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AN ELECTRON DIFFRACTION STUDY OF SOME PHASES IN THE Cu–Sb–S SYSTEM

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An electron diffraction study of the compound Cu_3SbS_4 has established that there are two modifications: I a rhombic, enargite type (a = 6.615, b = 7.46, c = 6.37 Å; Z = 2; space group, $Pnm2$) and II, a tetragonal luzonite type (a = 5.31, c = 10.62 Å; Z = 2; space group, $I\bar{4}2m$). The parameters of the latter structure have been more accurately defined: x = 0.269; z = 0.130. An electron diffraction study of tetrahedrite, Cu_3SbS_3 (a = 10.24 Å; Z = 8; space group $I\bar{4}3m$) showed that the the S atoms at the origin and the center of the elementary cell are excess.

In spite of many x-ray and electron diffraction studies [1-5] the relationship between the structure and the chemical composition of some phases in the Cu–Sb–S system remains somewhat vague. The published data indicate that the following phases exist in the Cu–Sb–S system: $CuSbS_2$, Cu_3SbS_4, and Cu_3SbS_3.

According to [6] the orthorhombic $CuSbS_2$ structure is an ordered phase with a unit cell: a = 6.00, b = 3.78; c = 14.45 Å; Z = 4; space group, Pnma. There a contradictory account of the symmetry and the unit cell of the Cu_3SbS_4 phase. Thus, according to Gaines [1] Cu_3SbS_4 has the luzonite (Cu_3AsS_4)-type structure (tetragonal, a = 5.29, c = 10.465 Å; Z = 2; space group $I\bar{4}2m$), while Alieva et al. [5] established that there are two modifications of Cu_3SbS_4; a high-temperature disordered sphalerite type with a = 5.28 Å and a low-temperature ordered cubic structure with a = 10.74 Å (space group Fm3m).

The tetrahedrite (Cu_3SbS_3) structure is based on the zincblende structure with a doubled period ($2a_{ZnS}$ = 10.84 Å) [3]. Accordingly 8 formula units are contained in the elementary cell of this Cu_3SbS_3 structure. Wuensch [3] considered that the Cu_3SbS_3 structure contained 26 S atoms (2 additional S atoms arranged at the corners and at the center of the elementary cube), i.e., the composition of the phase was $Cu_{24}Sb_8S_{26} = 2Cu_{12}Sb_4S_{13}$. The structure of tetrahedrite (Cu_2SbS_3) was recently refined by Machatschki [2] and Wuensch [3] and in the corresponding syntheses the two additional atoms under discussion were present. It is important to emphasize that in the case of these two S atoms the value of the electron density is lower than that of the other S atoms although in the (000) and ($\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$) positions the atoms were given full weight. The distance of the Cu_I to the central S atom calculated from the more accurate data is less than that to the other S atoms in spite of an increase in the coordination.

For these reasons we repeated the determination of the structures of Cu_3SbS_4 and Cu_3SbS_3 using electron diffraction.

EXPERIMENT

The specimens were prepared by fusing stoichiometric proportions of the components in evacuated quartz ampoules (vacuum $\sim 10^{-4}$ mm Hg). The films for electron diffraction were obtained by vacuum evaporation of the composition (from a tungsten spiral) onto both heated and cold NaCl substrates. At the maximum rate of evaporation of Cu_3SbS_4 onto NaCl substrates at room temperature, dispersed films were obtained. After these films had been annealed at above 150°C for one hour, films were obtained which produced sharp electron-diffraction photographs from the polycrystalline aggregate and were indexed on the basis of the cubic Cu_3SbS_3 cell with a = 10.24 Å, in good agreement, within the limits of experimental accuracy, with the data in [2]. A further increase in the annealing time resulted in the formation of single crystal films of Cu_3SbS_3 giving electron-diffraction photographs which we used to define the cell constant a more accurately. It can be assumed that, in our case, part of the S atoms evaporated during the evaporation of the source or vacuum annealing of the films and the composition approximated then to Cu_3SbS_3. Therefore, in order to obtain films with the composition Cu_3SbS_4, melts were prepared with excess sulfur (1 or 2%). After such melts had been evaporated on NaCl and the films annealed at 100°C for 15-30 min electron-diffraction photographs were produced from the polycrystalline aggregate which were indexed on the basis of an orthorhombic cell with a = 6.615, b = 7.46, c = 6.37 Å. Weak reflections belonging to the cubic phase of Cu_3SbS_3 were also observed in the electron-diffraction photographs. It is natural to compare these data with the corresponding values for Cu_3AsS_4: a = 6.46, b = 7.43, c = 6.18 Å; space group Pnm2; Z = 2. Within the limits of measurement errors the ratios of the periods a : b : c = 1 : 0.869: 1.047 of both phases are the same. Thus, it seems that in the Cu–Sb–S system there is an orthorhombic Cu_3SbS_4 phase analogous to Cu_3AsS_4 with two molecules in the elementary cell. Since additional weak reflections from the Cu_3SbS_3 phase were observed in the electron-diffraction photographs we did not define more accurately the atomic parameters. When the annealing temperature of the films in question was raised to 180-200°C the cubic phase of Cu_3SbS_3 with a = 10.24 Å again developed. A further increase in temperature led to degradation of the Cu_3SbS_3 and it was possible to identify the lines of the Cu_2S phase (a = 5.30 Å) in the diffraction photographs.

