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MINERALOGICAL CRYSTALLOGRAPHY

The Crystal Structure of Alumoklyuchevskite, $K_3Cu_3AlO_2(SO_4)_4$

S. V. Krivovichev, S. K. Filatov, and P. N. Cherepansky
St. Petersburg State University, Universitetskaya nab. 7/9, St. Petersburg, 199034 Russia

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Abstract—The crystal structure of the unstable mineral alumoklyuchevskite $K_3Cu_3AlO_2(SO_4)_4$ [monoclinic, $I2$, $a = 18.772(7)$, $b = 4.967(2)$, $c = 18.468(7)$ Å, $\beta = 101.66(1)°$, $V = 1686(1)$ Å] was refined to $R_1 = 0.131$ for 2450 unique reflections with $F \geq 4\sigma F_{\rm hkl}$. The structure is based on oxocentered tetrahedrons ($\rm OAlCu_3^{7+}$) linked into chains via edges. Each chain is surrounded by SO_4 tetrahedrons forming a structural complex. Each complex is elongated along the *b* axis. This type of crystal structure was also found in other fumarole minerals of the Great Tolbachik Fissure Eruption (GTFE, Kamchatka Peninsula, Russia, 1975–1976), klyuchevskite, $K_3Cu_3Fe^{3+}O_2(SO_4)_4$; and piypite, $K_2Cu_2O(SO_4)_2$.

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INTRODUCTION

Alumoklyuchevskite, $K_3Cu_3AlO_2(SO_4)_4$, described for the first time by Gorskaya et al. (1995), is an aluminum analogue of klyuchevskite, $K_3Cu_3Fe^{3+}O_2(SO_4)_4$ (Vergasova et al., 1989). Klyuchevskite and alumoklyuchevskite are minerals of volcanic exhalations from the second cinder cone of the Great Tolbachik Fissure Eruption (GTFE, Kamchatka Peninsula, Russia, 1975–1976).

Alumoklychevskite occurs as dark green small prismatic crystals up to 1 mm long and less than 0.1 mm wide. In a natural environment, the mineral was found as aggregates along with fedotovite, $K_2Cu_3O(SO_4)_3$; tenorite CuO, langbeinite $K_2Mg_2(SO_4)$; and lammerite, $Cu_3[(As,P)O_4]_2$.

In its behavior, alumoklyuchevskite is very similar to klyuchevskite; both minerals are extremely unstable in air. For example, the crystals of alumoklyuchevskite are covered by a white coating after remaining in air for a week, probably owing to hydration (Gorskaya et al., 1995), and this extremely hampers its examination.

EXPERIMENTAL

An X-ray single-crystal study of alumoklyuchevskite was carried out on a Bruker SMART APEX CCD system at the Laboratory of Environmental Mineralogy and Crystal Structures, Notre Dame University, Indiana, United States. The set of intensities was recorded for about 24 h, and the crystal was partially hydrated over this time. The unit-cell dimensions were refined by the least-squares method on the basis of 432 unique reflections. Absorption correction was introduced with approximation of the crystal morphology by ellipsoid. The intensities were processed and structural factors were calculated with the SAINT program. The structure was refined by direct methods in space group $I2$ on the basis of 1292 unique reflections with $|F_0| \geq 4\sigma_F$ to a convergence factor of $R_1 = 0.13$. The crystal chemical data on alumoklyuchevskite and refined structural parameters are given in Table 1; atomic coordinates and isotropic displacement parameters, in Table 2; and selected bond lengths, in Table 3.

CRYSTAL STRUCTURE

Coordination polyhedrons and their interrelations.

The Cu, Al, and S coordination polyhedrons are shown in Fig. 1. Each of four S atoms in the structure of alumoklyuchevskite is surrounded by four O atoms located in the apexes of the tetrahedron. The average bond lengths in the SO_4^{2-} tetrahedron are as follows, Å: 1.47 ⟨S(1)–O⟩, 1.47 ⟨S(2)–O⟩, 1.45 ⟨S(3)–O⟩, 1.46 ⟨S(4)–O⟩ (Table 3).

