

CRYSTAL STRUCTURE OF EUDIALYTE

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Translated from *Kristallografiya*, Vol. 17, No. 6,

pp. 1119-1123, November-December, 1972

Original article submitted July 12, 1972

The structure determination is presented for eudialyte, a complex silicate of Zr, Fe, Ca, and Na. The structural details are considered. The results on the structure obtained previously [1] are compared with the independent ones published somewhat later by Italian workers [2].

Following the first communication on the structure of eudialyte [1], there appeared a paper by Italian workers [2], in which the same structural pattern was given. Differences arose only over particular details of the structure and over the symmetry group, i.e., the framework in which the structure is described. The center group $R\bar{3}m$ proposed by [2] was used in our work in the first stages of the interpretation, but the final refinement was performed in a framework having no center of symmetry, namely, $R3m$, one of the subgroups of the original $R\bar{3}m$. Our approach to the structural determination inevitably led in our case to abandonment of holohedry. The mineral varies widely in composition with the source deposit, and there is no single general chemical formula, which makes it difficult to perform the structural interpretation, and it is necessary to assume that there exist, if not varieties, at least subtypes in the chemical formula of this mineral on account of the variable part, namely, the side chain as Vernadskii terms it.

The x-ray symmetry group is $\bar{3}mR$, which combines the three space groups $R\bar{3}m$, $R3m$ and $R32$; tests were performed at the Physics Faculty at Moscow University for the piezoelectric effect in single crystals, but the result was negative and so enabled us in the early stages to assume the holohedral group $R\bar{3}m$, with the rhombohedral setting ($a_T = 12.955 \text{ \AA}$, $\alpha_T = 66^\circ 44'$), is characterized by general 12-fold positions, particular 6-fold positions on 2-fold axes and on nether planes, by two 3-fold complexes at centers of symmetry, by 2-fold ones on $\bar{3}$ axes, and finally by two single-fold (inversion-point) ones on $\bar{3}$ axes, where the horizontal 2-fold axes meet the meridional nether planes. The chemical analysis of the specimen and the density required the rhombohedral cell to contain 3 Zr atoms, 3 Fe atoms (apart from an error due to a small amount of isomorphous components), 6 Ca atoms, 25 Si atoms, about 14 Na atoms, and about 80 anions, as well as small amounts of potassium and chlorine.

We deduced the coordinates of the heavy Zr, Fe, and Ca in the special positions in group $R\bar{3}m$ by anal-

ysis of the 3-dimensional Patterson function and elementary combination considerations; these coordinates were the point of departure in constructing the first electron-density distribution. This and the subsequent electron-density syntheses enabled us to construct a model for the structure. The usual refinement process reduced R only to 20%, and attempts to improve the model within the framework of the centered group $R\bar{3}m$ were without success.

A detailed examination of the electron-density syntheses revealed specific features in some of the peaks. Some peaks were elongated almost to the point where they were resolved into two peaks of approximately equal weight in the m planes, which indicated that the model was of excessively high symmetry, and at this stage we reconsidered the question of the space group. We did not employ statistical tests for a center of symmetry, because many of the atoms, in particular the heaviest ones, have special positions in the cell. To find the true symmetry we used superposition syntheses.

The basis for using these to revise the symmetry and also the structure model is that first of all one takes into account the minimal (obligatory) symmetry of the structure; within this group one defines the position of the heaviest atoms and constructs the minimization function via the corresponding interatomic vectors. The atomic configuration used in constructing this function is present in the structure without any relation to the actual symmetry. The resulting function produces an image of a structure, which is then refined by successive Fourier transformation and calculation of superposition syntheses [3, 4]. Consideration of the final superposition synthesis establishes whether particular symmetry elements are present or absent.

The mineral has three conceivable symmetry groups, $R\bar{3}m$, $R3m$, and $R32$, which include the $R3$ subgroup. This is the obligatory symmetry as given by the vectors between the Zr, Fe, and Ca atoms in conjunction with one of the most reliably established Si atoms, which gave a minimization function of rank 12.

