The Crystal Structure of Elpidite

Elio Cannillo, Giuseppe Rossi, and Luciano Ungaretti

C.N.R. Centro di studio per la cristallografia strutturale, Istituto di Mineralogia dell'Università, via Bassi 16, 27100 Pavia, Italy.

Abstract

The crystal structure of elpidite $Na_2ZrSi_6O_{15}\cdot 3H_2O$, $a = 7.14(2)$, $b = 14.68(1)$, $c = 14.65(1)$ Å, space group $Pbcm$, $Z = 4$, has been redetermined and found to agree essentially with that determined by Neronova and Belov. It consists of a framework formed by chains of Si-tetrahedra resembling epididymite connected by Zr-octahedra; the anion framework is saturated by sodium atoms. The most significant differences with respect to the structure analysis of Neronova and Belov are the doubling of the cell parameter b, the centric space group, and the improved accuracy of the atomic parameters. The refined structure, using Weissenberg data, yielded a final R index of 0.07.

Introduction

The crystal structure of elpidite $Na_2ZrSi_6O_{15}\cdot 3H_2O$ was solved by Neronova and Belov (1963) and described in the centrosymmetric space group $Pmcm$.[1] In a later paper, the same authors (1964) lowered the symmetry to $P2cm$ in order to explain certain features of the electron density map. The least squares refinement carried out on the basis of this latter space group led to a final discrepancy factor of 0.21. It was impossible for the Russian authors to obtain a more satisfactory R factor and accurate values of interatomic distances using the imperfect, twinned crystals from Lovozero, Kola Peninsula, U.S.S.R. Elpidite was recently found in silicate veins and vugs of the nepheline syenite of Mt. St. Hilaire (Quebec, Canada) and described by Chao (1967), who reported the following lattice parameters: $a = 7.14$, $b = 14.68$, $c = 14.58$ Å; the b cell parameter is twice the value of Russian elpidite. The availability of perfect single crystals of elpidite from Mt. St. Hilaire suggested a revision of the crystal structure of this mineral.

Experimental

A long prismatic crystal (cross section 0.05×0.08 mm) was used for the collection of the X-ray diffraction data. In-tegrated equi-inclination Weissenberg photographs (rotation axis a) of seven reciprocal lattice layers were taken with Ni filtered CuKα radiation, using the multiple film technique. A total of 1501 hkl reflections or 82 percent of the 1832 present in the CuKα limiting sphere were inspected. The reflections with $k = 2n + 1$ are very weak, so only 119 of the 748 inspected were measured, the remainder being too faint for accurate measurement. For reflections with $k = 2n$, 753 were measured and 166 were considered as unobserved. The intensities were corrected for the Lorentz-polarization and absorption factors and for incipient but incomplete α_1-α_2 spot doubling. The absorption factors were obtained through the formulas given by Cannillo and Mazzi (1967) and ranged from 1.56 to 2.49 ($\mu = 120$ cm^{-1}).

The cell parameters, as redetermined through oscillation and Weissenberg photographs, are: $a = 7.14(2)$, $b = 14.68(1)$, $c = 14.65(1)$ Å, in good agreement with those given by Chao. The space group is $Pbcm$, $Z = 4$.

Crystal Structure Analysis

The first step of the structure analysis was a check of the correctness of the structural model proposed by Neronova and Belov. At this stage only the reflexions with $k = 2n$ were considered and the problem of the true structure (with $b = 14.68$ Å) was delayed to a later step. Two cycles of full matrix least squares were carried out using the positional parameters given by the Russian authors, referred to the centric space group $Pmcm$. After two cycles the R factor dropped to 0.096, confirming the essential structural features of this mineral. An attempt to determine the true structure of elpidite in

---

[1] Here and elsewhere in the text the settings of crystallographic axes used by various authors are changed in order to obtain the orientation used in this paper; this orientation is consistent with the standard setting of the International Tables of X-ray Crystallography.

the space group *Pbcm* with $b = 14.68$ Å through the examination of the Patterson synthesis proved unsuccessful. On the other hand, the trend showed by the reflections with $k = 2n + 1$, for which the strongest intensities occur at high angles, and the features of the Patterson synthesis suggested that the doubling of the b cell parameter originated from small shifts of all the atoms rather than from ordering of cations or vacancies.

