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THE CRYSTAL STRUCTURE OF VLASOVITE

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A complete x-ray diffraction study has been made of the mineral vlasovite, $Na_4Zr_2[Si_8O_{22}]$. Vlasovite is a monoclinic mineral, a = 10.98, b = 10.00, c = 8.52 A, β = 100°24'; group C_{2h}^6-C2/c. The structure of vlasovite is a new type of silicate with infinite chains–ribbons of $[Si_8O_{22}]_\infty$.

The discovery of each new mineral is an important event, especially if this mineral belongs to a group of natural compounds which has few representatives. This is the case with vlasovite $Na_2ZrSi_4O_{11}$ [1], a new silicate from a small group composed of zirconium minerals. The thorough study of vlasovite has included a detailed x-ray diffraction study of this mineral.

The investigation was carried out on specimens presented to the authors by R. P. Tikhonenkova. Transparent isometric grains measuring 0.2-0.3 mm were used to prepare the x-ray diffraction patterns. In accordance with the optical biaxiality of the mineral, x-ray goniometry [2] established the Laue class 2/m, thereby, reliably fixing the monoclinic symmetry of vlasovite. The parameters and the type of Bravais lattice were determined in the RKOP and KFOR cameras: a base-centered (C) lattice, a = 10.98 ± 0.04, b = 10.00 ± 0.04, c = 8.52 ± 0.03 A, β = 100°24'. The number of formula units was 3.87 ≈ 4. The unit cell therefore contains eight atoms of Na, 4 Zr, 16 Si and 44 atoms of oxygen.

With Mo-radiation scannings were obtained of the zero to third layer lines by rotation about the $\underline{b}$ and $\underline{c}$ axes. On these x-ray diagrams there were only reflections of hkl with $h + k = 2n$ and $h0l$ with $l = 2n$. The systematic extinctions point to the x-ray group 2/m C –1c, in which there are two space groups–Cc and C2/c. In the subsequent analysis convincing proof was obtained favoring the centrosymmetrical group C_{2h}^6-C2/c in the framework of which all further investigation was conducted.

The intensities of reflections on the x-ray diagrams were measured visually using standards. The values of F^2 were obtained by a standard method with an allowance for the Lorentz factors and the polarization factor. The small dimensions of the particles investigated indicated that the absorption effect was very small.

The next stage in the investigation was provided by the Patterson syntheses, which were especially useful due to the presence of "heavy" Zr atoms. From 129 independent nonzero reflections of hk0 and 139–h0l Patterson projections were plotted in P (uv) and P (uw). In the analysis of these projections it was first established that a satisfactory interpretation of the maxima is only possible on the basis of the centrosymmetrical group C_{2h}^6. Especially convincing was the strong peak at P (uw) with accurate (!) coordinate $^1/_4$ $^1/_4$: in the group Cc all positions are general [3] and, therefore, the appearance of a peak with these coordinates is not very probable. To confirm the group C2/c we analyzed the statistics of intensities [4] of reflections of the zone h0l. The shape of the distribution curve for the experimental intensities agreed well with the corresponding theoretical curve for a centrosymmetrical crystal, which could be considered a final proof of the group C2/c.

TABLE 1. Coordinates of Basis Atoms in the Structure of Vlasovite

Atoms	x	y	z	Atoms	x	y	z
(4) Na_I	0	0.081	0.750	(8) O_{II}	0.147	0.103	0.504
(4) Na_{II}	0	0.412	0.750	(8) O_{III}	0.111	0.358	0.418
(4) Zr	0.250	0.250	0	(8) O_{IV}	0.054	0.239	0.965
(8) Si_I	0.265	0.072	0.638	(8) O_V	0.243	0.137	0.800
(8) Si_{II}	0.049	0.216	0.431	(8) O_{VI}	0.296	0.088	0.158
(4) O_I	0	0.166	0.250				

On the basis of a crystal-geometrical analysis using data obtained from the Patterson projections we found that the most probable position of the four Zr atoms in the structure is nonparametric—in one of two (it is immaterial which) systems of centers of inversion, lying in glide no planes [3]. Localization of the Zr atoms involved determining the approximate coordinates of the Si atoms which were next in "weight." The projections of the interatomic vectors which were then plotted confirmed the arrangement of Zr and Si atoms in the cell. Further analysis was conducted on the assumption that the Zr and Si atoms determine most of the signs of the structure amplitudes F_{hkl}.

