# DERIVATION OF THE STRUCTURE OF LOVOZERITE FROM SECTIONS OF THE THREE-DIMENSIONAL PATTERSON FUNCTION

V. V. Ilyukhin and N. V. Belov
Institute of Crystallography, Academy of Sciences

Translated from Kristallografiya, Vol. 5, No. 2, pp. 200-214, March-April, 1960
Original article submitted January 6, 1960

The structure of lovozerite, $Na_2ZrSi_6O_{15} \cdot 3H_2O \cdot 0.5\ NaOH$, has been deduced from sections of the electron-density pattern. The silicon-oxygen radical is shown to be a $[Si_6(O, OH)_{18}]$, ring; silicon-oxygen tetrahedron contains five or six OH groups.

Lovozerite, an extremely rare mineral, was first found in 1935, as grains associated with eudialite in the Lovozero alkali complex (central Kola peninsula) by Gerasimovskii, who described it in 1939 [1].

Specimens much altered by weathering have a black color and fracture irregularly. The specific gravity is 2.394 (pycnometer), the hardness is about 5, and cleavage is not observed. Powder patterns taken with Fe radiation showed no lines; on the basis of optical data (negative uniaxial with $n_\gamma = 1.560$, $n_\alpha = 1.549$) it has been assigned to the hexagonal system [1]. Gerasimovskii proposed an empirical formula

$$[H, Na, K]_2O \cdot (Ca, Mg, Mn)O \cdot (Zr, Ti)O_2 \cdot 6SiO_2 \cdot 5H_2O \rightarrow Na_2CaZrSi_6O_{16} \cdot 5H_2O,$$

from analyses of grains deriving from an occurrence on the River Muruai; that formula is the one given in the literature [2].

In composition lovozerite is similar to other Zr silicates of the eudialite-catapleiite group, especially to eudialite $Na_{4-5}CaFeZr(OH,Cl)Si_6O_{18}$, eucolite (eudialite containing much divalent metal and Nb), and mesodialyte [3] (which is intermediate in composition); its distinguishing features are a larger amount of water and a smaller amount of alkali. Studies on material found later in other localities here (by Tikhonenkov, in the Kola peninsula) and abroad (Greenland) have given similar results. Semenov [4] has reported single-crystal fragments of brown-red color occurring as overgrowths on eudialite. These latter crystals were in a much better state of preservation; they gave a more exact specific gravity (2.64) and a powder pattern (Fe radiation). The optical constants were confirmed, and a new analysis was obtained (analyst I. Razina), which showed a much higher content of alkali (12.4%) as against 5.6-6%), more silica (55.6% instead of 52%), and less water (8.23% against 13-15%). Rare-earths were also detected.

The most probable composition is

$$Na_2ZrSi_6O_{15} \cdot 3H_2O$$

with additional NaOH (about half a molecule).

This formula is close to that of elpidite ($Na_2ZrSi_6O_{15} \cdot 3H_2O$) and to that of dalyite ($K_2ZrSi_6O_{15}$); which contains no water; these two representatives of the eudialite group differ from the other Zr silicates in containing either Na alone or K alone (within the usual limits of purity for any mineral).

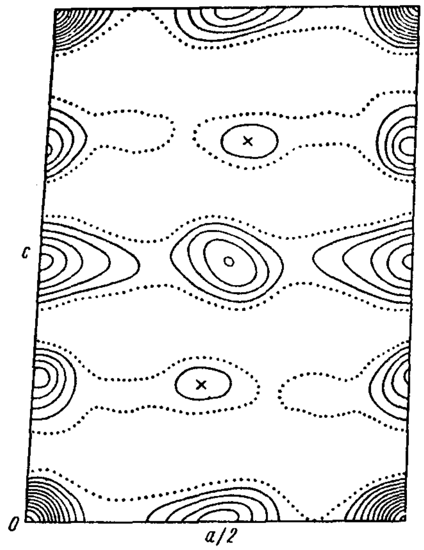

Fig. 1. The p(xz) Patterson projection. The contours are in arbitrary units. Negative contours have been omitted.

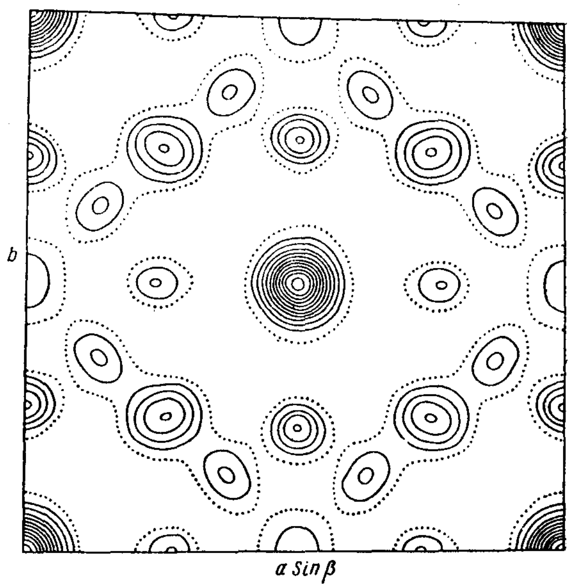

Fig. 2. Projection of the Patterson function on the xy plane. The contours are in arbitrary units. Negative contours have been omitted.

## I

The irregular single-crystals received from E. I. Semenov included three of roughly spherical shape (0.3-0.8 mm in size), which gave good Laue patterns as well as oscillation and rotation photographs; from these the class was found to be $C_{2h} = 2/m$, the cell parameters being a = 10.48, b = 10.20, c = 7.33 A, $\beta$ = 92°30′ with two (1.96) formula units in the unit cell.

The Weissenberg photographs (Mo radiation) showed absences only for h + k = 2n + 1, which corresponds to the x-ray group 2/mC – / –; that group includes one space group having a center of symmetry and two (Cm, C2) lacking such center.

The intensities were estimated on the usual blackening scale modified to have close intervals of $\sqrt[4]{2}$. Those spots falling at small $\vartheta/\lambda$ were concealed by the clamp in the goniometer cassette; these were estimated separately from patterns recorded with Cu radiation. As the crystals were nearly spherical, the corrections for absorption must be nearly the same for all the main zones, so they were neglected.

