

AN ELECTRON - DIFFRACTION STUDY OF Cu_3SbS_4

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Thin films of Cu_3SbS_4 are used. Disordered (I) and ordered (II) phases are detected and their structures are established: I. $a = 5.28 \text{ \AA}$, $Z = 1$, ZnS type; II. $a = 10.74 \text{ \AA}$, $Z = 8$, space group Fm3m, Cu at 24 (d), Sb at 8 (c), and S at 32 (f); $z = 1/8$ for S.

The x-ray information on Cu_3SbS_4 is incomplete. It has been found [1] that enargite Cu_3AsS_4 is isomorphous with famatinite, which is a phase based on Cu_3SbS_4 and having the antimony partly replaced by arsenic and the copper partly by iron or zinc. There are several papers on the structure of enargite, which has [2, 3] an orthorhombic unit cell whose constants are $a = 6.46$, $b = 7.43$, and $c = 6.18 \text{ \AA}$; $V = 296.5 \text{ \AA}^3$, $Z = 2$; space group Pnm. The structure is made up of almost regular tetrahedra, which contain the As and Cu atoms.

Hocart and Weil [4] have described results for luzonite (a mineral of approximate composition $\text{Cu}_3(\text{AsSb})\text{S}_4$, but they give no analyses.

This mineral is pseudocubic and has $a \approx 5.29 \text{ \AA}$, $V \approx 148 \text{ \AA}^3$, $Z = 1$. The three lattice constants differ by less than 0.5%; the structure is of ZnS type, and the atoms of copper and arsenic (antimony) lie in equivalent positions that correspond to Zn.

The structures of Cu_3VS_4 and Cu_3PS_4 are known; The first [1] is cubic ($a = 10.75 \text{ \AA}$, $V = 1240 \text{ \AA}^3$, $Z = 8$, space group Fm3m) and consists of VS_4 tetrahedra, while the Cu atoms lie in symmetry planes and have in-plane (not tetrahedral) coordination. However, these results have not been confirmed [5]; a is found as 5.37 \AA , the symmetry is $\text{P}\bar{4}3\text{m}$, the V atoms lie at the corners of cubes (which have the Cu atoms at the middle of the edges), and the S atoms are slightly displaced from the centers of the octants ($x_s = 0.235$). The basic structure consists of VS_4 tetrahedra, which are connected via copper atoms (also with tetrahedral coordination). Further, Cu_3PS_4 is orthorhombic; the structure and constants are almost exactly those of Cu_3AsS_4 .

The components (43.4 at.% Cu, 27.5% Sb, and 29.1% S) were melted together under vacuum at 1000°C ; the product was annealed for 3 hr at that temperature. The density (measured at room temperature) was 4.71 g/cm^3 . The films were made and examined in the Electron-Diffraction Laboratory of the Department of

Semiconductors at Azerbaijan State University. The apparatus was a prototype of the EG model [6] made at the Institute of Crystallography, Academy of Sciences of the USSR; the calculated distance $L \approx 700 \text{ mm}$, and the accelerating voltage was 60 kv [7].

The films of Cu_3SbS_4 were made by distilling pieces of the alloy onto freshly cleaved faces of NaCl crystals. Figure 1 shows the pattern given by such a film as transferred on collodion from the crystal to the apparatus without annealing. Figure 2 shows a pattern from an annealed film. The alloy must be distilled over completely; partial distillation results in Sb_2S_3 (Fig. 3).

The pattern of Fig. 1 can be indexed to a cubic cell ($a = 5.28 \pm 0.06 \text{ \AA}$) with $Z = 0.955 \approx 1$. The structure factors were calculated from the measured line intensities. The structure is of sphalerite type, in which the equivalent positions (those of the Zn atoms) are filled randomly by copper and antimony. The unannealed material thus has a structure resembling that of luzonite.

The pattern of Fig. 2 can be indexed to a cubic cell ($a = 10.74 \text{ \AA}$). The pattern shows only reflections with unmixed indices, so group Fm3m was selected. The unit cell contains eight Cu_3SbS_4 units. The intensities of the strong lines were measured on the microphotometer; those of the weak lines were estimated visually. The Φ_0^2 were used to calculate a Φ^2 series on [111], which showed peaks at $1/8$ and $1/4$; this indicates that de Jong's model for Cu_3VS_4 can be used [1]. The positions assigned to the atoms in group Fm3m are Cu at 24 (d), i.e., in symmetry planes, Sb at 8 (c), i.e., at centers of symmetry, and S at 32 (f) with $x = 1/8$; the sulfur atoms in each octant form a tetrahedron.

