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Figure 1. Stephanite Ag_5SbS_4. Projection xy.

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Abstract

Full Text

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CRYSTALLOGRAPHY

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THE CRYSTAL STRUCTURE OF STEPHANITE Ag_5SbS_4

Stephanite (black silver ore) Ag_5SbS_4—a complex Ag,Sb sulfide (sulfosalt)—in the sulfide handbook [1] was assigned to compounds of the chain type a priori, before structural determination.

The object of our investigation was Freiberg iron-black short-prismatic crystals, kindly provided by I. A. Pen' kov. The always-noted extraordinary tendency of stephanite to twinning (on (110), up to the formation of aragonite-type pseudohexagonal triples, but sometimes on (130) and even (100) and (010) [2, 3]) greatly hampered the obtaining of a set of X-ray intensities [4, 5]. Of 500 unbounded fragments of the mineral, only one ($0.4 \times 0.3 \times 0.4$ mm^3) was suitable for single-crystal photography.

The parameters of the orthorhombic cell (URS-50 diffractometer, CuKα radiation):
$a = 7.830 \pm 0.002$, $b = 12.450 \pm 0.005$, $c = 8.538 \pm 0.002$ Å—agree with those given in [6], but differ somewhat from [4, 5]. At density $\rho = 6.28$–6.32, $Z = 4Ag_5SbS_4$.

Fig. 1. Stephanite Ag_5SbS_4. Projection *xy*. Ideal scheme of two layers of hexagonal packing of S atoms (*a*). The isolated base-centered (pseudo-orthorhombic) cell is shown. Triangles are bases of Sb prisms. *b* and *c* are Sb atoms located at $z = 0$ and 1/2, respectively; *e* are cations AgI,III belonging to the first layer, *d* to the second. In each cation layer ($Ag_I + 2Ag_{III}$ + Sb) they form an almost regular hexagonal pattern, shifted relative to the pattern of anions ($S_1 + 2S_2 + S_3$).

The intensities of 488 nonzero reflections $0kl - 6kl$ and $hk0 - hk2$ (Weissenberg X-ray goniometer, MoKα, $\sin\vartheta/\lambda \leq 0.8$ Å^{-1}) were estimated on the $\sqrt[4]{I}$-scale of blackening standards, without correction for absorption. The base-centered X-ray group $mmmC - c$—includes three Fedorov groups:

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Fig. 2. Stephanite Ag5SbS4. A –paired rods (hatched walls) of AgII tetrahedra; darker tetrahedra correspond to the level z = 0, lighter ones to z = 0.5; B –axonometry

Figure 2: Fig. 2. Stephanite Ag5SbS4. A –paired rods (hatched walls) of AgII tetrahedra; darker tetrahedra correspond to the level z = 0, lighter ones to z = 0.5; B –axonometry

$D_{2h}^{17} = Cmcm$, $C_{2v}^{16} = C2cm$, and $C_{2v}^{12} = Cmc2_1$.
The morphology of the crystals [5], the geometry of the maxima $P(xyz)$, and the determination of the piezoelectric effect made it possible to settle on the last one–$Cmc2_1$.

Analysis of the Patterson peaks according to S. V. Borisov [7] made it possible to localize the heavy Ag and Sb. The lighter S atoms were found at the stage of electron-density syntheses. The discrepancy factor at this stage is $R = 0.15$, with a general isotropic thermal correction $B = 1.6$ Å^{-2}. The coordinates of the 7 basis atoms of the structure are given in Table 1; interatomic distances, in Table 2.

The rodlike (along c) character of stephanite requires beginning the description of the structure with the "supporting" architectural columns of Sb atoms triangulo-

of its section, which extend parallel to the c axis in pairs: one pair at the beginning of the C cell, and the other at its center. In each column, trigonal prisms with Sb and empty prisms alternate along the c axis. For Sb one usually assumes one unshared pair of electrons, and accordingly Sb is displaced toward the base in all prisms in one direction along c (hemimorphism), i.e., Sb^{3+} is characterized by triple umbrella coordination SbS_3 with an angle S—Sb—S ≈ 100°.

Fig. 2. Stephanite Ag_5SbS_4. **A** –paired rods (hatched walls) of Ag_{II} tetrahedra; darker tetrahedra belong to the level $z = 0$, lighter ones to $z = 0.5$; **B** –axonometric view.

The occupied prisms alternate with empty ones in neighboring columns in a checkerboard pattern because of the glide planes c and n that link the columns (Fig. 1). At the centers of the spacious rhombic channels between the supporting SbS_3 rods, triples of atoms $1Ag_I + 2Ag_{III}$ are strung on an axis of S-tetrahedra of the pseudohexagonal structure of stephanite ($b : a = 1.6$ instead of 1.73) according to the law of a pseudo-sixfold mirror axis (Fig. 1), and therefore somewhat more densely than in millerite NiS (8) and heazlewoodite Ni_3S_2 (9), which are characterized by the same triples (nests) in rhombohedra.