The 116 nonzero h0$l$ reflections, 117 similar hk0, and 78 similar 0k$l$ gave us three basic Patterson projections, but only the xz one showed a set of three peaks [5] characteristic of a centrosymmetric projection. Statistical analysis of the experimental structure factors [6] confirmed that the xz distribution is centrosymmetric and that the other two are not. There is one heavy atom in the independent part of the cell [7]; allowance for that did not alter the results deduced from [6]. The intensity distribution calculated from all the hk$l$ also lacked a center of symmetry, while the one-dimensional Harker trace taken along y through the three-dimensional pattern showed none of the peaks it ought to if there were an m plane normal to b.

So, although the crystal shows no piezoelectric effect, it would appear that there is no m plane, the most probable space group being $C_2^3 = C2$, with screw and rotation axes alternating. The independent part of the cell contains only two kinds of twofold positions having each a single parameter (on crystallographically different twofold rotation axes); the other positions are general and have three parameters. The chemical formula would imply that one of the one-parameter positions must be occupied by Zr and the other by Na, the other atoms being in general positions.

Figures 1 and 2 show the xz and xy projections respectively. The primitive cell contains one heavy atom ($Z_{Zr} = 40$); the restrictions placed on the symmetry of the group are such as to cause us to hope that the structure might be deducible directly from the projections, because the Zr-X vector system gives peaks much stronger than those given by the Na-X, Si-X, etc. systems. But, unfortunately the pattern of peaks is regular on account of the special configuration of the structure; peaks are superimposed because atoms overlap (the axes of the cell are large), and many peaks are broadened on account of the nearness to a centrosymmetric array; in consequence we can draw no reliable conclusion about the positions of the atoms.

The xz projection (b = 10.2 A) has its peaks arranged in bands parallel to the coordinate axes. The sole peak in p(xz) suitable for use in the superposition method [8] is the Zr-Si one (x in Fig. 1); but even $M_2(xz)$ retains all the peaks in p(xz)[$M_1(xz)$ does as well, of course], so no conclusion can be drawn. This result is confirmed by Simonov's [9] test for the possibility of locating the atoms:

$$Z_x Z_{\max} > 4b\sqrt{|\bar{P}|^2}. \quad \text{where } |\bar{P}|^2 = \frac{1}{S^2}\sum F^4_{h0l}$$

(with allowance for the zeroth term). We refer the $|F_{h0l}|$ to the absolute scale and estimate $|\bar{P}|^2$; we get

$$Z_x Z_{\max} > 3880\ e^2/A^2$$

Now the strongest Zr-Si peak has [23] a strength of 550 $e^2/A^2$; four peaks are superimposed in the synthesis (on account of the resemblance to a centered structure), but still 4 × 550 < $Z_x Z_{\max}$.

The higher symmetry of the xy and xz projections (the traces of two symmetry planes are present) does not make them convenient for minimalization. At first sight the xy projection appears suitable (c = 7.33 A along the axis), but it lacks single peaks and has a very pronounced diagonal bands, so it also fails to give a sharp $M_n(xy)$. Again, the yz projection fails because two structures are superimposed in the M function; those structures are generated by that function, which is centrosymmetric.

In view of the presence of a horizontal mirror plane in the vector space we replaced the usual projections

$$\int_0^b P(xyz)\cos 2\pi ky/b\,dy \quad \text{and} \quad \int_0^b P(xyz)\sin 2\pi ky/b\,dy.$$

by modified ones [10]

$$\int_0^{b/2} P(xyz)\cos 2\pi ky/b\,dy \quad \text{and} \quad \int_0^{b/2} P(xyz)\sin 2\pi ky/b\,dy$$

(and by the sum and difference of those), for which purpose we used h0*l* and h2*l* reflections. The peaks were broad and clearly overlapped, so we could not interpret them correctly. The statistical method [11, 12] also failed.

In view of these successive failures we were forced to use P(xyz), the three-dimensional Patterson function. For that purpose we had results for 13 planes normal to the axes in the reciprocal lattice, namely seven layer lines for b, five for c, and one (equatorial) for a. In all there were 1850 reflections corrected for angle factors and referred to a single scale.

The three-dimensional function has been applied with success for centrosymmetric structures [13-15], but for structures lacking centers (space groups $P2_1$, $P2_12_12_1$, $P6_12$) use has been made only of Harker sections [16-18] or of sections of the function showing peaks caused by pairs of atoms related by symmetry elements [19].

The peaks in the xy and xz projections were such as to indicate that suitable sections would be ones taken normal to the twofold axis at heights (in hundredths of b) of 0, 8, 10, 12, 13, 15, 17, 20, 22, 23, 25, 27, 28, 30, 33, 35, 37, 38, 40, 42, 50.*

Figure 3 shows the independent parts of the more important sections (those containing the strongest peaks). Fig. 4 shows all the main vectors from Zr by means of a dimetric projection of a sphere [20]. The size of a spot indicates the strength of the peak; the number indicates the length of the vector; and the orientation may be

---

*We wish to thank Professor G. S. Zhdanov and his colleagues in the computing division of the Karpov Institute of Physical Chemistry for permission to use their 'Kristall' computer.