The coordinates of the Si and Na atoms and some oxygen atoms were established from the ordinary and weighted projections of the electron density along the y and z axes. The impossibility of reliably determining the coordinates of some O atoms due to their overlapping on the total projections led us to revert to electron density electron of a part of the cell. We notice that the

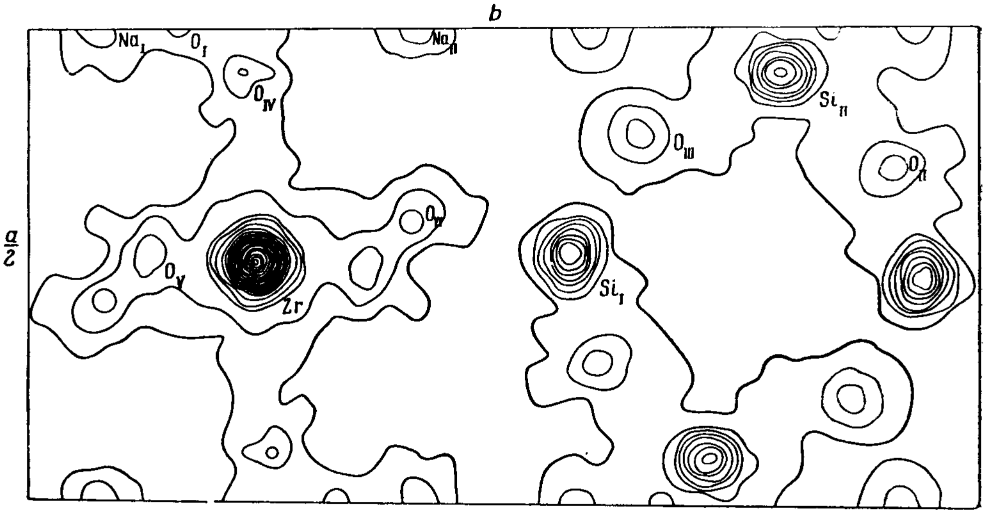

Fig. 1. Zone electron density projection of a half cell along the Z axis. Middle level of projected layer—zero. Contours drawn through 6 electrons/A^2.