There are three independent Cu^{2+} atoms in the structure. In all Cu(1)–Cu(3) polyhedrons, four short equatorial Cu–O bonds are recognized; their average values are, Å: 1.99 ⟨Cu(1)–O⟩, 1.95 ⟨Cu(2)–O⟩, and 1.96 ⟨Cu(3)–O⟩. The fifth bond is significantly longer, Å: 2.52 Cu(1)–O, 2.57 Cu(2)–O, and 2.60 Cu(3)–O (Table 3). The sixth bond is 0.5 Å longer than fifth for Cu(1) and Cu(3); therefore, these polyhedrons can be considered fivefold (Fig. 1). The sixth bond for Cu(2) is only 0.2 Å longer than the fifth bond, and therefore, Cu(2) polyhedrons can be considered a strongly distorted octahedron (Fig. 1).

An A1 atom has a much more regular octahedral coordination with an average ⟨Al–O⟩ bond length of 1.96 Å (Fig. 3).

Corresponding author: S.V. Krivovichev. E-mail: skrivovi@mail.ru

Table 1. Crystal chemical data on the structures of alumoklyuchevskite, klyuchevskite, and piypite

Parameter	Alumoklyuchevskite	Klyuchevskite	Piypite
a, Å	18.772(7)	18.6670(70)	13.60(2)
b, Å	4.967(2)	4.94(2)	13.60(2)
c, Å	18.468(7)	18.405(7)	4.98(1)
β°	101.66(1)	101.5(2)	90
V, $Å^3$	1686(1)	1663.15	921.1
Symmetry	Monoclinic	Monoclinic	Tetragonal
Space group/*Z*	*I*2/4	*I*2/4	*I*4/2
Density, g/cm^3	3.04	2.98	2.76
μ, mm^{-1}	7		6.73
Radiation, λ/Å	Mo_{K_α}/0.71073	Mo_{K_α}/0.71073	Mo_{K_α}/0.71073
Total reflections	7114		1234
Unique reflections	2450		706
Reflections with $F \geq 4\sigma_F$	1292	715	654
R_1, %	13.1	12	3.5
S	1.152		

Polyhedrons of K atoms are variable. K(1) is surrounded by eight oxygen atoms linked in pairs by symmetry elements; bond lengths range from 2.72 to 3.14 Å, average 2.91 Å. K(2) is surrounded by four oxygen atoms, which are also in pair symmetric; bond lengths varies from 2.65 to 2.79 Å, average 2.72 Å. Each of the K(3) and K(4) atoms is surrounded by seven oxygen atoms. For K(3), the shortest bond is 2.64 Å and the longest one is 3.15 Å—the average is 2.89 Å; for K(4), these values are 2.34Å, 3.15 Å, and 2.88 Å, respectively (Table 3).

Alumoklyuchevskite is attributed to a group of minerals based on complexes of oxocentered tetrahedrons (Krivovichev and Filatov, 2001). The structure can be described on the basis of chains of oxocentered $[OAlCu_3]^{7+}$ tetrahedrons, in the center of which one of two additional O17 or O18 atoms is located. Oxocentered tetrahedrons are linked into chains via edges (Fig. 3a).

Via Cu–O and Al–O bonds, oxocentered tetrahedrons are linked with SO_4^{2-} tetrahedrons. The chains are arranged along the *b* axis (Fig. 3a). K^+ cations are localized between the chains. A view of the chain in the plane perpendicular to elongation is shown in Fig. 2.

Valence balance. The bond valence balance was calculated for the coefficients published by Breese and O'Keefe (1991). The sums of the valence bonds were close to the nominal valence values: 1.98–2.18 Cu, 6.08–6.36 S, 0.83–1.29 K, and 1.79–2.26 O. For A1, the

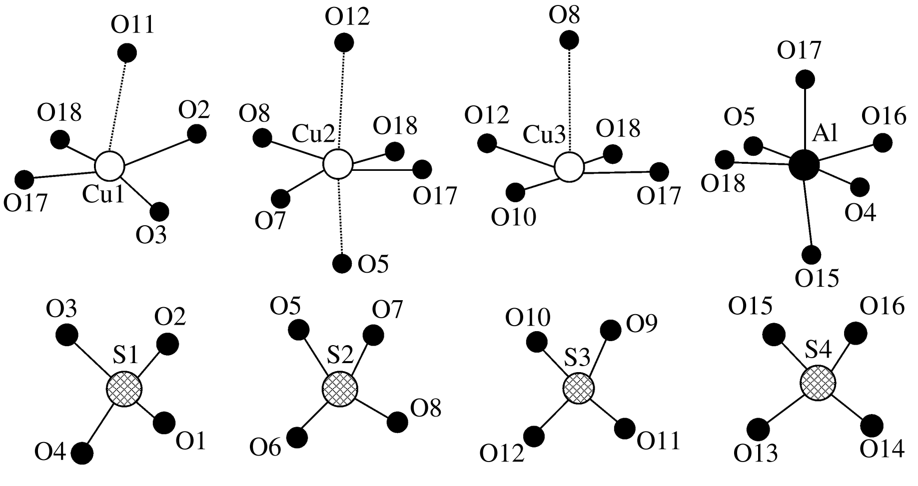

Fig. 1. Coordination polyhedrons of Cu, Al and S in the crystal structure of alumoklyuchevskite.