TABLE 1. Coordinates of the Basis Atoms in Eudialyte (hexagonal setting)

Atom		Symmetry group $R\bar{3}m$			Symmetry group $R\bar{3}m$ [2]						
symbol and multiplicity	symbol and multiplicity in [2]	x/a	y/b	z/c	x/a	y/b	z/c				
Zr(9)	Zr ₁ (9)	0.001	0.500	0.4991	0	0.5	0.5				
Fe(9)	Fe(9)	0.988	0.494	0.0017	0	0.5	0				
Si ₁ (9)	Si ₃ (18)	-0.069	0.069	0.0809	0.0698	-0.0698	0.9168				
Si ₂ (9)		0.071	-0.071	0.9155							
Si ₃ (9)	Si ₂ (18)	-0.124	0.124	0.4071	0.1239	-0.1239	0.5926				
Si ₄ (9)		0.125	-0.125	0.5920							
Si ₅ (18)	Si ₁ (36)	0.338	0.275	0.5687	0.3392	0.2752	0.5703				
Si ₆ (18)		-0.339	-0.277	0.4593							
Ca(18)	Ca(18)	-0.072	0.330	0.3309	-0.0733	0.3333	0.3333				
Na ₁ (9)	Na ₁ (18)	0.247	-0.247	0.4652	0.2317	-0.2317	0.5078				
Na ₂ (9)		-0.223	0.223	0.4885							
Na ₃ (9)	Na ₂ (18)	0.114	-0.114	0.7203	-0.106	0.106	0.2836				
Na ₄ (9)		-0.098	0.098	0.2852							
O ₁ (9)	O ₇ (18)	-0.272	0.272	0.4091	0.2719	-0.2719	0.5896				
O ₂ (9)		0.270	-0.270	0.5862							
O ₃ (9)	O ₆ (18)	-0.099	0.099	0.1285	0.093	-0.093	0.8671				
O ₄ (9)		0.096	-0.096	0.8662							
O ₅ (9)	O ₅ (18)	-0.223	0.223	0.2839	0.2186	-0.2186	0.7116				
O ₆ (9)		0.217	-0.217	0.7125							
O ₇ (18)	O ₁ (36)	0.291	0.367	0.3772	0.2875	0.3661	0.3777				
O ₈ (18)		-0.278	-0.358	0.6194							
O ₉ (18)	O ₃ (36)	-0.049	-0.277	0.4392	0.0513	0.2824	0.5609				
O ₁₀ (18)		0.053	0.289	0.5601							
O ₁₁ (9)	O ₄ (18)	0.163	-0.163	0.4487	-0.1574	0.1574	0.5530				
O ₁₂ (9)		-0.154	0.154	0.5484							
O ₁₃ (18)	O ₂ (36)	0.437	0.373	0.5436	0.4351	0.3672	0.5418				
O ₁₄ (18)		-0.435	-0.365	0.4571							
O ₁₅ (9)	O ₆ (18)	0.154	-0.154	0.6364	0.1531	-0.1531	0.6401				
O ₁₆ (9)		-0.153	0.153	0.3611							
O ₁₇ (9)	O ₅ (18)	-0.059	0.059	0.3973	0.0600	-0.0600	0.5964				
O ₁₈ (9)		0.062	-0.062	0.5888							
0.5Si ₁₇ (3)	0.36Zr ₂ (3)	0	0	0.4177	0	0	0.6231				
0.5Si ₁₈ (3)		0	0	0.5799							
0.5OH ₁ (3)		0	0	0.5227							
0.5OH ₂ (3)		0	0	0.4724							
(OH) ₃ (3)		0	0	0.7492							
0.5Cl(3)		0.63Cl(3)	0	0				0.2315	0	0	0.2374
			0	0				0			

The Fourier transform of this allowed us to construct a superposition synthesis that contained most of the atoms in the structure and decided the question of the symmetry. This synthesis clearly revealed a nether plane and also deviation from 2-fold symmetry. This result is to be compared with the above features of the electron-density synthesis made within the framework of group $R\bar{3}m$, which gave the unambiguous conclusion that there was no 2-fold rotation in axes and no center of symmetry, i.e., the space group was unambiguously $R\bar{3}m$. Note that the pseudosymmetry $R\bar{3}m$ was retained to a large extent. Most of the atoms in the structure are placed in a centrosymmetric fashion, but there is also substantial deviations. Table 1 gives the final coordinates of the basis atoms. For convenience, the adjacent columns give the atoms related by the pseudo-center of symmetry. The coordinates of the Na atoms deviate substantially from centrosymmetric, since they lie in a mirror plane. The final coordinates were obtained by refining the model by least squares within the framework of group $R\bar{3}m$ via 783 independent non-zero structure factors. We used a common isotropic temperature parameter $B = 0.54 \text{ \AA}^{-2}$, which gave $R =$

10.9%. Table 2 gives the cation-anion distances in the principal polyhedra. These distances do not lie outside the usually accepted limits. Our results in Table 1 are given together with values converted to a common origin for the basis atoms as given in [2].