The structure was solved through the application of direct methods. As the normalized structure factor E's of reflections with $k = 2n + 1$ had very low values, they did not contribute to the determination of signs by the application of Sayre's equations. The reflections were therefore divided in two sets: one including the reflections with $k = 2n$ and the other those with $k = 2n + 1$. The normalized structure factors of the latter set were multiplied by a factor which satisfied the condition that $E^2 = 1.0$. In this way the normalized structure factors of the two sets entered Sayre's equations with the same weight.

The sign determination was carried out using the program written by R. E. Long (1965). The set of signs with the highest consistency, containing 183 E's of $k = 2n$ reflections and 22 E's of $k = 2n + 1$ reflections, was used to compute a three-dimensional E map in space group *Pbcm*. This map gave the coordinates of all the atoms consistent with the crystal structure determined by Neronova and Belov, but deviated from the *Pmcm* symmetry in such a

TABLE 3. INTERATOMIC DISTANCES AND TETRAHEDRAL BOND ANGLES FOR ELPIDITE.*

Si(1)-O(1)	1.63(2) Å	Si(3)-O(1)	1.58(2) Å	Na(2)-O(3)	**2.52(2) Å
	O(2) 1.64(2)		O(7) 1.61(1)		O(9) **2.58(2)
	O(3) 1.57(2)		O(8) 1.66(1)		W(1) **2.34(1)
	O(4) 1.60(2)		O(9) 1.61(2)		
				Zr -O(3)	**2.09(2)
					O(6) **2.07(1)
Si(2)-O(4)	1.65(2)	Na(1)-O(2)	2.70(2)		O(9) **2.08(2)
	O(5) 1.63(1)		O(5) 2.42(2)		
	O(6) 1.57(1)		O(6) **2.73(1)	W(1) -W(2)	**2.84(2)
	O(7) 1.66(2)		O(8) 2.40(2)		O(7) 2.92(2)
			O(9) **2.91(2)	W(2) -O(8)	2.99(3)
			W(2) 2.31(3)		

O(1)Si(1)O(2)	110.4(9)°	O(4)Si(2)O(5)	108.1(9)°	O(1)Si(3)O(7)	105.7(8)°
	O(3) 111.7(8)		O(6) 112.0(6)		O(8) 111.0(9)
	O(4) 104.2(8)		O(7) 108.8(6)		O(9) 113.3(8)
O(2)Si(1)O(3)	109.0(10)	O(5)Si(2)O(6)	107.5(6)	O(7)Si(3)O(8)	106.1(9)
	O(4) 107.8(11)		O(7) 107.1(9)		O(9) 112.1(8)
O(3)Si(1)O(4)	113.4(9)	O(6)Si(2)O(7)	113.0(8)	O(8)Si(3)O(9)	108.4(10)
Si(1)O(1)Si(3)	162.5(8)	Si(1)O(4)Si(2)	146.5(12)	Si(2)O(7)Si(3)	133.8(9)
Si(1)O(2)Si(1)	136.0(14)	Si(2)O(5)Si(2)	153.4(11)	Si(3)O(8)Si(3)	140.7(14)

*Estimated standard deviations are given in parentheses to immediate right of interatomic distance or bond angle.
**The distance occurs twice.

way as to justify the very weak reflections with $k = 2n + 1$. Three least squares cycles with isotropic temperature factors for all the atoms lowered the R factor to 0.083. A subsequent cycle with anisotropic temperature factors was unsatisfactory, probably because of the small number of measured reflections with $k = 2n + 1$. Thus only Zr was treated anisotropically and the final discrepancy factor was 0.07 for the 706 observed reflections. A secondary extinction correction ($g = 2.12 \times 10^{-6}$) was introduced in the final least squares cycle (Zachariasen, 1963). A modified version of the program ORFLS (Busing *et al.*, 1962) was utilized for the least squares refinement using the atomic scattering factors for neutral atoms given by Hanson *et al.*, (1964). The scattering factor of Z_r was corrected for anomalous dispersion according to Cromer and Liberman (1970).

Final atomic coordinates and thermal parameters are given in Table 1. The final observed and calculated structure factors are compared in Table 2.[1] Bond distances and angles as well as their standard deviations are given in Table 3.