Table 2. Atomic coordinates, isotropic displacement parameters U_{iso}, Å, and sums of valence bonds V,v.u. (valent units) in the structure of alumoklyuchevskite $K_3Cu_3(Al, Fe)O_2(SO_4)_4$

Atom	*x*	*y*	*z*	U_{iso}	*V*
Cu(1)	0.1866(2)	0.0018(16)	0.5327(2)	0.0211(13)	1.98
Cu(2)	0.2600(2)	–0.0137(15)	0.4098(2)	0.0139(12)	2.18
Cu(3)	0.1693(2)	0.4850(14)	0.4167(2)	0.0129(11)	1.99
Mc*	0.3025(4)	0.514(3)	0.5282(4)	0.020(3)	3.01
S(1)	0.1835(5)	0.503(3)	0.6259(5)	0.029(3)	6.12
S(2)	0.3309(4)	0.487(3)	0.3649(5)	0.014(2)	6.08
S(3)	0.0728(4)	–0.015(3)	0.3692(5)	0.013(2)	6.36
S(4)	0.4059(5)	0.024(3)	0.6022(5)	0.019(3)	6.25
K(1)	1/2	0.483(5)	1/2	0.031(3)	1.08
K(2)	0	0.464(4)	1/2	0.025(3)	0.83
K(3)	0.3700(4)	0.519(3)	0.7465(4)	0.020(2)	1.02
K(4)	0.4294(5)	0.037(3)	0.2776(5)	0.034(3)	1.29
O(1)	0.1838(15)	0.460(9)	0.7051(10)	0.04**	1.79
O(2)	0.1338(18)	0.356(7)	0.5718(19)	0.04**	2.24
O(3)	0.1607(14)	0.786(4)	0.6087(15)	0.017(7)	2.07
O(4)	0.2603(9)	0.480(8)	0.6170(12)	0.017(6)	2.09
O(5)	0.3563(11)	0.560(5)	0.4428(12)	0.005(6)	2.15
O(6)	0.3894(13)	0.434(7)	0.3248(15)	0.04**	2.08
O(7)	0.3124(17)	0.777(4)	0.3569(19)	0.033(9)	2.15
O(8)	0.2650(13)	0.329(6)	0.3417(17)	0.034(9)	1.98
O(9)	0.0067(17)	–0.048(9)	0.3160(18)	0.049(10)	2.01
O(10)	0.0901(17)	0.700(4)	0.3594(18)	0.034(9)	2.26
O(11)	0.0650(13)	0.024(8)	0.4453(10)	0.031(7)	1.85
O(12)	0.1311(18)	0.156(7)	0.3551(19)	0.036(9)	2.14
O(13)	0.4734(9)	0.028(7)	0.5763(12)	0.018(7)	2.00
O(14)	0.4147(12)	–0.005(9)	0.6823(13)	0.023(6)	1.92
O(15)	0.3845(16)	0.310(4)	0.5831(17)	0.028(8)	1.99
O(16)	0.3476(13)	0.8556(5)	0.5651(15)	0.025(8)	2.18
O(17)	0.232(2)	0.732(9)	0.480(2)	0.04**	2.23
O(18)	0.233(2)	0.231(9)	0.476(2)	0.04**	2.13

Notes: * Site occupation Al 0.64 and Fe 0.36.
** Values were established by refining.

calculation was performed taking into account that this site is occupied by 64% Al and 36% Fe^{3+}. The sum of valence forces on the A1 atom is 3.01 and almost equal to the formal valence of Al 3+.