The Φ were corrected for the temperature factor, in which the B used was that found from the medium and weak reflections (0.6). The Wilson-Vainshtein scattering law was tested from the theoretical Σf and Σf^2 by means of the $\bar{\Phi}_0^2$; the scattering was found to

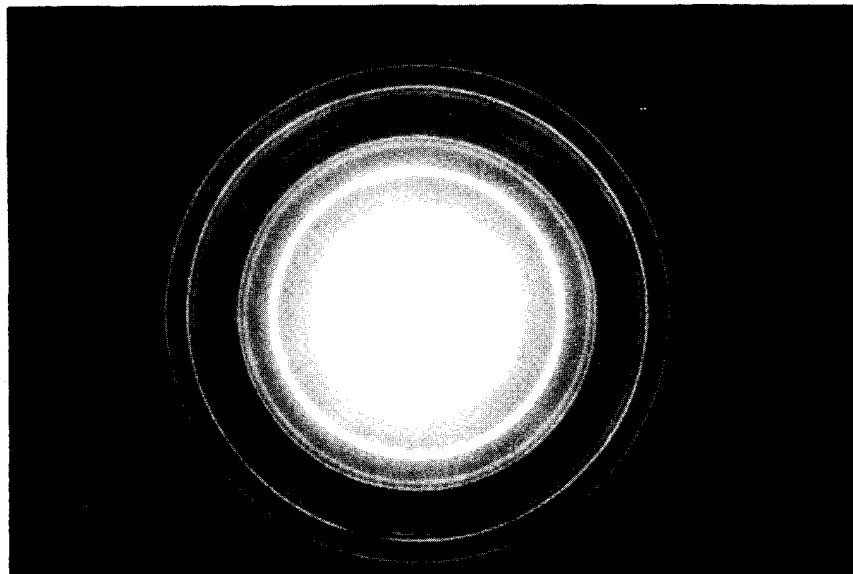


Fig. 1. Electron-diffraction pattern from disordered Cu_3SbS_4 .

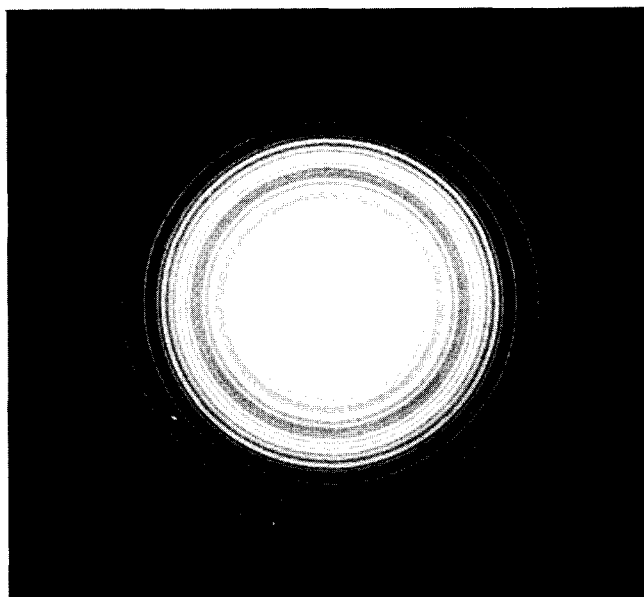


Fig. 2. Electron-diffraction pattern from ordered Cu_3SbS_4 .

be purely kinematic. Then the structure factors were normalized to their absolute values in terms of the strong and medium reflections. This gave $R = 11.9\%$, which shows that the structure has been established correctly.

The normalized Φ_0 were used to calculate one-dimensional and two-dimensional sections of the Φ series. Figure 4 shows the section on (110), in which the lines are at 150- v intervals. The peaks have the following heights:

$$\varphi_{\text{Cu}}(0) = 950 \text{ v}; \varphi_{\text{Sb}}(0) = 1320 \text{ v}; \varphi_{\text{S}}(0) = 515 \text{ v}.$$

These show also that the structure model is correct.