Description and Discussion of the Structure

As pointed out by Neronova and Belov, the characteristic feature of the crystal structure of elpidite

TABLE 1. ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS FOR ELPIDITE.*

Atom	x/a	y/b	z/c	B(Å²)
Zr	0.4950(5)	0.2500	0.5000	0.40[a]
Si(1)	.7720(10)	.3854(4)	.6462(4)	0.40(12)
Si(2)	.5086(10)	.0476(2)	.6613(2)	0.51(7)
Si(3)	.2170(10)	.3928(4)	.6435(4)	0.49(12)
O(1)	.9966(26)	.4047(7)	.6392(7)	1.46(20)
O(2)	.7156(32)	.3538(14)	.7500	1.33(40)
O(3)	.7077(23)	.3099(13)	.5772(14)	1.38(36)
O(4)	.6781(21)	.4825(11)	.6277(12)	1.53(32)
O(5)	.5285(31)	.0713(10)	.7500	0.93(27)
O(6)	.4904(26)	.1405(7)	.5886(7)	1.20(18)
O(7)	.3029(19)	.4888(9)	.6119(9)	0.51(26)
O(8)	.2881(29)	.3770(13)	.7500	0.79(34)
O(9)	.2928(20)	.3097(11)	.5823(12)	0.80(31)
Na(1)	.4362(17)	.2299(8)	.7500	2.07(25)
Na(2)	-0.0027(23)	.2500	.5000	2.02(28)
W(1)	.0104(28)	.1130(9)	.5810(9)	2.61(25)
W(2)	.1233(38)	.1895(17)	.7500	3.04(46)

[a] Zr was treated anisotropically in the refinement. The β_{ij} values in the expression $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ are: $\beta_{11} = 0.0029(8)$, $\beta_{22} = 0.0002(1)$, $\beta_{33} = 0.0005(1)$, $\beta_{12} = \beta_{13} = 0.0$, $\beta_{23} = -0.0001(1)$. The value listed in this Table corresponds to the equivalent isotropic temperature factor (Hamilton, 1959).

*Estimated standard deviations (esd) are enclosed in parentheses and refer to the last decimal place cited. For example, 0.4950(5) indicates an esd of 0.0005 whereas 0.7720(10) indicates an esd of 0.0010.

is the presence of double chains of tetrahedra of the epididymite type (Robinson and Fang, 1970) connected by Zr atoms in octahedral coordination. The silicate chains and Zr octahedra form an anionic framework saturated by sodium atoms (Figs. 1 and 2). The double chains of tetrahedra are parallel to [100], the elongation axis of the crystals.

Comparison of the double chains of epididymite and elpidite is of interest. In epididymite the differences in bond lengths of Si with bridging and non-bridging oxygens are rather sizeable for the three independent tetrahedra, whereas in elpidite the rule is well respected for Si(1) and Si(2) but the Si(3)–O(1) distance of 1.58 Å is shorter than the silicon non-bridging oxygen distance of the same tetrahedron. However, it should be noted that O(1) is involved in a large Si–O–Si angle which justifies the short Si(3)–O(1) bond. The Si–O–Si angles in epididymite range from 139° to 152° whereas in elpidite the extreme values are 134° and 163°. In general, the silicate chain of epididymite seems to be more "regular" than that of elpidite. Both minerals possess a pseudo-mirror plane normal to the chain direction. In elpidite the oxygens form nearly perfect octahedra around Zr.

Two independent sodium atoms are present in the

FIG. 2. The crystal structure of elpidite projected on (001). The projection plane has been slightly rotated about [001] in order to avoid superposition of the tetrahedra.

crystal structure of elpidite. Na(2) has an octahedral coordination formed by four oxygens of the tetrahedra and two symmetrically equivalent water molecules W(1). The octahedra around Na(2) and Zr form a column running parallel to [100]. The other

FIG. 1. Partial projection along [010] with +b down, showing the epididymite-like chains in elpidite together with Zr and Na(2) which form chains of octahedra parallel to a. The y coordinates range from about ¼ to ¾. Na(1) and the water molecules are omitted for clarity.
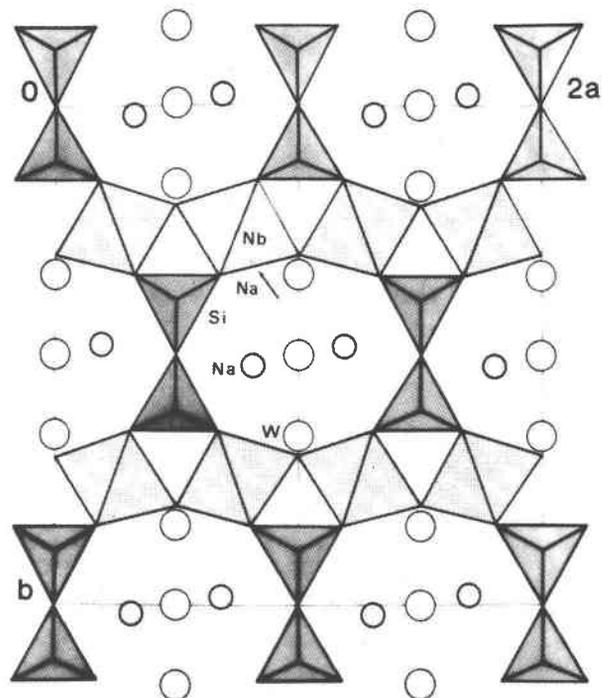
FIG. 3. Schematic partial projection of the crystal structure of nenadkevichite along [001] with +c down. The tetrahedra form four-membered rings through a mirror plane parallel to (001).