Similar structures. Alumoklychevskite is isostructural with klyuchevskite, $K_3Cu_3Fe^{3+}O_2(SO_4)_4$, and similar in structure to piypite, $K_3Cu_3O(SO_4)_2$. In comparison to alumoklyuchevskite, Fe^{3+} is subsituted for the majority of Al atoms in klyuchevskite. Because of the close ion radii of Al (0.53 Å) and Fe^{3+} (0.64 Å) (Shannon, 1976), this substitution does not result in differences in unit-cell dimensions significantly exceeding measurement errors (Table 1).

The common motif integrates the structural types of klyuchevskite and piypite (Figs. 2, 3). Like klyuchevskite, the crystal structure of piypite is based on the chains of oxocentered edge-sharing tetrahedrons surrounded by SO_4 tetrahedrons.

Distortions of edge-sharing tetrahedrons. Stable variations in the length of the shared edge and supported central bond angles are characteristic features of the edge-sharing tetrahedrons (Krivovichev and Filatov, 2001). As was shown in the cited work, the integration of two OA_4 tetrahedrons via the shared AA edge (Fig. 3a) leads to central oxygen atoms approaching. The oxygen atoms forcibly converging in this way and having the same charge sense and appreciable degree of ionic O–A bond in tetrahedrons are repulsed, i.e., tending to move away from each other and decrease the effect of Coulomb repulsion. The problem is partially solved by a decrease in central AOA angles supported on the shared AA edge with a decrease in its length (Fig. 4). The value of this effect substantially depends on the dimensions of metal A atoms located in the apices of tetrahedra (ligands): the lesser the ligand A, the closer the central O atoms converge and the greater the degree by which they are repulsed with distortion of tetrahedrons, i.e., with a decrease in the shared edge and the supported valence angles. Figure 4 shows that the effect of distortion is weak in the case of large ligands A (Fig. 4b) and strong in the case of small ligands (Fig. 4a).

The crystal structure of alumoklyuchevskite gives a specific example of distorted OA_4 tetrahedrons (A = Cu, Fe^{3+}, Al) due to their integration into the chain via shared edges. For example, the A1–O(18)–Cu(3) angle is 95° (Fig. 4a), much less than the angle in a regular tetrahedron (109.5°), and less than average value (105.3°) of central angles in the OCu_3Al tetrahedron. Another central A1–O(17)–Cu(3) angle of 102° also supported by the shared Al–Cu(3) edge (Fig. 3a) is less in comparison with average value.

The increase in valence angles supported by unshared edges in a perpendicular plane (Fig. 4a) is the consequence of the aforementioned decrease in valence angles along the chain axis. For example, the Al–O(17)–Cu(1) angle is 121°. In all truth, this tendency is not universal and the Cu(3)–O(17)–Cu(2) angle (103°) is less than the average value of 109.5°.

As concerns the unshared A1–Cu(3) edge in alumoklyuchevskite (Fig. 3a), its length is 2.904 Å. Thus, the edge is shorter in comparison with the average value 3.078 Å in a tetrahedron like the length of the other unshared Cu–Cu edge, 2.884 Å (Fig. 3a; Table 4).

The comparison of the three above-described cognate minerals of similar structure and the same origin is especially indicative. All distortions of the edge-sharing tetrahedrons identified in the structure of alumoklyuchevskite are almost perfectly reproduced in the structures of klyuchevskite and piypite (Table 4). In fact, the effect of metal atom size on the distortion value cannot be estimated from these minimal differences in length of shared edges and values of angles supported by them. Since alumoklyuchevskite and klyuchevskite are isostructural, even small differences between them may be revealed.

As was noted above, the distortion of edge-sharing tetrahedrons is the greater the less the metal–ligand ionic radius (Fig. 4). In the Al (053 Å) and Fe^{3+} (0.64 Å) pair, the former is less. Hence, it can be expected that

