$_4$ atoms (Table IV), which in our opinion prevents participation of these undersaturated atoms in a hydrogen bond with molecules of zeolite water, which we were unable to locate, but which may well be present according to the chemical analysis results.

An interesting feature of zorite is the noncoincidence of the direction of elongation of the crystals along the b axis with the direction of the silicate chains, and also the cleavage which separates these chains. In structures with mixed radicals we rather often observe this apparent lack of correspondence between the character of the silicate radical and the "internal" properties of the mineral. A similar phenomenon is observed in structures of the tuhualite type,[11] in dalyite,[12] and in lemoinite,[13] and has been discussed in more detail in Ref. 14. These facts emphasize the equivalent functional roles of anion complexes and complexes (polyhedra) which play the part of an anion in radicals of the mixed type in which the silicate components must be regarded as fragments of a more general radical. In this respect mixed tetrahedral radicals (aluminum silicate frameworks, especially zeolites) have long been a classic case. When they are present, such "paradoxes" as perfect cleavage are not unusual.

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1) In this article we use the terminology and methods of the theory of OD structures.[2]

2) "Aq" denotes the oxygen atom of a water molecule.

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