The framework has the composition $\text{Na}_{12}\text{Ca}_6\text{Fe}_3\text{Zr}_3[\text{Si}_3\text{O}_9]_2[\text{Si}_9\text{O}_{24}(\text{OH})_3]_2$, which is practically the same in [1] and [2]. The discrepancies occur in the population of zeolite-type cavities that extend along the 3-fold axis; moreover, electron-density syntheses were similar in the two cases as regards number, disposition, and height of the peaks, and agreed closely in a narrow region directly around the 3-fold axis. The difference in the interpretation arose on account of differences in the processing of the chemical analysis results. The Italian workers [2] converted the analyses to the content of the rhombohedral cell on the basis that the cell contained 24 silicon atoms. The six different analyses that they considered were transformed to the rhombohedral cell on that basis; the lack of care in this approach is demonstrated by the values given in that paper [2] for the observed and calculated densities. A cursory glance at the last two columns in Table 7 from [2] shows

TABLE 2. Basic Interatomic Distances (Å) in Eudialyte

Zr-octahedron		Ca-octahedron		Fe-polyhedron			
Zr—O ₄	2.00	Ca—O ₅	2.31	Fe—O ₈	1.98		
Zr—O ₃	2.03	Ca—O ₁₅	2.38	Fe—O ₈ *	1.98		
Zr—O ₁₃	2.03	Ca—O ₇	2.38	Fe—O ₇	2.14		
Zr—O ₁₃ *	2.03	Ca—O ₆	2.39	Fe—O ₇ *	2.14		
Zr—O ₁₄	2.13	Ca—O ₁₆	2.42				
Zr—O ₁₄ *	2.13	Ca—O ₈	2.43				
Si ₁ -tetrahedron		Si ₂ -tetrahedron		Si ₃ -tetrahedron		Si ₄ -tetrahedron	
Si ₁ —O ₈	1.57	Si ₂ —O ₅	1.54	Si ₃ —O ₁₆	1.57	Si ₄ —O ₁₅	1.53
Si ₁ —O ₃	1.61	Si ₂ —O ₄	1.62	Si ₃ —O ₁₇	1.64	Si ₄ —O ₁₈	1.55
Si ₁ —O ₁	1.64	Si ₂ —O ₂	1.67	Si ₃ —O ₉	1.64	Si ₄ —O ₁₀	1.70
Si ₁ —O ₁ *	1.64	Si ₂ —O ₃ *	1.67	Si ₃ —O ₆ *	1.64	Si ₄ —O ₁₀ *	1.70
Si ₅ -tetrahedron		Si ₆ -tetrahedron		Si ₇ -tetrahedron		Si ₈ -tetrahedron	
Si ₅ —O ₈	1.55	Si ₆ —O ₇	1.61	Si ₇ —(OH) ₂	1.65	Si ₈ —(OH) ₁	1.72
Si ₅ —O ₁₀	1.59	Si ₆ —O ₉	1.63	Si ₇ —O ₁₇ (OH)	1.58	Si ₈ —O ₁₈ (OH)	1.57
Si ₅ —O ₁₃	1.60	Si ₆ —O ₁₄	1.57	Si ₇ —O ₁₇ *(OH)	1.58	Si ₈ —O ₁₅ *(OH)	1.57
Si ₅ —O ₁₂	1.68	Si ₆ —O ₁₁	1.64	Si ₇ —O ₁₇ *(OH)	1.58	Si ₈ —O ₁₆ *(OH)	1.57
Na ₁ -polyhedron		Na ₂ -polyhedron		Na ₃ -polyhedron		Na ₄ -polyhedron	
Na ₁ —O ₄	2.50	Na ₂ —O ₁₂	2.49	Na ₃ —O ₇	2.49	Na ₄ —O ₁₆	2.66
Na ₁ —O ₄ *	2.50	Na ₂ —O ₁	2.68	Na ₃ —O ₇ *	2.49	Na ₄ —O ₃	2.70
Na ₁ —O ₁₁	2.55	Na ₂ —O ₃	2.72	Na ₃ —O ₆	2.56	Na ₄ —O ₃ *	2.70
Na ₁ —O ₁₄	2.56	Na ₂ —O ₃ *	2.72	Na ₃ —O ₁₁	2.58	Na ₄ —O ₁₃	2.79
Na ₁ —O ₁₄ *	2.56	Na ₂ —O ₁₃	2.77	Na ₃ —O ₁₄ *	2.58	Na ₄ —O ₁₃ *	2.79
Na ₁ —O ₂	2.71	Na ₂ —O ₁₃ *	2.77	Na ₃ —O ₁₅	2.71	Na ₄ —O ₅	3.11
Na ₁ —(OH) ₃	3.29	Na ₂ —O ₉	2.87	Na ₃ —(OH) ₃	2.97	Na ₄ —Cl	2.91
		Na ₂ —O ₉ *	2.87				

Asterisks denote atoms related by symmetry to the basal ones.

that the calculated density in all six cases was substantially less than the observed density. The chemical analysis of the specimen examined in [2] was converted by the Italian workers on the basis of 24 silicon atoms in the unit cell, which led to a computed density of 2.76 g/cm², while the observed density was 2.90. Observed density requires the contents of the cell to be increased by 5% and in particular gives an additional Si atom.