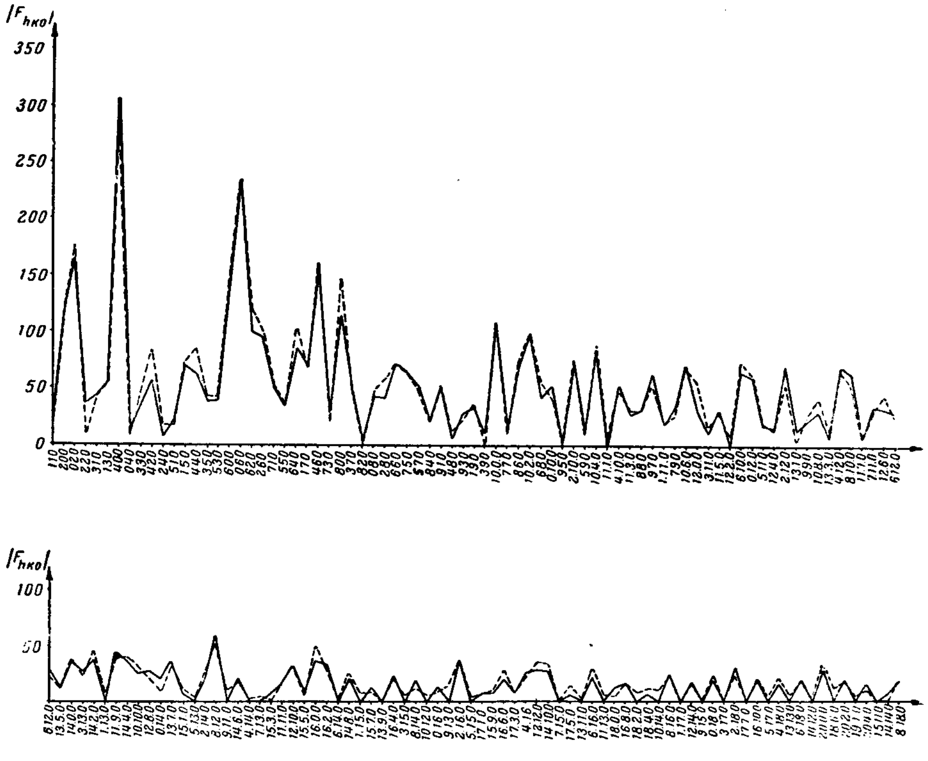

Fig. 2. A comparison of the experimental (—) and calculated (-----) values of F_{hk0}.

structure of vlasovite was very suitable for the application of the zone projection method, especially when projecting a cell along the z axis. The electron density projections of a half cell along the Y and z axes were plotted from 253 independent reflections of $h0l$, $h1l$, and $h3l$ and also from 487 reflections of hk0, hk1, and hk3. From a second approximation of these zone projections the previously established coordinates were made more accurate and the missing coordinates of the atoms in the structure were determined, except for the z coordinates of the atoms O_{IV} and O_{VI} (Table 1).

The vertical coordinates of these latter were established on the basis of crystal chemistry considerations. Figure 1 shows a zone projection along the z axis, in which all atoms of the structure are well resolved. The basis coordinates of the atoms in the vlasovite structure, determined by 24 parameters, are given in Table 1. The values of the coefficients R for reflections of the zones hk0 and $h0l$ without allowing for $F_e = 0$ are equal to 15.3 ($\sin \vartheta/\lambda \leq 1.03$) and 17.3% ($\sin \vartheta/\lambda \leq 1.06$). The inclusion of $F_e = 0$ up to $\sin \vartheta/\lambda \leq 0.90$ leads to values of R equal to 16.8 and 16.5%, respectively. Figures 2 and 3 show graphs for the agreement between the experimental and theoretical values of the structure amplitudes F_{hk0} and F_{h0l}.

The silicon oxygen radical in the vlasovite structure had the formula $[\mathrm{Si_4O_{11}}]_\infty$ and is an infinite chain-ribbon stretched along the [101] or, which is the same, parallel to the edge of the monoclinic I-cell. The links of the chains are quadruple rings of Si-tetrahedra, connected to one another in such a way that in the formation of the chain each of the original rings $[\mathrm{Si_4O_{12}}]$ loses one atom of oxygen (Fig. 4b). The centers of the rings coincide with the inversion centers of the structure, and two neighboring rings in the chain are connected to one another by a twofold axis. The planes of the quadruple rings are not parallel to the common direction of the chain-ribbons, but are almost parallel to the edge a of the noncentered cell. The latter fact was the reason for selecting the C-aspect in describing the structure of vlasovite, since in this case the specific "stepwise" character of the silicon oxygen strip is more clearly followed.

The basis of the vlasovite structure is caused by the arrangement of the Si-chains and the unconnected Zr-octahedra on each of which four chains converge. Figure 5 shows a layer of structure which is one quadruple ring thick and cut parallel to the xz plane. A layer which is similar in thickness and parallel to the yz is shown in Fig. 6. Here, each of the four chains of $[\mathrm{Si_4O_{11}}]_\infty$, converging on the Zr-octahedra is represented by one quadruple ring—a link of the chains. The planes of the rings of two neighboring chains are sharply inclined to one another, which gives the impression of exactly the same actual orientation of neighboring links in each of the chains.