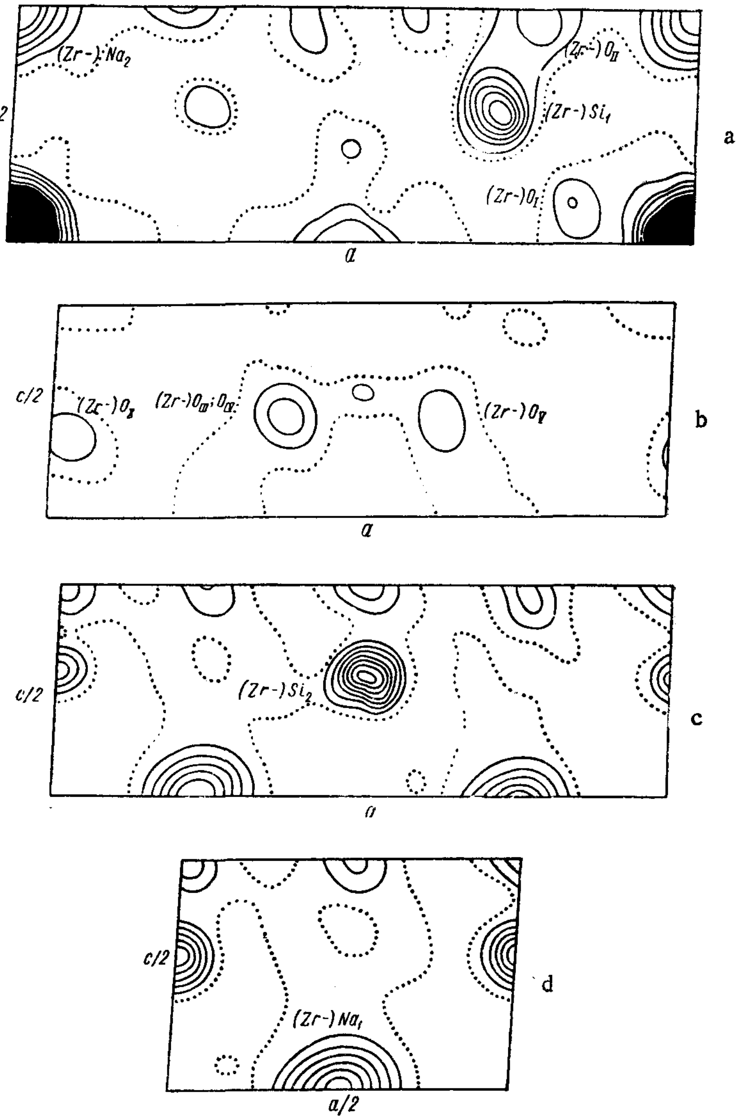

Fig. 3. Sections of P(xyz), the three-dimensional Patterson function.
a) y = 0; b) y = 0.13; c) y = 0.22; d) y = 0.25.

read in $\rho$, $\varphi$ coordinates from the equiangular grid. The two unique Zr atoms in the side-centered cell are related by an oblique translation; one may be considered as being at the origin 000 (the other is at $-\frac{1}{2}\frac{1}{2}0$), so that Zr-X peak gives the absolute coordinates of the X atom. The sign of $r_X$ (the orientation to be chosen from the two possible ones) is to established from considerations of chemical crystallography and so on (i.e., by trial and error).

The assignment of any peak was checked by calculating (by means of integral characteristics [21]) the absolute height of that peak at its center:

$$P_{ij}(0) = \frac{1}{2\pi^2}\int_0^\infty f_i(s)\,f_j(s)\,s^2\,ds$$

and the shape of the peak

$$P_{ij}(r) = \frac{1}{2\pi^2}\int_0^\infty f_i(s)\,f_j(s)\,s^2\frac{\sin sr}{sr}\,ds \approx \frac{1}{2\pi^2}\sum_{k=1}^{K_{\max}} f_i(s_k)\,f_j(s_k)\,s_k^2\frac{\sin s_k r}{s_k r}\,\Delta s_k$$

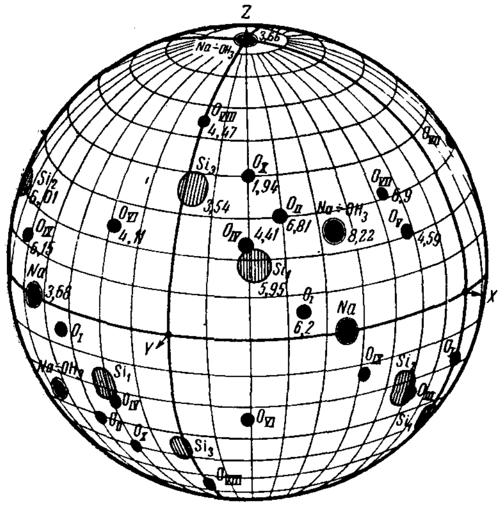

Fig. 4. The main Zr-X interatomic vectors.

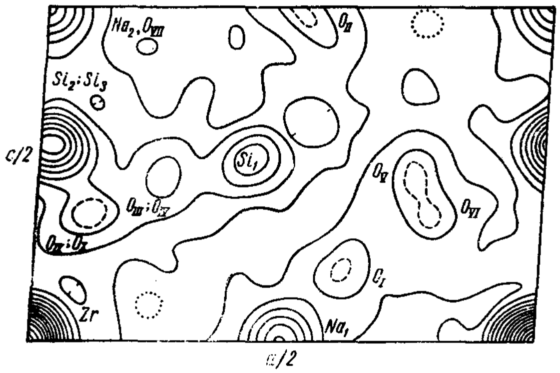

Fig. 5. Electron-density synthesis σ(xz). The contours are at intervals of 7 e/A$^2$, or of 3.5 e/A$^2$ for the partly overlapping O atoms.

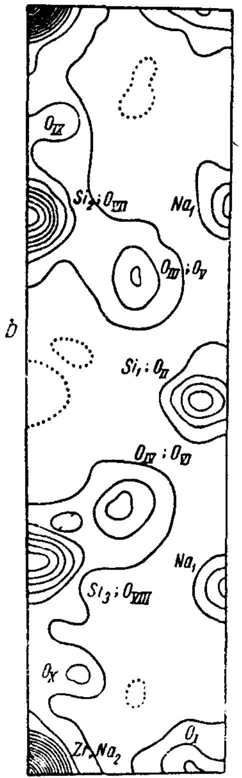

Fig. 6. Electron-density synthesis σ(xy). The contours are at intervals of 7e/A$^2$.

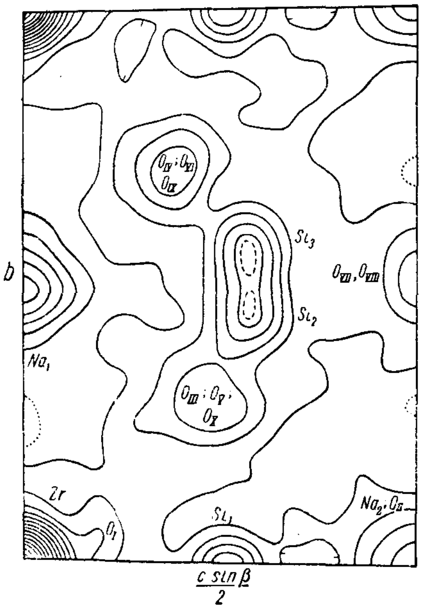

Fig. 7. Electron-density synthesis σ(yz). The contours are at intervals of 7 e/A$^2$, or 3.5 e/A$^2$ for adjacent Si atoms.

this process was applied to the Zr-Si, Zr-Na, Zr-O, Si-Si, Si-O, O-O peaks subject to a certain amount of averaging (over h0*l* , hk*l* , hk0, 0k*l* zones and the whole of the space of the reciprocal lattice hk*l* ) for the temperature factor B computed by means of Wilson's method [22]. For this purpose we took the mean isotropic temperature factor for all atoms to be B = 1.75 A$^2$.