The structure of ordered Cu_3SbS_4 is as follows. The sulfur atoms form a regular tetrahedron in each octant of the unit cell. Two adjacent tetrahedra are related by a symmetry plane that passes between them. The Sb atoms lie at the centers of the tetrahedra, while the above symmetry planes contain the Cu atoms, which have four nearest neighbors (S atoms at the corners of a rectangle); Fig. 5 shows the orientation of the tetrahedra.

The structure may also be described in a setting with a vertical threefold axis; the SbS_4 tetrahedra form a centered hexagonal array. Layers having the direc-

Formula	Phase	Volume per mol., A^3	Tabulated tetrahedral radius, A
Cu_3AsS_4 (enargite)	Orthorhombic	148.5	As - 1.18
$\text{Cu}_3(\text{AsSb})\text{S}_4$ (luzonite)	Cubic $a = 5.29 \text{ A}$	148	Sb - 1.36
Cu_3VS_4	Cubic $a = 5.37 \text{ A}$	154	V - ?
Cu_3PS_4	Orthorhombic	148.5	P - 1.10
Cu_3SbS_4	Cubic, ordered $a = 10.75 \text{ A}$	156	Sb - 1.36

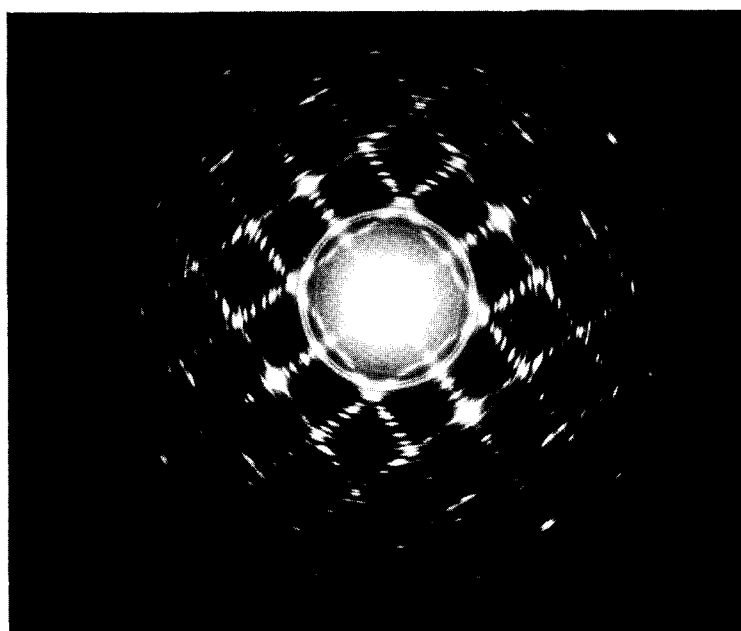


Fig. 3. Electron-diffraction pattern from Sb_2S_3 . The crystals form axial textures having their axes mutually perpendicular.

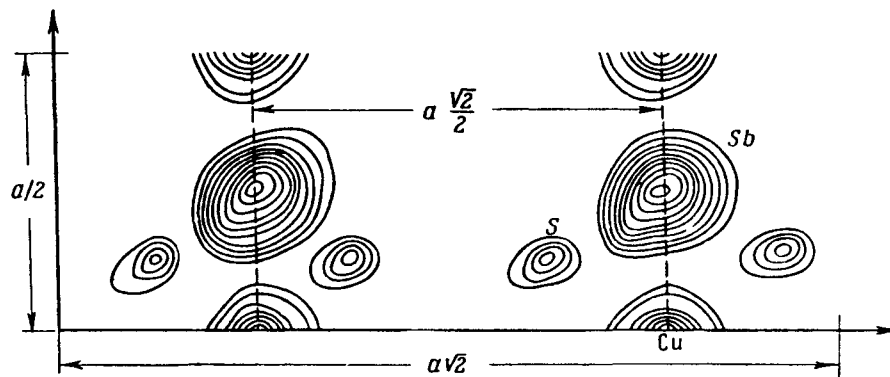


Fig. 4. Section of the three-dimensional potential on (110) for ordered Cu_3SbS_4 .