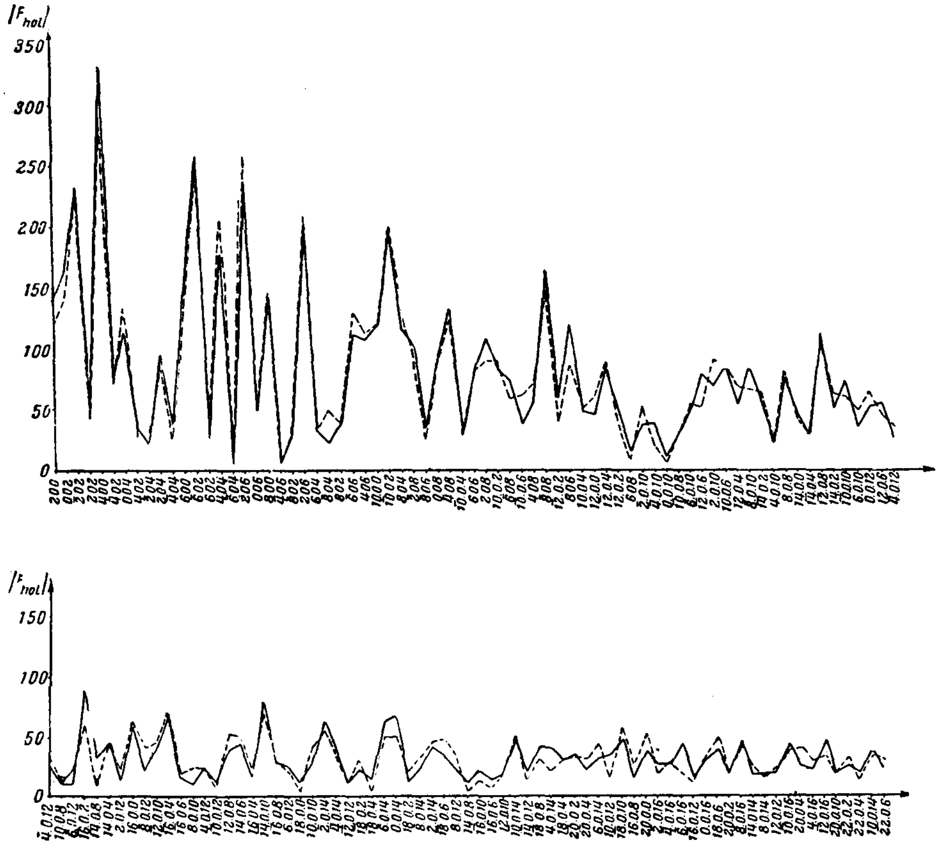

Fig. 3. A comparison of the experimental (—) and not calculated (-----) values of F_{h0l}.

For two crystallographically nonequivalent positions of the Na atoms in the vlasovite structure there are different coordination polyhedra. The Na_I atoms are in septahedra, close to typical polyhedra established for Ca and Na atoms in the structures of ilvaite, narsarsukite, eudidimite, and other minerals. This polyhedron, characteristic for Ca and Na atoms, can be described as a trigonal prism with a pyramid built on one of its tetragonal faces. The obtained polyhedron, therefore, has 7 apices, 13 edges, and 8 faces. The vlasovite septahedron differs from a dismantled typical polyhedron in that the number of faces of the first is reduced to 6 due to both bases of the prism merging with the faces of the pyramid adjoining them. As a result , we have a polyhedron with 7 apices, 11 edges, and 6 faces. The coordination polyhedra of the Na_{II} atoms are distorted octahedra. The polyhedra of both kinds are connected in pairs along an edge and these pairs in their turn are on rotational axes of the second order. These groups of septahedra and octahedra connected with one another do not have common elements with pairs similar to them, but are joined along the edges with Zr octahedra in such a way that infinite columns are formed, stretched parallel to the Si chains. Figure 7a shows a complete Na–Zr column. If from it (for convenience of representation) we remove the Na_{II} octahedra and view it from the side, then we arrive at Fig. 7b. Here, there is alternation of Zr octahedra and Na_I polyhedra, the latter being turned toward the observer alternately showing the base and the sharp apex. This figure can serve as an illustration of the concept of the main "architecture" role of bars of polyhedra about large cations, put forward by Belov [5]. In fact, in the chain of $[Si_4O_{11}]_\infty$ elements of rigidity and elements of elasticity are combined. The links of the chain