The peaks on P(xyz) were referred to the absolute scale. For that purpose we used a slightly modified formula from [23]:

$$KP\,(000)_0 = \sum_{i=1}^{N} P_{ii}\,(0) - \frac{F^2_{000}}{V}\,.$$

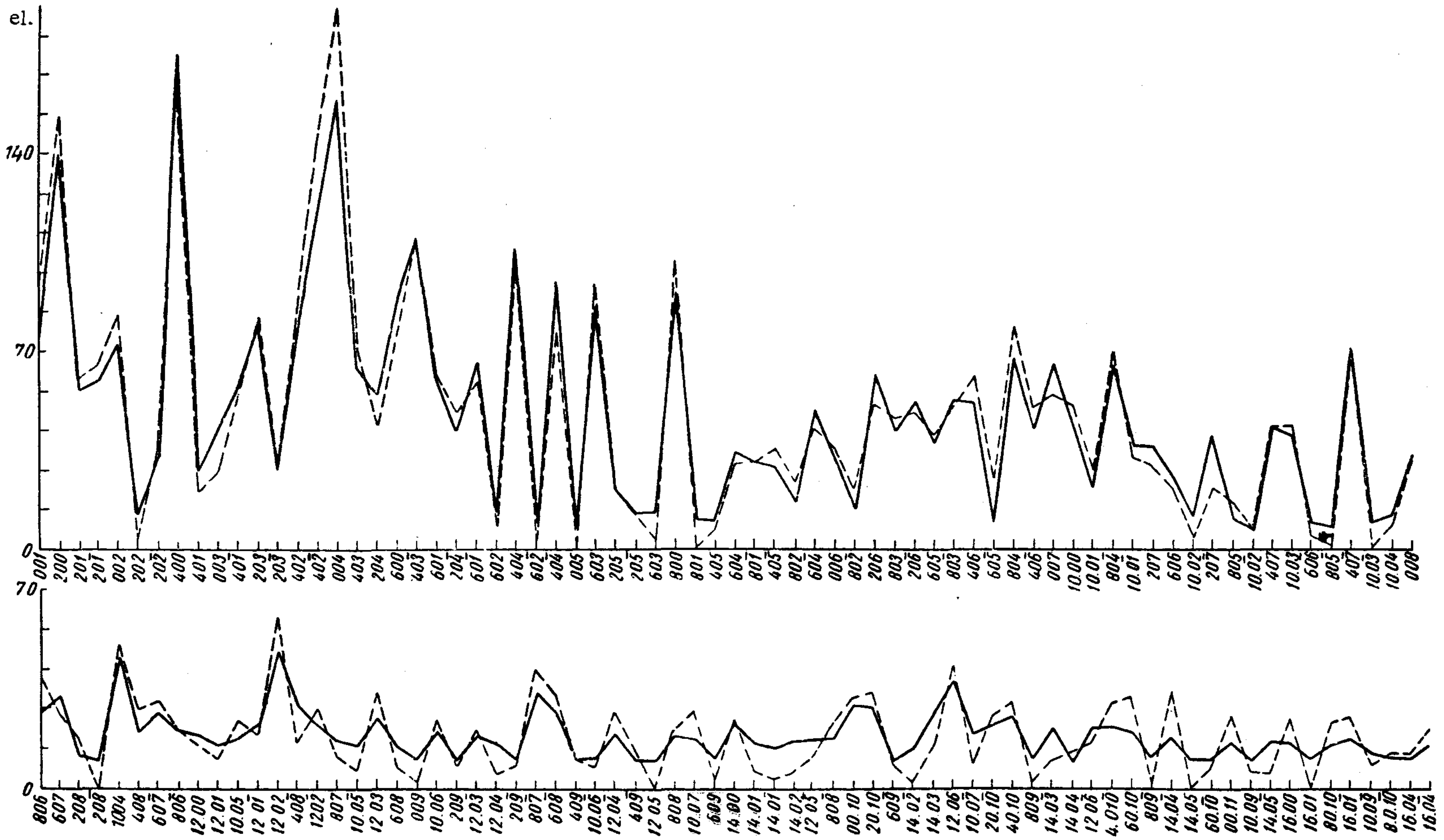

Fig. 8. Structure amplitudes for the h0$l$ zone.

—— $F_0$ ---- F.