Table 3. Selected bond lengths in the structure of alumoklyuchevskite

Bond	Bond length, Å	Bond	Bond length, Å
Cu(1)–O(18)	1.88(4)	S(2)–O(8)	1.455(18)
Cu(1)–O(3)	1.90(3)	S(2)–O(6)	1.467(17)
Cu(1)–O(17)	1.95(4)	S(2)–O(5)	1.47(2)
Cu(1)–O(2)	2.21(4)	S(2)–O(7)	1.486(18)
Cu(1)–O(11)	2.52(2)	⟨S(2)–O⟩	1.47
Cu(1)–O(4)	3.02(4)		
⟨Cu(1)–O⟩ (4)*	1.99	S(3)–O(12)	1.45(3)
⟨Cu(1)–O⟩ (5)**	2.09	S(3)–O(11)	1.456(16)
⟨Cu(1)–O⟩ (6)***	2.25	S(3)–O(10)	1.474(18)
		S(3)–O(9)	1.43(3)
Cu(2)–O(7)	1.84(3)	⟨S(3)–O⟩	1.45
Cu(2)–O(18)	1.86(4)		
Cu(2)–O(17)	1.95(4)	S(4)–O(16)	1.438(17)
Cu(2)–O(8)	2.13(3)	S(4)–O(13)	1.442(15)
Cu(2)–O(12)	2.57(3)	S(4)–O(14)	1.46(3)
Cu(2)–O(5)	2.77(2)	S(4)–O(15)	1.498(18)
Cu(2)–O⟩ (4)*	1.95	⟨S(4)–O⟩	1.46
⟨Cu(2)–O⟩ (5)**	2.07		
⟨Cu(2)–O⟩ (6)***	2.19	K(1)–O(5)	2.72(2) × 2
		K(1)–O(13)	2.76(3) × 2
Cu(3)–O(18)	1.92(4)	K(1)–O(15)	3.02(3) × 2
Cu(3)–O(17)	1.92(4)	K(1)–O(13)	3.14(4) × 2
Cu(3)–O(10)	1.96(3)	⟨K(1)–O⟩	2.91
Cu(3)–O(12)	2.04(3)		
Cu(3)–O(8)	2.60(3)	K(2)–O(2)	2.65(3) × 2
Cu(3)–O(11)	3.12(3)	K(2)–O(11)	2.79(3) × 2
⟨Cu(3)–O⟩ (4)*	1.96	K(2)–O⟩	2.72
⟨Cu(3)–O⟩ (5)**	2.09		
⟨Cu(3)–O⟩ (6)***	2.26	K(3)–O(1)	2.64(4)
		K(3)–O(9)	2.65(3)
Al–O(17)	1.80(4)	K(3)–O(4)	2.83(2)
Al–O(16)	1.96(3)	K(3)–O(14)	2.85(4)
Al–O(15)	1.95(3)	K(3)–O(14)	3.05(4)
Al–O(4)	1.97(2)	K(3)–O(3)	3.07(3)
Al–O(18)	2.02(4)	K(3)–O(1)	3.15(4)
Al–O(5)	2.05(2)	⟨K(3)–O⟩	2.89
⟨Al–O⟩	1.96		
		K(4)–O(6)	2.34(3)
S(1)–O(2)	1.42(4)	K(4)–O(10)	2.61(3)
S(1)–O(1)	1.478(17)	K(4)–O(14)	2.88(2)
S(1)–O(3)	1.486(18)	K(4)–O(13)	2.94(2)
S(1)–O(4)	1.487(15)	K(4)–O(9)	3.09(4)
⟨S(1)–O⟩	1.47	K(4)–O(12)	3.12(4)
		K(4)–O(7)	3.15(3)
		⟨K(4)–O⟩	2.88

Note: Data on the 4(*), 5(**), and 6(***) shortest Cu–O bonds are given.

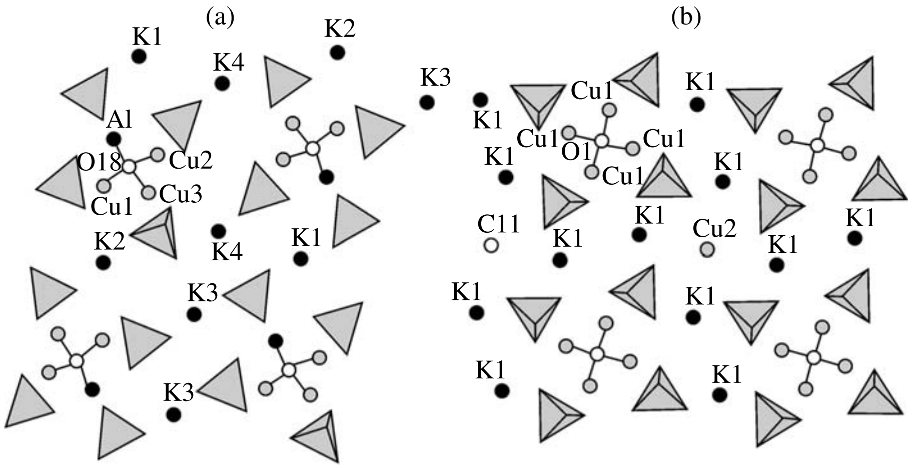

Fig. 2. Structures of (a) alumoklyuchevskite and, as in much the same way, klyuchevskite and (b) piypite in the plane perpendicular to chains of oxocentered tetrahedrons.