sodium atom, Na(1), occurs in a cavity formed by adjacent double chains of tetrahedra. It is bonded to seven oxygens and water molecule W(2) with distances ranging from 2.31 to 2.91 Å. Na(1) and the water molecule bonded to it are the atoms with the greatest deviation from symmetry *Pmcm*.

If the tetrahedral chains in elpidite are visualized as rings of four tetrahedra connected together by Si_2O_7 groups, an interesting comparison can be made with the crystal structure of nenadkevichite (Perrault *et al.*, 1972). The chemical formula of this mineral is $Na_2(Nb, Ti)_2(O, OH)_2Si_4O_{12} \cdot 4H_2O$ and its lattice parameters are very close to those of elpidite ($a = 7.42$, $b = 14.20$, $c = 7.15$ Å; space group *Pbam*). The main structural feature of nenadkevichite, like that of elpidite, is an anion framework formed by Si-tetrahedra and Nb octahedra saturated by Na atoms. The nenadkevichite framework is derived from that of elpidite by eliminating the Si(2) and O(5) atoms and by doubling the number of octahedra (compare Fig. 2 and Fig. 3). The additional octahedron found in nenadkevichite restores the missing connections resulting from the elimination of the two Si atoms. Two peculiar features of the nenadkevichite structure are the zig-zag columns of Nb octahedra parallel to [100] and the slightly different disposition of the non-octahedral sodium atoms occupying the cavity caused by the absence of the Si_2O_7 groups.

Acknowledgments

References

BUSING, W. R., K. O. MARTIN, AND H. A. LEVY (1962) ORFLS, a Fortran crystallographic least-squares program. *U. S. Nat. Tech. Inform. Serv.* **ORNL-TM-305.**

CANNILLO, E., AND F. MAZZI (1967) Absorption correction for some elongated prismatic crystals. *R. Acc. Naz. Linc.* **42,** 888–893.

CHAO, G. Y. (1967) Leucophanite, elpidite and narsarsukite from the Desourdy Quarry, Mont St. Hilaire, Quebec [abst.]. *Can. Mineral.* **9,** 286.

CROMER, D. T., AND D. LIBERMAN (1970) Relativistic calculation of anomalous scattering factors for X-rays. *J. Chem. Phys.* **53,** 1891–1896.

HAMILTON, W. C. (1959) On the isotropic temperature factor equivalent to a given anisotropic temperature factor. *Acta Crystallogr.* **12,** 609–610.

HANSON, H. P., F. HERMAN, J. D. LEA, AND S. SKILMANN (1964) HFS atomic scattering factors. *Acta Crystallogr.* **17,** 1040–1044.

LONG, R. E. (1965) *The Crystal and Molecular Structure of Cyclopropanecarboxamide.* Ph.D. Thesis, University of California, Los Angeles.

NERONOVA, N. N., AND N. V. BELOV (1963) The crystal structure of elpidite. Dimorphism of dimetasilicate radicals. [In Russian]. *Dokl. Acad. Nauk SSSR.* **150,** 3.

——— (1964) Crystal structure of elpidite. [In Russian]. *Kristallografiya.* **9,** 828–834. [Transl. *Sov. Phys. Crystallogr.* **9,** 700–705].

PERRAULT, G., C. BOUCHER, J. VIGAT, E. CANNILLO, AND G. ROSSI (1972) La structure cristalline de la nenadkevichite (in press).

ROBINSON, P. D., AND J. H. FANG (1970) The crystal structure of epididymite. *Amer. Mineral.* **55,** 1541–1549.

ZACHARIASEN, W. H. (1963) The secondary extinction correction. *Acta Crystallogr.* **16,** 1139–1144.