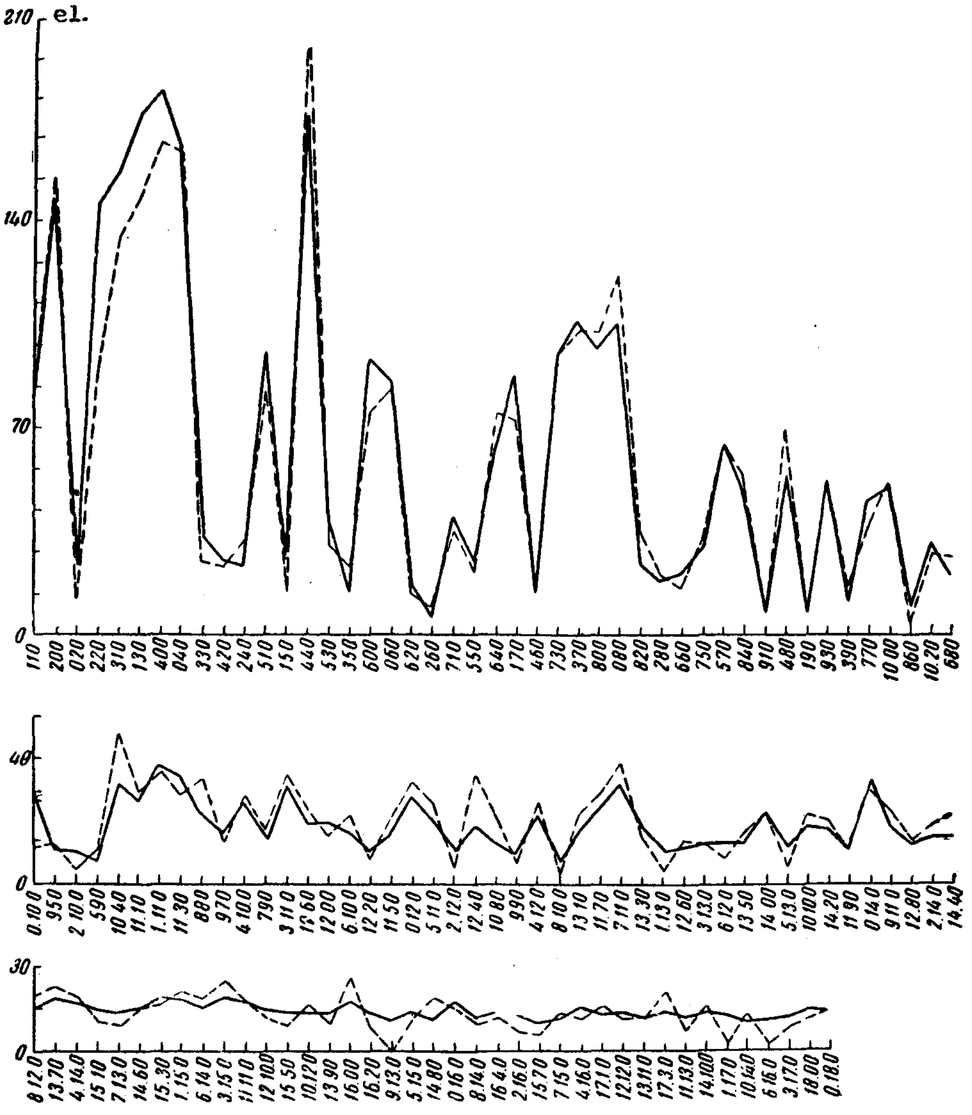

Fig. 9. Structure amplitudes for the hk0 zone. —— $F_0$ ---- F.

TABLE 1

| Atom | x* | y* | z* | Atom | x* | y* | z* |
|---|---|---|---|---|---|---|---|
| Zr | 0 | 0 | 0 | $O_{VI}$ | 61.0 | 84.0 | 81.3 |
| $Si_1$ | 21.1 | 49.5 | 26.5 | $O_{VII}$ | 50.0 | 27.5 | 50.0 |
| $Si_2$ | 49.5 | 23.2 | 70.9 | $O_{VIII}$ | 50.0 | 74.5 | 50.0 |
| $Si_3$ | 48 | 78.2 | 70.9 | $O_{IX}$ | 4.0 | 85.5 | 17.6 |
| $O_I$ | 18.8 | 2.0 | 89.3 | $O_X$ | 6.6 | 13.5 | 19.6 |
| $O_{II}$ | 23.0 | 49.5 | 53.0 | $Na_1'$ | 24.8 | 24.6 | 00.0 |
| $O_{III}$ | 37.1 | 13.5 | 74.0 | $Na_1''$ | 25.2 | 74.6 | 00.0 |
| $O_{IV}$ | 37.5 | 87.0 | 78.0 | $(OH_3)\,Na_2$ | 00.0 | 1.5 | 50.0 |
| $O_V$ | 62.8 | 17.0 | 75.4 | | | | |

---

*Coordinates given in hundredths of a, b, and c.

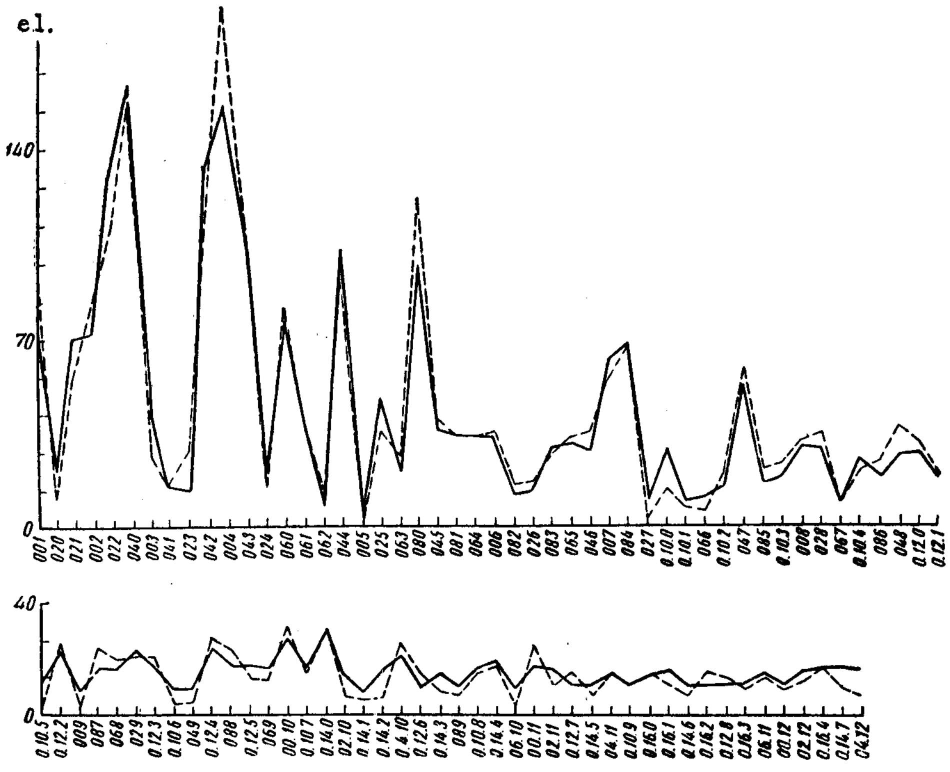

Fig. 10. Structure amplitudes for the 0k*l* zone.
—— $F_0$ ---- F.

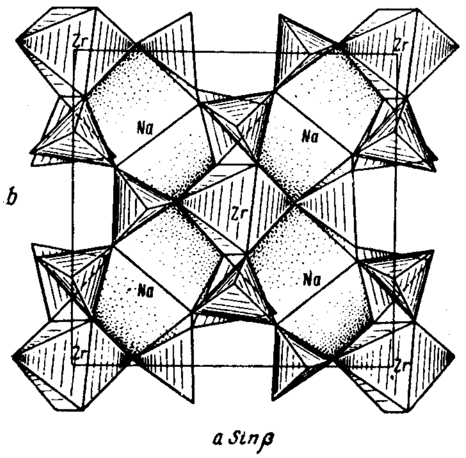

Fig. 11. Projection of the structure of lovozerite (in polyhedra) on the xyplane.