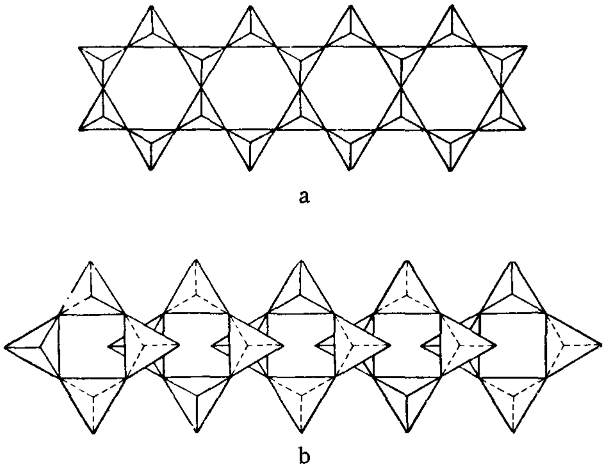

Fig. 4. Diagram of silicon oxygen chain-ribbons with formula of the radical $[Si_4O_{11}]_\infty$. a) Amphibole, b) vlasovite.

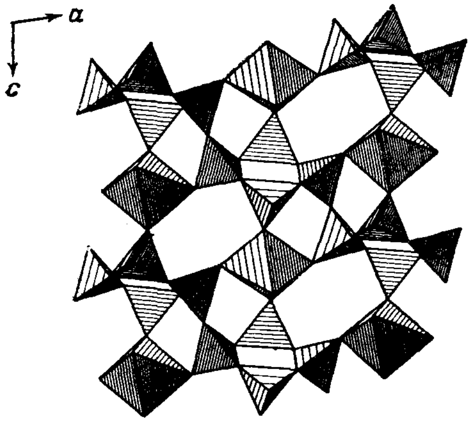

Fig. 5. The axonometry of a layer of the vlasovite structure parallel to the xz plane.

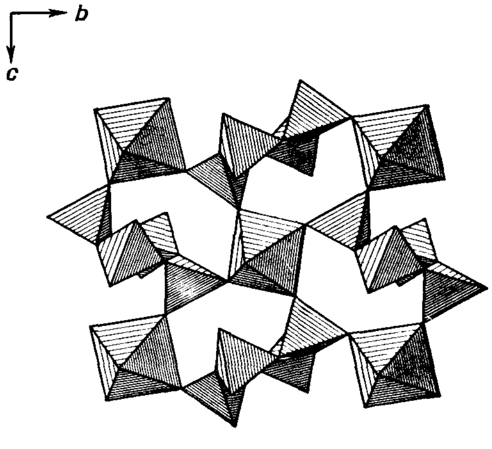

Fig. 6. A layer of the vlasovite structure parallel to the yz plane.

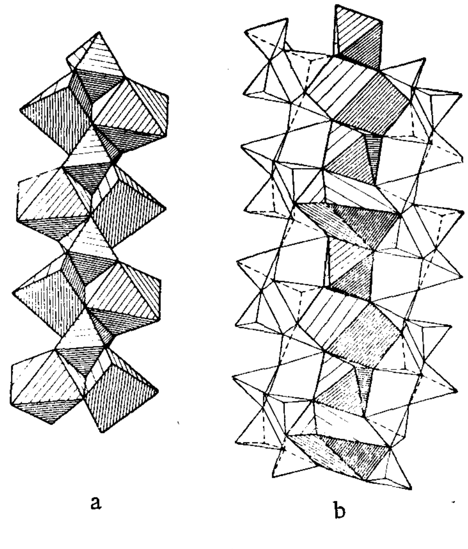

Fig. 7. Two aspects of a column of Na–Zr polyhedra in the vlasovite structure.