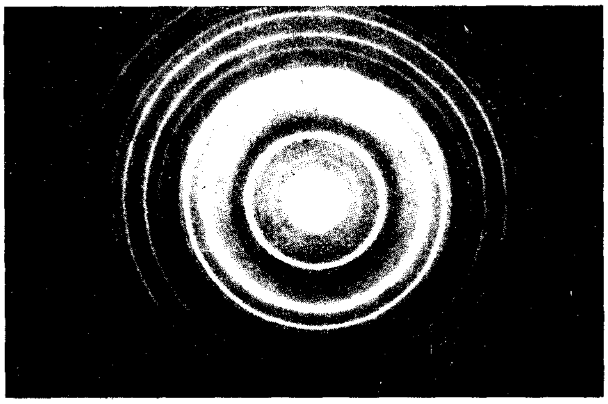
Fig. 1. Electron-diffraction photograph from the polycrystalline aggregate of the tetragonal phase of Cu_3SbS_4.

Thus the orthorhombic phase of Cu_3SbS_4 is unstable and on raising the annealing temperature it decomposes: $2Cu_3SbS_4 \rightarrow 2Cu_3SbS_3 + S_2\uparrow \rightarrow 2Cu_3SbS_3 \rightarrow 3Cu_2S + Sb_2S_3\uparrow \rightarrow 3Cu_2S$.

We failed to make the tetragonal luzonite-type phase of Cu_3SbS_4 [1] under these experimental conditions. In order to eliminate the degradation of the film during higher temperature annealing, the Cu_3SbS_4 specimens were annealed in evacuated sulfur present to ensure an excess vapor pressure above the surface of the specimen (annealing temperature 200-260°C). Such films gave diffraction photographs of a polycrystalline aggregate (Fig. 1) which were indexed on the basis of a body-centered tetragonal cell with a = 5.31, c = 10.62 Å. Films composed of Cu_3SbS_4 with an analogous structure were obtained also from a mixture containing 1-2 % As. It is clear that a trivial arsenic content in Cu_3SbS_4 stabilizes this phase and indeed this is associated with the existence of the $Cu_3(As, Sb)S_4$ minerals containing various percentages of Sb or As.

The refinement of the structure of the tetragonal phase of Cu_3SbS_4. Approximately 90 reflections (up to $\sin\theta/\lambda \approx 0.980$ Å^{-1}) were recorded on the electron-diffraction photographs from the tetragonal phase of Cu_3SbS_4 (Fig. 1). The intensities of the main reflections were measured microphotometrically. The intensities of the weak and more distant reflection were evaluated visually. A qualitative comparison of the intensity of the reflections from the tetragonal phase of Cu_3SbS_4 and the x-ray data for Cu_3AsS_4 [1] indicates that the structures are of the same type. Thus the atoms in the Cu_3SbS_4 structure are tetrahedrally coordinated and occupy the following positions in the space group $I\bar{4}2m$:

$$2Cu_I - 2(b);\ 4Cu_{II} - 4(d);\ 2Sb - 2(a);\ 8S - 8(i).$$

The values of the x and z parameters of the S in the Cu_3AsS_4 structure were: $x_S = 0.250$, and $z_S = 0.125$. The divergence factor R for this model was 28.8%.

The structure was refined using the KSP-68 program and a Ural-2 computer. The R factor was minimized using a random-search method [7]. A continuous search for the R-factor minimum in refining the atomic parameters was undertaken by a programmed separation using the ratio of their calculated amplitudes, of the combined experimental structural amplitudes. Each group of re-

TABLE 1. Interatomic Distances, Å

Compound	Cu—S	Sb—S	Reference
CuS	2.19		[9]
Sb_2S_3		2.49—2.57	[10]
$CuSbS_2$	2.25—2.33	2.44—2.57	[6]
Cu_3SbS_3	2.22—2.29	2.41	Present work
Cu_3SbS_4	2.19	2.42	" "

flections separated in this way was described in the original information in the table of indices. The total and individual temperature factors were accurately determined by a minimization of the divergence factor R and by a sampling method. The final divergence factor R was 27.2%. We should note that the high value of the divergence factor for this structure is evidently conditioned by the fact that reflections from Cu_2S were superimposed on eight strong reflections of those from Cu_3SbS_4. If the added contribution of these reflections from Cu_2S to the intensity is taken into account, then R = 23.4%. The accurately determined parameters of the S atoms are: $x_S = 0.269$, $z_S = 0.130$. The shortest interatomic distances are shown in Table 1.