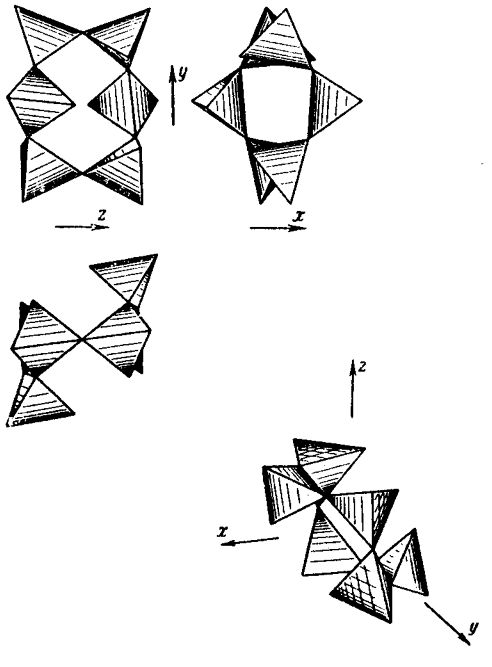

Fig. 12. Ring of silicon-oxygen tetrahedra (projections on the xz, xy, and yz planes, and axonometric projection).

TABLE 2

| | Neglecting zero reflections (%) | With zero reflections (%) | No. of zeros |
|---|---|---|---|
| $R_{h0l}$ | 18.0 | 20.2 | 24 |
| $R_{hk0}^{*}$ | 18.5 | 19.5 | 12 |
| $R_{0kl}^{*}$ | 18.0 | 19.4 | 15 |

in which $P(000)_0$ is the value of the function (unnormalized) at the origin of the Patterson cell, $F^2_{000} = \left(\sum_{i=1}^{N} Z_i\right)^2$

V is the volume of the cell, and $P_{ii}(0)$ is calculated from certain formulas [21, 21]. Then the absolute value of P(xyz) is

$$P(x, y, z)_{\text{abs}} = KP(xyz)_0 + \frac{F^2_{000}}{V}$$

The extra term $\frac{F^2_{000}}{V}$ appears because the zeroth term cannot be incorporated in $P(xyz)_0$ since it cannot be given in relative units.

The peaks agreed well in height and shape with those found from experiment, so we were able to assign preliminary coordinates to Si, Na, and some of the oxygen atoms; in that way we obtained a first rough model.

TABLE 3

| Anion | Cation | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Zr | $Na_1$ | $Na_1$ | $Si_1$ | $Si_2$ | $Si_3$ | $Na_2$ | $\Sigma \frac{w_i}{n_i}$ |
| $O_I$ | $^4/_6$ | $^1/_6\ (^1/_7)$ | | $^4/_4$ | | | | $2-\frac{1}{6}\left(\frac{1}{7}\right)$ |
| $O_{II}$ | | | | $^4/_4$ | | | $^1/_6$ | $1+\frac{1}{6}$ |
| $O_{III}$ | | $^1/_6\ (^1/_7)$ | | $^4/_4$ | $^4/_4$ | | | $2+\frac{1}{6}\left(\frac{1}{7}\right)$ |
| $O_{IV}$ | | | $^1/_6\ (^1/_7)$ | $^4/_4$ | | $^4/_4$ | | $2+\frac{1}{6}\left(\frac{1}{7}\right)$ |
| $O_V$ | | $^1/_6\ (^1/_7)$ | | | $^4/_4$ | | | $1+\frac{1}{6}\left(\frac{1}{7}\right)$ |
| $O_{VI}$ | | | $^1/_6\ (^1/_7)$ | | | | | $1+\frac{1}{6}\left(\frac{1}{7}\right)$ |
| $O_{VII-VIII}$ | | | | | $^4/_4$ | | $^1/_6$ | $2+\frac{1}{6}$ |
| $O_{IX}$ | $^4/_6$ | $^1/_6\ (^1/_7)$ | | | $^4/_4$ | | $^1/_6$ | $2\left(2-\frac{1}{42}\right)$ |
| $O_X$ | $^4/_6$ | | $^1/_6\ (^1/_7)$ | | | $^4/_4$ | $^1/_6$ | $2\left(2-\frac{1}{42}\right)$ |

We calculated a series of electron-density syntheses for the xz (centrosymmetric) projection*, for which purpose a was divided into 120 parts and c into 60 parts; then we proceeded to the xy and yz projections (in the first we divided b and a into 60 parts; in the second, b into 120 parts and c into 60 parts). Six successive synthesis were performed for σ(x, z), four for σ(y, z), and two for σ(x, y) (Figs. 5-7); as a result we established the coordinates of all the main atoms and were able to allow for displacement arising from overlapping [24]. Table 1 gives the coordinates resulting from syntheses carried to the points at which R attained the values given in Table 2.

---

*The work was done at first manually and later on the 'Strela' universal computer in the Computing Center at Moscow State University; we are deeply indebted to the team at the Center (especially V. I. Simonov) for his assistance.

TABLE 4

**Zr-Octahedron** (A)

$Zr - O_{I} = 2.16$
$O_{IX} = 2.05$
$O_{X} = 2.13$

$O_{I} - O_{IX} = 3.15$
$- O_{X} = 2.87$
$- O^{*}_{IX} = 3.00$
$- O^{*}_{X} = 3.00$
$O_{IX} - O^{*}_{IX} = 3.26$
$O_{X} - O^{*}_{X} = 2.79$
$O_{IX} - O_{X} = 2.88$

**$Si_{I}$ Tetrahedron** (A)

$Si_{1} - O_{I} = 1.62$
$O_{II} = 1.64$
$O_{III} = 1.67$
$O_{IV} = 1.61$

$O_{I} - O_{II} = 2.72$
$- O_{III} = 2.55$
$- O_{IV} = 2.66$
$O_{II} - O_{III} = 2.60$
$- O_{IV} = 2.74$
$O_{III} - O_{IV} = 2.73$

**$Si_{2}$ Tetrahedron** (A)

$Si_{2} - O_{III} = 1.65$
$O_{V} = 1.58$
$O_{VII} = 1.60$
$O_{IX} = 1.57$

$O_{III} - O_{V} = 2.72$
$- O_{VII} = 2.68$
$- O^{*}_{IX} = 2.53$
$O_{V} - O_{VII} = 2.58$
$- O^{*}_{IX} = 2.63$
$O_{VII} - O^{*}_{IX} = 2.56$

**$Si_{3}$ Tetrahedron** (A)

$Si_{3} - O_{IV} = 1.54$
$O_{VI} = 1.69$
$O_{VIII} = 1.60$
$O_{X} = 1.72$

$O_{IV} - O_{VI} = 2.50$
$- O_{VIII} = 2.77$
$- O^{*}_{X} = 2.52$
$O_{VI} - O_{VIII} = 2.77$
$- O^{*}_{X} = 2.78$
$O_{VIII} - O^{*}_{X} = 2.57$