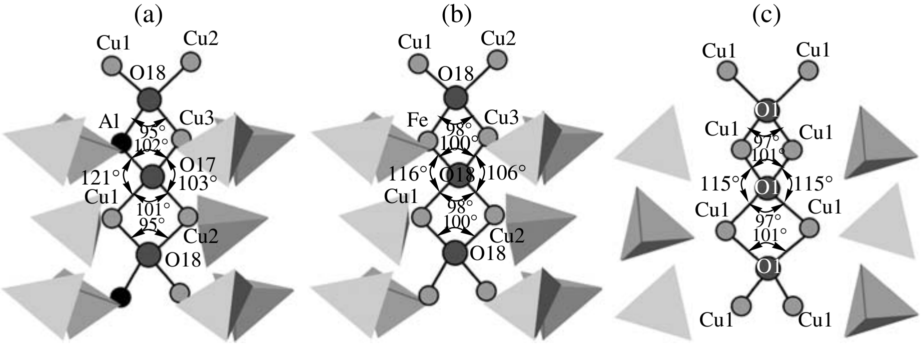

Fig. 3. Bond angles on oxygen in oxocentered tetrahedrons in the structures of (a) alumoklyuchevskite, (b) klyuchevskite, and (c) piypite.

the distortions will be greater in alumoklyuchevskite (at least a little). Indeed, Table 4 shows that the shared Al–Cu edge (2.904 Å) in alumoklyuchevskite is shorter than the Fe–Cu edge (2.918(6) Å) in klyuchevskite, although this difference is within the limits of measurement error. In addition, it could be caused by a lesser average length of edges in the tetrahedron OCu_3Al (3.08 Å) than in the tetrahedron OCuFe (3.10 Å). As concerns the average Al–O–Cu and Fe–O–Cu angles supported by shared edges, they are practically indiscernible (98.5° and 99°).

The search for weak distinctions in comparison with piypite (Table 4) is hampered to a much greater extent, because alumoklyuchevskite and klyuchevskite, on the one hand, and piypite, on the other, belong to different structural types, while the dimensions of metal ions are comparable: the ionic radius $R(Cu^{2+})$ for a coordination number (CN) of 5 is 0.65 Å; for the square coordination

Table 4. Characteristics of distorted oxocentered OA_4 tetrahedrons having shared edges in the crystal structures of alumoklychevskite and similar compounds

Parameter	Alumoklyuchevskite		Klyuchevskite		Piypite
	$O(17)Cu_3Al$	$O(18)Cu_3Al$	$O(17)Cu_3Fe$	$O(18)Cu_3Fe$	OCu_4
A_s–O–A, deg	99	98	99	99	99
A_s–O–A_s, deg	112	112	111	110	115
$\langle A_s \ldots A_s \rangle$, Å	2.904(9)	2.904(9)	2.918(6)	2.918(6)	2.936(4)
	2.884(6)	2.884(6)	2.899(4)	2.899(4)	
$\langle A \ldots A \rangle$, Å	3.022	3.042	3.031	3.022	3.089