TABLE 2. Balance of Valences in the Vlasovite Structure

Atoms	Na_{I}	Na_{II}	Zr	Si_{I}	Si_{II}	Σ
O_{I}	${}^{1}/_{7}$	—	—	—	2	$2+{}^{1}/_{7}$
O_{II}	${}^{1}/_{7}$	—	—	1	1	$2+{}^{1}/_{7}$
O_{III}	—	${}^{1}/_{6}$	—	1	1	$2+{}^{1}/_{6}$
O_{IV}	${}^{1}/_{7}$	${}^{1}/_{6}$	${}^{4}/_{6}$	—	1	$2-{}^{1}/_{42}$
O_{V}	${}^{1}/_{7}$	—	${}^{4}/_{6}$	1	—	$2-{}^{4}/_{21}$
O_{VI}	—	${}^{1}/_{6}$	${}^{4}/_{6}$	1	—	$2-{}^{1}/_{6}$

TABLE 3. Interatomic Distances in the Vlasovite Structure

Polyhedron	Interatomic distances, A		
Zr octahedron	$Zr - O_{IV} = 2.13$	$O_{IV} - O_{V} = 2.90$	$O_{IV} - O^{*}_{VI} = 2.73$
	$Zr - O_{V} = 2.04$	$O_{IV} - O^{*}_{V} = 2.99$	$O_{V} - O_{VI} = 3.04$
	$Zr - O_{VI} = 2.11$	$O_{IV} - O_{VI} = 3.24$	$O^{*}_{V} - O_{VI} = 2.82$
Si_{I} tetrahedron	$Si_{I} - O_{II} = 1.60$	$O_{II} - O^{*}_{III} = 2.65$	$O^{*}_{III} - O^{*}_{VI} = 2.65$
	$Si_{I} - O^{*}_{III} = 1.68$	$O_{II} - O_{V} = 2.58$	$O_{V} - O^{*}_{VI} = 2.67$
	$Si_{I} - O_{V} = 1.58$	$O_{II} - O^{*}_{VI} = 2.70$	
	$Si_{I} - O^{*}_{VI} = 1.64$	$O^{*}_{III} - O_{V} = 2.67$	
Si_{II} tetrahedron	$Si_{II} - O_{I} = 1.62$	$O_{I} - O_{II} = 2.54$	$O_{II} - O^{*}_{IV} = 2.65$
	$Si_{II} - O_{II} = 1.61$	$O_{I} - O_{III} = 2.57$	$O_{III} - O^{*}_{IV} = 2.52$
	$Si_{II} - O_{III} = 1.59$	$O_{I} - O^{*}_{IV} = 2.70$	
	$Si_{II} - O^{*}_{IV} = 1.58$	$O_{II} - O_{III} = 2.66$	
Na_{I} polyhedron	$Na_{I} - O^{*}_{I} = 2.47$	$O^{*}_{I} - O_{II} = 3.93$	$O_{IV} - O^{*}_{IV} = 3.64$
	$Na_{I} - O_{II} = 2.88$	$O^{*}_{I} - O_{V} = 4.01$	$O_{IV} - O_{V} = 2.90$
	$Na_{I} - O_{IV} = 2.41$	$O_{II} - O^{*}_{IV} = 2.65$	
	$Na_{I} - O_{5} = 2.69$	$O_{II} - O_{V} = 2.58$	
Na_{II} octahedron	$Na_{II} - O^{*}_{III} = 2.86$	$O^{*}_{III} - O^{*}_{III} = 3.41$	$O^{*}_{VI} - O^{*}_{III} = 4.41$
	$Na_{II} - O_{IV} = 2.51$	$O^{*}_{III} - O_{IV} = 4.11$	$O^{*}_{VI} - O^{*}_{III} = 2.65$
	$Na_{II} - O^{*}_{VI} = 2.24$	$O_{IV} - O^{*}_{IV} = 3.64$	$O^{*}_{VI} - O_{IV} = 3.90$
		$O_{IV} - O^{*}_{VI} = 2.73$	

Note. The asterisk indicates atoms which are not included in the number of basis atoms.