**$Na_{1}$ Polyhedron** (A)

$Na_{1} - O_{I} = 2.52$
$O_{III} = 2.60$
$O_{IV} = 2.46$
$O_{V} = 2.40$
$O_{VI} = 2.25$
$O_{IX} = 2.66$
$O_{X} = 2.68$
$O_{I} = 3.00$

$O_{I} - O_{III} = 2.55$
$- O_{V} = 3.64$
$- O_{X} = 2.87$
$O_{III} - O_{V} = 3.72$
$- O^{*}_{VI} = 3.51$
$- O^{*}_{IX} = 2.52$
$O_{IV} - O^{*}_{VI} = 2.91$
$- O_{X} = 2.50$
$- O^{*}_{I} = 2.66$

$O_{V} - O^{*}_{IX} = 3.76$
$- O_{X} = 3.25$
$- O^{*}_{I} = 3.78$
$O^{*}_{VI} - O^{*}_{IX} = 3.70$
$- O_{X} = 3.54$
$- O^{*}_{I} = 3.60$
$O_{IX} - O^{*}_{I} = 3.14$
$O^{*}_{IV} - O_{V} = 3.30$

$Na_{2}$ — **$OH_{3}$-Polyhedron** (A)

$Na_{2} - O_{II} = 2.44$
$O_{VII} = 2.46$
$O_{VIII} = 2.36$
$O_{X} = 2.65$
$O_{IX} = 2.93$

$O_{II} - O^{*}_{VII} = 3.32$
$- O^{*}_{VIII} = 3.53$
$- O_{IX} = 3.64$
$- O_{X} = 3.37$
$O^{*}_{IX} = 3.09$
$O^{*}_{X} = 4.03$

$O_{IX} - O^{*}_{VII} = 2.55$
$- O_{X} = 2.88$
$O^{*}_{VIII} - O_{X} = 2.60$

---

Note. The stars denote atoms other than the basic ones, to which they are related by the symmetry elements, however.

These values are roughly equal for the three independent projections on account of the method of estimating the intensities**, and of the isometric nature of the structure, which is responsible for the identical absorption (see description of structure).

---

** At first we tried to use the xy and yz projections, supposing that the derivative from central symmetry would fail to make itself felt. But, five successive revisions of the coordinates would not reduce R below 45% We obtained satisfactory values of R only when the symmetry was reduced to C2.

The coordinates are determined by 41 parameters. The three $\rho$ (r), projections were supplemented from the weak peaks in P(xyz) in order to revise the coordinates of overlapping atoms.

The error [23] varies somewhat from one projection to another:

$h0l$, $0kl$: Zr ± 0.0013 A; Si ± 0.005 A; Na ± 0.0065 A; O ± 0.0012 A
$hk0$: Zr ± 0.001 A; Si ± 0.004 A; Na ± 0.0055 A; O ± 0.01 A.

Figures 8-10 give the experimental structure amplitudes calculated from the coordinates given in Table 1 and referred to the absolute scale.

The structure of the first Zr silicate of the eudialite group (catapleiite, $NaZr[Si_3O_9]2H_2O$) was established (in 1936) by B. K. Brunovskii in this laboratory [25]; its symmetry $D^4_{6h} = P6_3/mcm$. It consists of almost flat layers of cations joined by a hexagonal array of Zr octahedra and Na decahedra; the layers are separated by gaps of 5 A, which is about half c. Between the layers there are triple (single-layer) rings of $[Si_3O_9]$tetrahedra. Two $H_2O$ molecules are distributed randomly over three possible positions (2/3 in each).

Our description of the structure of the second mineral in this group (lovozerite) must start with the xy projection (Fig. 11). It is clear that Zr octahedra and Na polyhedra alternate along the [110] diagonals of the cell to form an almost exactly tetragonal array having a square of side 7.31 A. In the xy projections two such identical squares are related by an oblique translation of group C2. The Zr atom lies at the center of a slightly distorted oxygen octahedron (at the corner of a square); the Na atom (at the middle of a side) is surrounded by a characteristic figure having seven vertices, which is made up a trigonal prism and half an octahedron joined on a common square face [compare Ca (Na) in sphene, durangite, epidote, etc.] The eighth (somewhat more remote) anion gives a figure composed of two distorted trigonal prisms joined at their bases. That figure is very convenient to use in representing the structure (Fig. 8), although in fact each rectangular face is bent along its diagonals. The flat grids are separated vertically by c sin $\beta$, i.e., along the axis c = 7.33 A but with a displacement through the angle $\beta$. At half c, between Zr atoms, lies another Na atom (that appearing in the second part of the formula); but chemical analysis gives a half molecule of NaOH in the 'side chain', and the structure factors indicate that this Na atom is replaced in half the instances by OH or (more probably) by $OH_3$.*

The main feature of lovozerite is the three-dimensional lattice of Zr octahedra lying at the corners of dubic cells 7.31 A × 7.31 A × 7.33 A having a slight monoclinic inclination relative to the base along a diagonal ($\beta$ is 92°30', not 90°). At the middle of each edge there is an Na atom, which along c are replaced in half the cases by OH or $OH_3$. This isometric framework is responsible for the lack of cleavage.

A silicon-oxygen radical of closed type lies within each (almost) cubic cell. It is a six-member ring of silica units $[Si_6O_{18}]$, (not a three-member ring, as in catapleiite and is of the type found in beryl and dioptase. The related Zr silicate elpidite has been supposed (but not shown) to contain a two-level trigonal ring (doubled catapleiite ring). This six-member ring may also be considered as being two catapleiite rings (the doubling causes the distance between the cation layers to rise to $1.5 \times 5 \approx 7.33$ A), but the rings are not closed, the two being related by a horizontal twofold axis on [010] (Fig. 12). This six-member ring may also be represented as two $Si_2O_7$ groups parallel to c and closed only by two Si tetrahedra (one above, one below). The pseudo-sixfold axis of the ring lies along $[\bar{2}01]$. The two such rings in the monoclinic cell are parallel and are related by the oblique translation in that cell.

The mineral is to be reckoned as unstable on account of this structure of the silicon-oxygen radical, in conjunction with the mobile Na polyhedra and heavy Zr nodes (which together give the structure little strength); it is readily destroyed by weathering. A useful measure of this lack of strength is its constant B = 1.75, which is very high for a silicate; this value shows that the thermal oscillations are large even at room temperature (other Zr silicates have $B \leq 1$) and that the structure is open and of intermediate type.