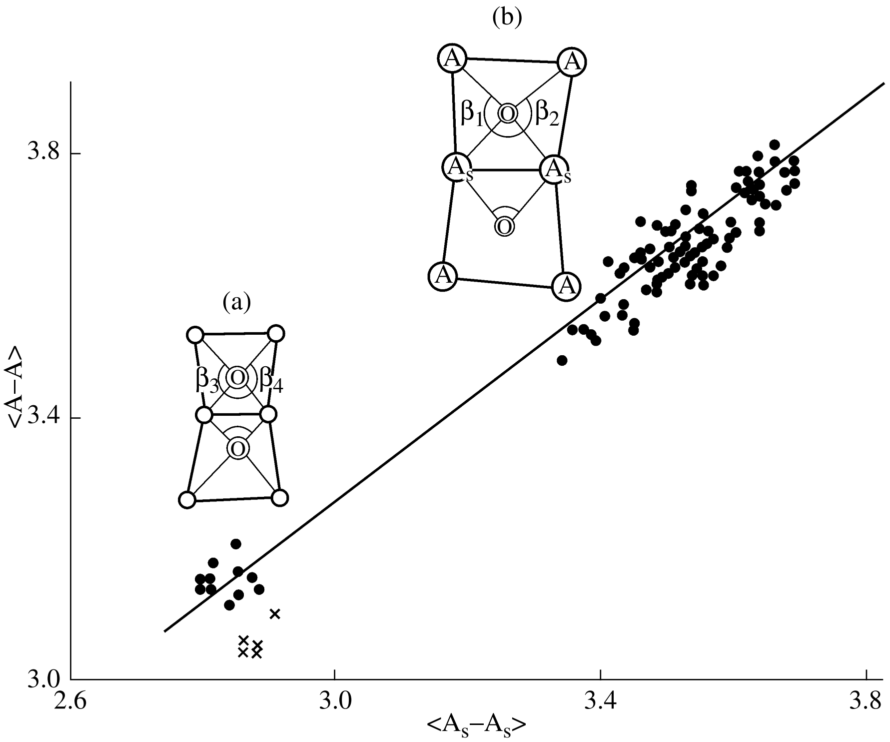

Fig. 4. The length, of A_s–A_s shared edge versus the average length of the A–A edge in anion-centered tetrahedrons and comparative distortion of oxocentered tetrahedrons for (a) small and (b) large cations, after Krivovichev and Filatov (2001). Crosses are the data for five oxocentered tetrahedrons in the structure of alumoklyuchevskite, klyuchevskite, and piyite.

by oxygen (CN 4), the ionic radius is 0.57 Å (Shannon, 1976).

In ending our consideration of distorted edge-sharing OA_4 tetrahedrons, the following can be concluded: (1) alumoklyuchevskite, klyuchevskite, and piypite constantly display underestimated lengths of shared edges and angles of central angles supported on them in comparison with the average values in a tetrahedron; (2) these deviations from average values are almost identical in the studied minerals due to close ionic radii of Al (CN 6), Fe^{3+} (CN 6), and Cu^{2+} (CN 4 or 5), which are 0.59 ± 0.06 Å.

In the monograph by Krivovichev and Filatov (2001), a similar analysis was performed for a wide range of ionic radii and the corresponding variations in the average distortions of tetrahedrons were obtained. In particular, for the small Cu^{2+} ion ($R_{IV} = 0.5$ Å), the distortions are greater (the shared edge is 2.82 Å at an average length of the edge in a tetrahedron of 3.14 Å; the central angle supported by the shared edge is 93.5Å at an average angle in the tetrahedron of 109.6°) than for the large Pb^{2+} ion ($R_{IV} = 1.19$ Å), whereas the shared edge is 3.61 Å at an average edge length in the tetrahedron of 3.76 Å; the central angle supported by the shared edge is 103.1° at an average angle in the tetrahedron of 109.5°. The average distortion is approximately 12% for small Cu^{2+} and 5% for large Pb^{2+}.

From an examination of 118 symmetrically independent tetrahedrons from 84 crystal structures, Krivovichev and Filatov (1999) plotted the length of the A_s–A_s shared edge versus average distance ⟨A–A⟩ for the oxocentered OA_4 tetrahedrons (Fig. 4). We plotted experimental points (crosses in Fig. 4) in this diagram for five independent oxocentered tetrahedrons in compliance with the data given in Table 4: alumoklyuchevskite (2), klyuchevskite (2), and piypite (1). It is seen that our data tightly cluster close to the previous plot, which regularly deviated toward the average lengths of edges in the OA_4 tetrahedron. Unfortunately, we failed to explain this small but regular anomaly.

CONCLUSIONS

The crystal structure of alumoklyuchevskite, $K_3Cu_3AlO_2(SO_4)_4$, a mineral of volcanic exhalations, was solved. As was expected (Gorskaya et al., 1995), the mineral is isostructural to klyuchevskite, $K_3Cu_3Fe^{3+}O_2(SO_4)_4$. The chains of edge-sharing oxocentered tetrahedrons are the pivotal ones of the structure. The chains are linked to each other via SO_4 tetrahedrons and K ions. The oxocentered OCu_2Al tetrahedrons are distorted in line with the concept of tetrahedron distortions bonded via a shared edge. Similar distortions were revealed in klyuchevskite and piypite, $K_4Cu_4O_2(SO_4)_4(Na,Cu)Cl$, two other minerals of the Tolbachik Eruption of 1975–1976.

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