TABLE 4. Some Bond Angles in the Vlasovite Structure

Bonds	Valence angles (in degrees)	
Si_{I} tetrahedron	$O_{II} - Si_{I} - O^{*}_{III}$ 108	$O^{*}_{III} - Si_{I} - O_{V}$ 110
	$O_{II} - Si_{I} - O_{V}$ 108	$O^{*}_{III} - Si_{I} - O^{*}_{VI}$ 106
	$O_{II} - Si_{I} - O^{*}_{VI}$ 113	$O_{V} - Si_{I} - O^{*}_{VI}$ 112
Si_{II} tetrahedron	$O_{I} - Si_{II} - O_{II}$ 104	$O_{II} - Si_{II} - O_{III}$ 113
	$O_{I} - Si_{II} - O_{III}$ 107	$O_{II} - Si_{II} - O^{*}_{IV}$ 113
	$O_{I} - Si_{II} - O^{*}_{IV}$ 116	$O_{III} - Si_{II} - O^{*}_{IV}$ 106
Si — O — Si	$Si_{I} - O_{II} - Si_{II}$ 145	$Si_{II} - O_{I} - Si^{*}_{II}$ 180
	$Si^{*}_{I} - O_{III} - Si_{II}$ 141	

are quadruple silicon oxygen rings and are very rigid structures, whereas, the points of connection of the neighboring rings with one another can be compared with hinged joints, permitting compression and extention of the chain as a whole without destroying the symmetry. The real configuration of the separate elements of the chain should, therefore, be considered as the result of the facility of a silicon oxygen disposition for concrete arrangement of the large cations.

In the vlasovite structure, the second Pauling rule is well satisfied: the maximum deviation from 2 of the sum of positive valency forces converging on the oxygen atoms (atoms O_V) is 9.5% (Table 2).

The interatomic distances in the vlasovite structure (Table 3) are close to the mean values observed in silicates. The exception is a certain increase in the distances in Na polyhedra, which is connected with considerable openness of the structure.

The valence angles in silicon oxygen chains of the structure are given in Table 4. A calculation was also made of the angle between the edges of the tetrahedra, forming the quadruple ring of the chains. This angle was 91° (89°) and, therefore, the internal shape of the quadruple rings is practically a square.

Vlasovite is a new structural type of silicate with infinite chains $[Si_4O_{11}]_\infty$. A similar formula of the radial is also shown by the classical representatives of the "first chapter" in the crystal chemistry of silicates [6]—amphiboles. However, between the silicon oxygen radicals of the amphiboles and vlasovite there is an important difference (Fig. 4): the amphibole band is the product of condensation of pyroxene chains of $[SiO_3]$, whereas, the infinite radical of the vlasovite structure is formed from finite groupings—quadruple rings.

Bearing in mind the periodicity (two rings) along the axis of the chains in the structure, the vlasovite formula should be written in the form $Na_4Zr_2[Si_8O_{22}]$.

The properties of vlasovite are in accordance with its structural features. The low specific gravity (2.97) corresponds to the friable (but strong) structure of the mineral. The middle plane of vlasovite with regard to cleavage is parallel to (010) and coincides with a somewhat crimped plane in the structure, intersecting only the Zr—O and Na—O bonds. The plane of the optic axes in the structure also coincides with (010) and at the same time is parallel to planes containing the axes of the chains. Finally, the closeness of the double-refractions of vlasovite and amphiboles is an indication of the band character of the silicon oxygen radical in their structures.

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