The radical has the formula $[Si_6O_{18}]$ found also for beryl and dioptase; in each of the six tetrahedra two oxygen corners are common to adjacent tetrahedra (the other two are connected to one Si atom only); but the rings in the two latter minerals are of high symmetry (6/m and $6^{\circ} = \bar{3}$), whereas the ring in lovozerite has only

---

*This 50% substitution of OH or $OH_3$ for Na causes R to fall by 1.5%.

a single twofold axis lying in its own plane. Each Si tetrahedron has only one of its O corners entering a Zr octahedron, so the formula for the mineral and the balance of the valences imply that one corner must be taken by an OH group; in all the ring contains six hydroxyl groups, which appear in the tetrahedra in very much the way for afwillite [26], pectolite [27], $Ca_2[SiO_3OH]OH$ [28], and epididymite [29]. The proper formula for the radical is $[Si_6O_{12}(OH)_6]$, which makes lovozerite the fifth silicate in which Si is joined, directly to hydroxyl. The number of groups in the radical may be reduced to five (randomly distributed over the six positions) if we assume that the groups replacing 50% of the Na atoms on the vertical edges are $OH_3$, rather than OH.

The R are very good, and so is the balance of the valences, in view of the unusual structure of the radical.

We saw above that the Na lie in figures with eight corners, but one O is further away from $Na_1$, and two from $Na_2$; it would be better to say that $\frac{1}{7}$ of the valence strength of $Na_1$ goes to each O($\frac{1}{6}$ for $Na_2$). For simplicity in the calculations we have taken the figure to be $\frac{1}{6}$ in both cases; in that case we get for each oxygen a sum differing from two (or one) by much less than 25% usually taken to be the limit permissible under Pauling's second rule. The deviation from balance is even less in every case (except for $O_{IX}$ and $O_X$, for which it becomes $^1/_{42}$) if we use $^1/_7$ instead of $^1/_6$. Three oxygen atoms ($O_{II}$, $O_V$, $O_{VI}$) are bonded to one Si only (are not bonded to Zr); the sum over the cations for each of them is about one, so they must be in OH groups.

Table 4 gives all the interatomic distances, which agree well with those found for other silicates.

The Zr octahedron has on its twofold axis three Zr-O distances, which are 2.05, 2.13, 2.16 A; now $Zr^{4+} + O^{2-} = 2.15$ A, so the edges of the octahedron are 2.79-3.26 A long.

The slight scatter about the means found for the Si tetrahedra (Si-O = 1.54-1.72 A and O-O = 2.50-2.78 A) are to be explained as caused by hydroxyl, even though the Si-OH distance is nearly equal to the Si-O one, as in afwillite and pectolite.

The two Na cations in the main part of the formula have seven neighbors at distances of 2.25-2.68 A and have eight at 3 A. Six Na-O distances for the additional Na are 2.34, 2.44, 2.65 A, with two further Na-O of 2.93 A.

An interesting point is that a slight deformation of (almost) cubic cell (to make it triclinic), if such as to join the free corners of the tetrahedra in one ring with similar corners in another, would make a chain of tetrahedra corresponding to the radical $[Si_6O_{15}]$ (here we have a possible model for dalyite $K_2ZrSi_6O_{15}$).

The closeness of the structure to cubic (especially to centrosymmetric) affects the $F^2$ syntheses very greatly; we have pointed out above how greatly the banding etc., hinder us in deducing the structure.

Lovozerite gives us another example of a mineral in which the directions of the principal refractive indices coincide with the diagonals of the x-ray cell (not with the axes). The identical array of Zr and Na atoms found along both diagonals of the (001) faces is responsible for making two refractive indices equal ($n_\gamma = 1.560$), the third being lower (on account of the weakening of the edges of the cube along c); the result is that the mineral was at first considered to be uniaxial, the symmetry being over-estimated as hexagonal or tetragonal.

## LITERATURE CITED

[1] V. I. Gerasimovskii, Doklady Akad. Nauk SSSR 25, 751 (1939).

[2] A. G. Betekhtin, Mineralogy [in Russian] (Moscow, 1950).

[3] M. D. Dorfman, Dissertation [in Russian] (1959).

[4] E. I. Semenov, Trudy Kol'sk. Fil. Akad. Nauk SSSR (1960).

[5] Kh. S. Mamedov and N. V. Belov, Doklady Akad. Nauk SSSR 106, No. 3 (1956).

[6] E. R. Howells, et al., Acta Cryst. 3, 210 (1950).

[7] G. A. Sim, Acta Cryst., 11, 123 (1958).

[8] M. J. Buerger, Acta Cryst., 4, 531 (1951).

[9] V. I. Simonov, Kristallografiya 4, No. 3 (1959).*

---

* [See Soviet Physics - Crystallography, vol. 4].

[10] I. M. Rumanova, Kristallografiya 3, No. 6 (1958).*

[11] W. H. Zachariasen, Acta Cryst. 5, 60 (1952).

[12] E. G. Fesenko, I. M. Rumanova, and N V. Belov, Kristallografiya 1, No. 2 (1956). **

[13] K. Robinson, Acta Cryst. 7, 494 (1954).

[14] P. G. Taylor and C. A. Beevers, Acta Cryst. 5, 341 (1952).

[15] J. A. Ibers, Acta Cryst. 9, 225 (1956).

[16] L Nitta, K. Sakurai, and Y. Tomiie, Acta. Cryst. 4, 289 (1951).

[17] A. E. Smith, Acta Cryst. 5, 224 (1952).

[18] S. v. Houten and E. H. Wiebenga, Acta Cryst. 10, 156 (1957).

[19] D. Harker, J. Chem. Phys. 4, 381 (1936).

[20] E. A. Glazunov and N. F. Chetverukhin, Axonometry [in Russian] (Moscow, 1953).

[21] V.V. Ilyukhin and S. V. Borisov, Strukt. Khim. 1, No. 1 (1960).

[22] A. J. C. Wilson, Nature 150, 152 (1942).

[23] B. K. Vainshtein, Zhur. Eksp i Teor. Fiz. 27, 44 (1954).

[24] A. D. Booth, Proc. Roy. Soc. A, 188, 77 (1946).

[25] B. K. Brunovskii, Acta Physicochem. USSR 5, 863 (1936).

[26] H. D. Megaw, Acta Cryst. 5, 477 (1952).

[27] M. J. Buerger, Z. Krist. 108, 248 (1956).

[28] L. Heller, Acta Cryst. 5 , 725 (1952).

[29] E. A. Pobedimskaya and N. V. Belov, Doklady Akad. Nauk SSSR 129, No. 4 (1959).