We use crystals kindly provided by M. D. Dorfman for which the content of the cell was determined via Z. M. Goroshchenko's chemical analysis, with an observed density of 2.87 and a volume of 1760 Å³ for the rhombohedral cell (Table 3). This gave 25 silicon atoms in the rhombohedral cell, not the 24 assumed in [2]. Our conclusion agrees with that due to Borneman-Starynkevich, which she drew on the basis of numerous chemical analyses of the mineral.

The additional Si atom can be based only on the 3-fold axes. Each of the 9-fold silicon-oxygen rings consists of three [Si₂O₇] groups and three [SiO₄] orthotetrahedra that combine these into a ring. These tetrahedra are slightly rotated around one edge (Figs. 1 and 2 in [1]), and they form a triangular area, the base for the additional cations in the side chains, which are located on the 3-fold axis. These varying inclinations enable one to adapt this fragment to accommodate cations of different sizes. In our case, the edges of the oxygen triangles in two of the 9-fold rings were 2.53 and 2.67 Å, respectively, while the distances of the cations from these oxygen atoms were 1.58 and 1.57 Å. These distances were increased to 1.685 Å in [2], while the neglected 25th Si atoms was replaced by Zr, which filled its position with a probability of 36% ($Z_{\text{eff}} = 40 \times 0.36 \approx 14$). The square coordination of the Fe atoms sur-

TABLE 3. Goroshchenko's Analysis and Cation Contents for the Rhombohedral Cell of Eudialyte

Oxide	wt. %	Content	Oxide	wt. %	Content
SiO ₂	59.14	25.22	MnO	0.60	0.26
TiO ₂	0.46	0.18	CaO	11.18	5.18
ZrO ₂	11.83	2.94	SrO	0.47	0.14
Nb ₂ O ₅	0.11	0.02	Na ₂ O	14.06	13.89
Al ₂ O ₃	0.07	0.04	K ₂ O	1.39	0.90
Fe ₂ O ₃	0.50	0.19	H ₂ O ⁻	0.12	4.05
TR ₂ O ₃	0.37	0.12	H ₂ O ⁺	1.07	4.05
FeO	5.32	2.27	S	0.04	0.04
MgO	0.24	0.18	Cl	1.82	1.64

prised us somewhat, but it was completely confirmed by the results of [2].

Borneman-Starynkevich concluded that the ratio of the cations to the silicone was variable in this mineral on the basis of numerous chemical analyses, and it is confirmed by the structural results. The minimum number of Si atoms in the rhombohedral cell is 24: There are two 3-fold and two 9-fold silicon oxygen rings. The mechanism that brings three oxygen atoms from the orthotetrahedra together enables one to assume that the middle part of the 9-fold rings contains the additional Si atom; then the [Si₉O₂₇] ring is transformed into a radical [Si₁₀O₂₈] of the type of a rounded platform. We get the maximum number of Si atoms in the mineral when we completely replace the 9-fold rings by platforms; the rhombohedral cell then contains 26 silicon atoms. Our specimen in this sense was intermediate, as it had 25 Si atoms in the cell. The heights of the peaks in the electron-density distributions and the low value for R makes it reasonable to say that the first and second types of radical are equally probable in our specimen.

The band of zeolite-type poles along the 3-fold axis passes through twelve layers of 6-fold rings of Ca octahedra. Within each such ring, which is covered above and below by $[\text{Si}_3\text{O}_9]$ radicals, there is a convenient place for the additional large cations, especially potassium. Another type of blockage in the elongated cavities is provided by the additional Si tetrahedra in the silicon-

oxygen radicals of platform type. Between these lie the additional anions, namely, $\text{Cl}(\text{OH})$ and also the Na cations, the latter being randomly distributed over the free chambers in the mineral.

We are indebted to the Italian workers for providing an offprint of their paper on the mineral.

LITERATURE CITED

1. V. M. Golyshev, V. I. Simonov, and N. V. Belov, *Kristallografiya*, 16, 93 (1971) [*Sov. Phys. - Crystallogr.*, 16, 70 (1971)].
2. G. Giuseppetti, F. Mazzi, and Carlo Tadini, *Tschermaks, Min. Petr. Mitt.*, 16, 105 (1971).
3. V. I. Simonov, *Acta Crystallogr.*, B25, No. 1, 1 (1969).
4. A. B. Tovbis and V. I. Simonov, *Kristallografiya*, 16, 1131 (1971) [*Sov. Phys. - Crystallogr.*, 16, 994 (1972)].