Table 1

Coordinates of the basis atoms

in the structure of stephanite

Atom	x/a	y/b	z/c
Ag_I	0.500	0.145	0.842
Ag_{II}	0.312	0.378	0
Ag_{III}	0.326	0.063	0.190
Sb	0	0.169	0.917
S_1	0.229	0.231	0.754
S_2	0	0.467	0
S_3	0.500	0.486	0.800

Table 2

Interatomic distances in stephanite (in Å)

Ag_I-tetrahedron	Ag_{III}-tetrahedron
Ag_I—S = 2.49	Ag_{III}—S_1 = 2.65
—S_2 = 2.58	—S_2 = 2.42
—S_2^* = 3.23	—S_2^* = 2.99
	—S_2 = 2.78
Ag_{II}**-tetrahedron**	**Sb-polyhedron**
Ag_{II}—S_1 = 2.54	Sb—S_1 = 2.39
—S_1^* = 2.88	—S_3 = 2.49
—S_2 = 2.68	
—S_3 = 2.64	

As in this latter compound, in the Ag triple in stephanite the vertical S–S edge is common, while the intersecting edges of the corresponding tet-

tetrahedra are formed by atoms S_1 and S_3 from the walls of the central SbS_3-rods*.

Using the same basic S atoms for their tetrahedral environment, the cations Ag_{II} (which account for 2/5 of the total amount of silver in stephanite) are arranged into beams, and further into corrugated walls (they are stretched on both sides over the glide planes n, Fig. 2), which pass parallel to the short axis of the primitive rhombi (in Fig. 1). The Ag_{II}-tetrahedra are connected with one another only by common vertices (all four, i.e., the formula of the network is $Ag_{II}-[Ag_{II}S_2]_\infty$), but they have common edges both with the Ag_{III} tetrahedra and with the SbS_3 umbrellas. The very strongly expressed metallic character of stephanite is determined by the large number of common edges in the Ag tetrahedra. This same feature is probably connected with the brittleness of stephanite (a brittle silver ore), which may be compared with the brittleness of

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Fig. 3. Stephanite Ag_5SbS_4. Projection xy. One layer of the structure is shown. The central Sb-prisms are indicated by dots, Ag_I-tetrahedra by checkerboard hatching, and Ag_{III}-polyhedra by linear hatching

Figure 3: Fig. 3. Stephanite Ag_5SbS_4. Projection xy. One layer of the structure is shown. The central Sb-prisms are indicated by dots, Ag_I-tetrahedra by checkerboard hatching, and Ag_{III}-polyhedra by linear hatching

pentlandite (Ni, Co) and sulvanite $CuVS_4$, which are distinguished by the same structural feature ([8],[9]). Despite the more or less regular tetrahedral environment of all three kinds of Ag by S atoms, not all Ag—S bonds can be ordinary covalent bonds for classical sulfides. In fact, 4 anions S^{2-} are able to provide 16 donor electron pairs; after subtracting 3 for the rod-like Sb^{3+}, 13 pairs remain for 5 Ag atoms, i.e., most Ag atoms have only two covalent (through electron pairs) bonds with S**. The predominance of "true" double coordination also contributes to the above-noted extraordinary brittleness of stephanite.

Fig. 3. Stephanite Ag_5SbS_4. Projection xy. One layer of the structure is shown. The central Sb-prisms are indicated by dots, Ag_I-tetrahedra by checkerboard hatching, and Ag_{III}-polyhedra by linear hatching.

The layer of Ag-tetrahedra distinguished in Fig. 3 makes it possible to understand the pseudohexagonal morphology of stephanite crystals and the formation of aragonite-type triplets.

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* In accordance with true rhombic symmetry, in these sixes of Ag-tetrahedra there is distinguished a metachain $[Ag'_2S_6]_\infty$ in the mirror plane with links connected by the glide plane c. The atoms (tetrahedra) Ag_{III}, paired through a common vertical edge, are also connected by the glide plane c, and together with Ag_I form triplets–steps of pseudohexagonal (6_3) three-start spiral staircases through the midpoints of the edges of the unit cell. Nevertheless, the pair Ag_{III} at 0.152 is higher than Ag_I.

** This inequality of bonds in the tetrahedra is manifested in the inequality of the Ag—S distances, namely:
Ag_I—$S = 2.49$ (2); 2.58; 3.23(?) Å;
Ag_{II}—$S = 2.54$; 2.64; 2.68; 2.88 Å;
Ag_{III}—$S = 2.42$; 2.65; 2.78; 2.99 Å.

Note: Figure translations are in progress. See original paper for figures.

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