The refinement of the tetrahedrite Cu_3SbS_3 structure. It has already been noted that the electron-diffraction photograph from this phase (Fig. 2) was indexed on the basis of a cubic cell with $a = 10.24$ Å. The observed extinctions lead to the space group $I\bar{4}3m$. Approximately 90 reflections were recorded (up to $\sin\theta/\lambda \approx 0.795$ Å^{-1}). The intensities were measured as described above and a kinematic formula was used to transform to $\Phi^{\exp}_{hkl}$. The divergence factor R was then calculated on the basis of the model proposed in [2], i.e., with the Cu, Sb, and S atoms occupying the following positions in the $I\bar{4}3m$ space group:

$$12Cu_{I} - 12(d);\ 12Cu_{II} - 12(e);\ 8Sb - 8(c);\ 24S - 24(g).$$

A comparison of the experimental and calculated structural amplitudes indicated that the scattering has a partially dynamic character (R = 36%).

The atomic parameters and the temperature factor for this structure were also refined by a random search method [7] and the final values of these parameters were as follows $x_{Cu_{II}} = 0.220$, $x_{Sb} = 0.270$; $x_S = 0.117$; $z_S = 0.360$; $B = 3.4$ Å^2. In this case the divergence factor R was 25.6%. After checking the extinction on the basis of the dynamic scatter theory in the two-wave approximation the divergence factor R was 20.5% [8] (average thickness of crystals H = 365 Å). The Cu–S and Sb–S interatomic distances in the Cu_3SbS_3 structure are shown in Table 1. They are all reasonably similar to the distances in the structures CuS, $CuSbS_2$, etc. [6, 9, 10]. To demonstrate the two supplementary S atoms a two-dimensional section $\varphi(xy0)$ was constructed without allowing for these atoms. It is clear from Fig. 3 that in this particular section this S atom does not appear at the (000) site. When these atoms are allowed for the S atom appears in the $\varphi(xy0)$ section but its height is lower relative to the other S atoms in the structure. This indicates that in the cubic tetrahedrite structure the two S atoms at the origin and in the center of the elementary cell are excess.

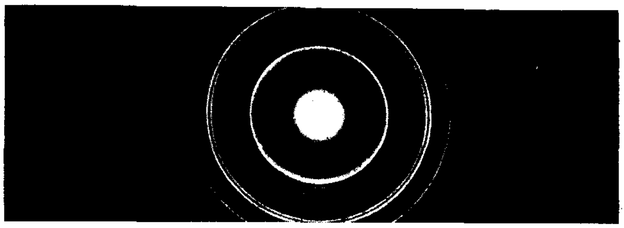

Fig. 2. Electron diffraction photograph from the polycrystalline aggregate of the cubic phase of Cu_3SbS_3.

DISCUSSION OF RESULTS

Electron-diffraction photography of the Cu_3SbS_4 compounds established the existence of two modifications: I, an orthorhombic enargite type; II, a tetragonal luzonite type. By comparing these results with the data obtained in [5] the following may be noted: the cubic phase with a period $a = 10.74$ Å in fact corresponds to the composition Cu_3SbS_3 and not as suggested in [5] to Cu_3SbS_4. The appearance of a phase on the substrate with a composition slightly different from the composition of the ori-

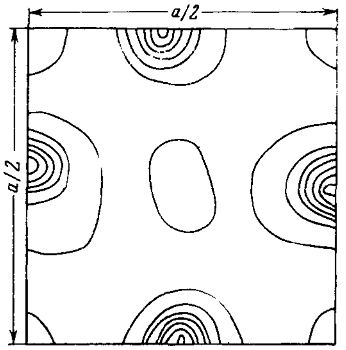

Fig. 3. The $\varphi(xy0)$ section of the Cu_3SbS_3 structure.

ginal material happens quite often in the electron-diffraction photographs. After evaporation and annealing, degradation of the Cu_3SbS_4 occurs according to the equation given above. Another disordered cubic phase of Cu_3SbS_4 with a = 5.28 Å, the electron-diffraction pattern of which was shown in [5], corresponds fully to the strong reflections obtained in our electron-diffraction photograph which, in combination with the weak reflections, is indexed as an orthorhombic cell. As for the chemical composition of the tetrahedrite, our data leads to the formula Cu_3SbS_3. The Cu atoms in these structures have a two-fold and a tetrahedral coordination. The possible coordination numbers for Cu in sulfides are discussed in greater detail in [11].

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