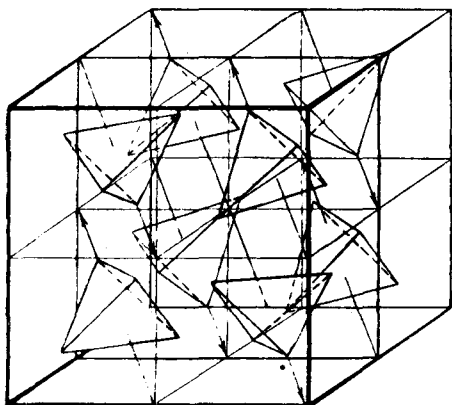


Fig. 5. Array of SbS_4 tetrahedra in ordered Cu_3SbS_4 ; setting with cubic axes.

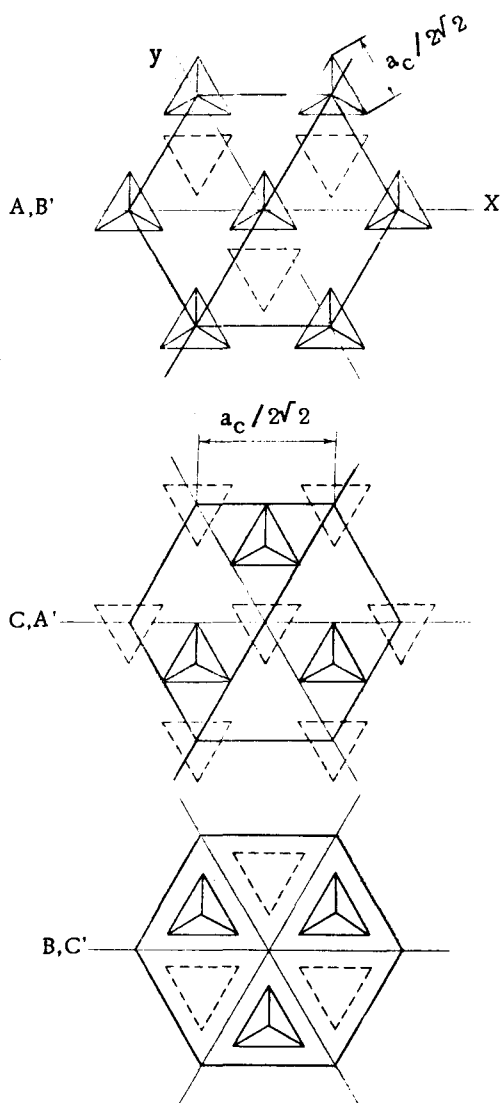


Fig. 6. Array of SbS_4 tetrahedra in the setting with hexagonal axes.

tions of the corners of their tetrahedra differing by 180° alternate along $[111]$. The repeat period on that axis covers layers; the planes passing through the Sb atoms are separated by $a\sqrt{3} : 6 = a/2\sqrt{3}$. Figure 6 shows the tetrahedra in each layer and the alternation of directions. The structure may be described in terms of hexagonal axes, whose constants are

$$a_h = a_c/\sqrt{2}, c_h = a_c \cdot \sqrt{3}.$$

The centers of the tetrahedra form a sequence

$$\dots AB'C' A'BC' \dots,$$

in which the prime denotes a direction turned through 180° ; adjacent layers present either their vertices or their bases. The copper atoms connecting the layers in the first case couple side edges; in the second, edges of the base.

Belov [8] describes the minerals $\text{Cu}_2\text{FeSnS}_4$, CuFeS_2 , Cu_3AsS_4 , $\text{Cu}_3(\text{FeGe})\text{S}_4$ in terms of layers of tetrahedra (copper, tin, etc).

Ordered Cu_3SbS_4 differs in two respects from Belov's structures. Firstly, the vertices alternate in direction (up and down) along $[111]$, whereas in sphalerite, stannite, etc. the tetrahedra all face the same way. Secondly, the coordination around the copper atoms is rectangular instead of tetrahedral. (In-plane coordination around Cu atoms occurs in some copper complexes.)

The interatomic distances agree with the tabulated atomic radii; the Cu-S distance is 2.33 Å (sum of the radii $1.30 + 1.04 = 2.34$ Å), the Sb-S distance is 2.33 Å ($1.36 + 1.04 = 2.40$ Å).

The molecular volumes in these structures are very reproducible (see Table).

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