ON THE STRUCTURE OF CERTAIN PHASES
IN THE COPPER—SULFUR SYSTEM

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Only one phase with a fcc lattice is known in the Cu−S system; this is $Cu_{2-x}S$ with a lattice constant of $a = 5.564 \pm 0.016$ Å [1]. However, in the electron-diffraction analysis of CuS samples obtained by evaporating the individual Cu and S components from two sources and subjecting them to heat treatment we observed a new phase with a fcc cell and a lattice constant of $a = 5.387 \pm 0.004$ Å, stable at 20 to 600°C. According to [2-4] the structure of $Cu_{2-x}S$ is of the fluorite type. The composition of this phase was determined in [5] as Cu_9S_5 or $Cu_{1.8}$S. The structure of this compound was studied by Rahlfs [1], who showed that $Cu_{2-x}S$ could not crystallize in the fluorite structure in view of the disagreement between I_{exp} and I_{calc}; he calculated the theoretical intensities for 19 different models with four $Cu_{1.8}$S molecules in the unit cell and compared these with experiment. None of the models considered gave satisfactory agreement between the calculated and experimental intensities. An attempt was made in [5] to identify this phase as rhombohedral with a period of $a = 16.16$ Å and an angle of $\alpha = 13°56'$, having one Cu_9S_5 molecule in the unit cell.

The present investigation is devoted to the refinement of the $Cu_{2-x}S$ structure and to a determination of the structure of the new cubic form with $a = 5.387$ Å. We obtained electron-diffraction pictures with multiple exposures from the corresponding samples. The intensities of the reflections were measured from microphotometer curves obtained in the MF-4. Comparison of the theoretical and experimental structure amplitudes for a model of antifluorite gave an R factor of 38.7% for the cubic phase with $a = 5.564$ Å, which confirms the conclusion of [1] regarding the unsuitability of this model for $Cu_{2-x}S$.

A one-dimensional section of the Φ^2 series in the [111] direction gave two peaks with coordinates $1/4$ $1/4$ $1/4$ and $1/2$ $1/2$ $1/2$; however, the height of the peak with $1/2$ $1/2$ $1/2$ was much smaller than that of the peak with $1/4$ $1/4$ $1/4$, from which it was concluded that not all eight octants were occupied by Cu atoms, but only four, and that some of the atoms lay in the $1/2$ $1/2$ $1/2$ position. Thus this structure is best described in the noncentrosymmetrical Fedorov group $F\bar{4}3m$. The S and Cu atoms occupy the following positions: 4S in 4(a), 4Cu in 4(c), and 3.2Cu in 4(b). We calculated the structure amplitudes for this model, allowing for the temperature factor (for B = 1.3 Å²). This gave an R factor of 19.7%, which suggested that the later model was the most probable. By minimizing the R factor, we refined the composition of the phase in question. The smallest value (19.2%) was obtained for a composition of $Cu_{1.9}$S (i.e., x = 0.1).

In order to determine the structure of the new phase with the period $a = 5.387$ Å, we plotted a one-dimensional section of the Φ^2 series for the directions [111] and [100]. In the first section we found only one peak with coordinates $1/4$ $1/4$ $1/4$. A complicating factor was the fact that even the composition of the structure being studied was unknown. If we suppose that for this particular phase, as in the case of $Cu_{2-x}S$, the framework of the desired structure consists of S atoms forming an fcc lattice, then the smallest S−S distance in this structure equals $a\sqrt{2}/2 = 3.80$ Å. However, according to [4] a distance of 3.80 Å between the anions S−S can only occur for a divalent cation. On the basis of this fact and also after carrying out an analysis of the interatomic function and minimization of the R factor, we proposed the composition CuS for the phase in question, with four molecules in the unit

cell. The Cu and S atoms are arranged in the following way within the $F\bar{4}3m$ Fedorov group: 4S in 4(a), 4Cu in 4(c). Comparison of the experimental structure amplitudes with the calculated ones (for B = 0.1 $\mathrm{\mathring{A}}^2$) gave R = 15.4%, supporting the model and composition of the phase in question.

In the literature there is only one known form of the compound CuS, having a hexagonal lattice with constants a = 3.80, c = 16.32 $\mathrm{\mathring{A}}$, and Fedorov group C6/mmc. Our cubic phase of the sphalerite type with a = 5.387 $\mathrm{\mathring{A}}$ may evidently be regarded as a new form of CuS. The spacings of the cubic and hexagonal lattices are related in the following simple way: $a_c = a_h \sqrt{2}$, $c_h/a_c \simeq 3$.

In the cubic lattice the shortest S–S distance is 3.80 $\mathrm{\mathring{A}}$ and the Cu–S distance 2.33 $\mathrm{\mathring{A}}$; in the hexagonal lattice the S–S distance in the (0001) plane also equals 3.80 $\mathrm{\mathring{A}}$, while the Cu has a tetrahedral coordination with two types of S atoms: $Cu-3S_{II}$ (2.31 $\mathrm{\mathring{A}}$) and $Cu-S_I$ (2.35 $\mathrm{\mathring{A}}$) [7], i.e., the average Cu–S distance is also equal to 2.33 $\mathrm{\mathring{A}}$. Thus in both forms of CuS the coordination of the Cu atoms and the interatomic distances Cu–S and S–S are preserved.

The process of forming the cubic CuS phase was observed in our experiments by the kinetic electron–diffraction method [8]. The hexagonal CuS phase, on heating in vacuo (t greater than 130°C), is enriched with copper owing to its partial dissociation and the evaporation of the more volatile component, sulfur. In this way the cubic form $Cu_{1.9}S$ is formed; this has excess S, and on subsequent annealing passes into the cubic form of CuS (sphalerite type) with a lattice constant of 5.387 $\mathrm{\mathring{A}}$. A microphotometer recording of the kinematic electron–diffraction picture, illustrating the process in question, appears in Fig. 1: CuS_{hex} → $Cu_{1.9}S$ → CuS_{cub}; from this we see that, on annealing the CuS films, in addition to the (11$\bar{2}$0) reflection of CuS_{hex} the (220) reflection of $Cu_{1.9}S$ appears. Then the intensity of the (11$\bar{2}$0) line diminishes and that of the (220) line of $Cu_{1.9}S$ increases. Then the intensity of the (220) line of $Cu_{1.9}S$ starts falling, and in the place of the (1120) we see the (220) line of
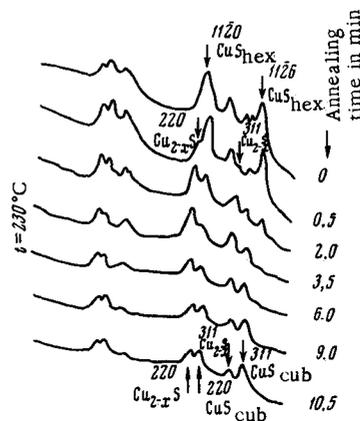

Fig. 1. Microphotometer recording from a kinematic electron-diffraction picture, showing the course of the CuS_{hex} → $Cu_{1.9}S$ → CuS_{cub} transformation process.

CuS_{cub} (since $a_c = a_h \sqrt{2}$ CuS). In addition to this, the existence of the new cubic phase of CuS is confirmed by the presence of an independent (311) reflection on the electron–diffraction picture.

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