

AN ELECTRON DIFFRACTION STUDY OF THE SEMICONDUCTOR CuAsSe_2

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Translated from *Kristallografiya*, Vol. 13, No. 3,

pp. 412-416, May-June, 1968

Original article submitted October 1, 1966

Thin films of CuAsSe_2 , obtained by evaporation of a "mix" at a pressure of $5 \cdot 10^{-5}$ mm Hg₂ were shown by electron diffraction to exist in two phases: a cubic sphalerite-type phase with a lattice constant $a = 5.75 \text{ \AA}$, and a hexagonal phase with $a = 4.05$, $c = 19.72 \text{ \AA}$, space group R3m, $Z = 3$. The hexagonal phase is based on a cubic close-packing of the Se atoms, with the Cu and As atoms occupying all the tetrahedral cavities. The shortest interatomic distances are: Cu-Se 2.42 and 2.45, As-Se 2.50 and 2.55, and Se-Se 3.94 and 4.16 \AA .

This investigation consists of an electron diffraction study of the structure of the compound CuAsSe_2 .¹ The specimens were prepared as thin films by the vacuum deposition of a mix of CuAsSe_2 in a vacuum of $5 \cdot 10^{-5}$ mm Hg. Rock salt crystal substrates were used. The films grew in the following forms, depending on the substrate temperature and the duration of heating: amorphous (deposition of CuAsSe_2 on a substrate below 160°C); polycrystalline (after annealing amorphous films for 7 h at 160°C, or by deposition onto a substrate at 180-220°C); laminar textured or mosaic crystals. The characteristic effect of arsenic is to increase considerably the tendency to the formation of the amorphous phase, and to decrease the speed of the order-disorder transformation and of crystallization.

Photographs of two types were obtained from the laminar textured form. Electron diffraction photographs of the first type, which showed only a small number of reflections, were obtained only by depositing the CuAsSe_2 melt onto substrates at 180-200°C and subsequently annealing in the same temperature range for 3-5 h, or by deposition onto substrates at 300°C. Electron diffraction photographs of the second type, which showed a much larger number of reflections, were obtained by depositing CuAsSe_2 onto substrates preheated to 230°C followed by annealing at 220-240°C for 4-5 h. These patterns differ from the diffraction patterns from the other structures in the sharper fall in the intensity of the reflections with an increase in $\sin \vartheta/\lambda$. These photographs, moreover, retain a

good contrast and they contain a sufficient number of reflections for structural investigation.

Diffraction photographs from the polycrystalline aggregates and from the laminar-textured films of the first type were indexed satisfactorily on the basis of a face-centered cell with $a = 5.75 \pm 0.04 \text{ \AA}$ (NH_4Cl standard). The crystals were arranged in the film with both the octahedral edge (texture axis [111]) and cube edge (texture axis [100]) (Fig. 1) parallel to the surface of the sub-

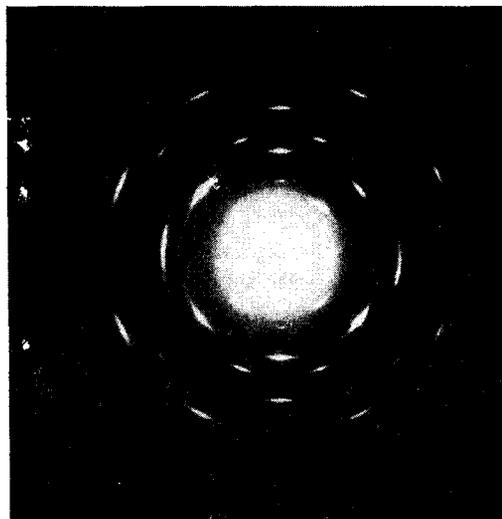


Fig. 1. Electron diffraction photograph of the cubic phase of CuAsSe_2 ; texture axis [100].

¹The CuAsSe_2 was kindly provided by A. Mal'gasov of the Institute of Physics, Academy of Sciences of the Azerbaïdzhan SSR.

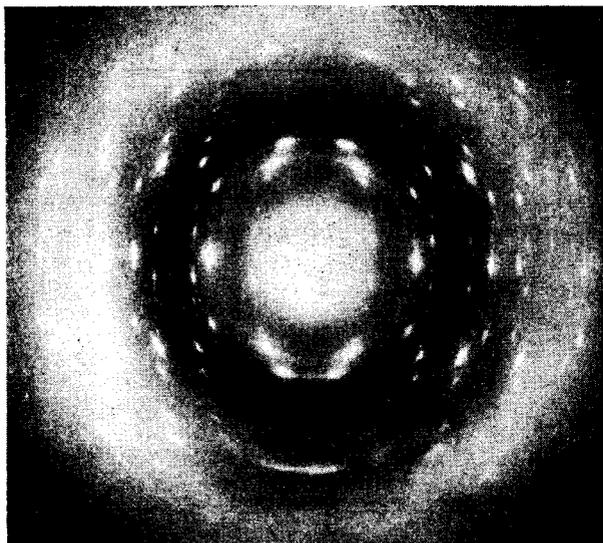


Fig. 2. Electron diffraction photograph of the hexagonal phase of CuAsSe_2 ; texture axis $[0001]$.

strate. The diffraction patterns of the laminar textured form of the second type were indexed on the basis of a hexagonal cell with $a = 4.05 \pm 0.02$, $c = 19.72 \pm 0.06 \text{ \AA}$ (Fig. 2).

A simple analysis of the intensity of the reflections in the diffraction pattern of the cubic single crystals of CuAsSe_2 (reflections of the type $h+k+l = 4n$, $4n+1$ strong, but $h+k+l = 4n \pm 2$ weak) indicates that it has a structure of the sphalerite type (space group $T_d^2 - F\bar{4}3m$). The density of the original material, measured by a pycnometric method, was 5.25 g/cm^3 , which is sufficiently accurate to deduce that there are two formula units of CuAsSe_2 in the unit cell.²

From the absence in the space group of any two-fold positions the Cu and As atoms must be statistically distributed: 2Cu and $2\text{As} - 4(a)$; $4\text{Se} - 4(c)$. A total of 40 independent reflections up to $\sin \vartheta/\lambda = 0.850 \text{ \AA}^{-1}$ were recorded. The intensity of the reflections in the patterns from the oblique textures was determined visually and microphotometrically. The conversion of intensities into structural amplitudes was done by standard methods.

For $B = 0.5 \text{ \AA}^2$ the divergence factor R for all reflections was 15.3%. It should be noted that on some photographs, for the $h+k+l = 4n \pm 2$ type reflections, Φ_{exp} systematically exceeded Φ_{calc} . Some suggested explanations of this anomaly can be put forward. In the first place, in the sphalerite type of structure all the octahedral cavities are unoccupied, and surplus atoms of one of the components can be accommodated therein. However, in addition to interstitial solid solutions, vacancy solid solutions can be formed. In fact a whole series

of compounds of the zinc sulfide structure type are known, in which up to 33% of the cation positions are unoccupied: Ga_2S_3 , Ga_2Se_3 , In_2Te_3 , etc. Secondly, it may be assumed that the anomalous behavior of the reflections with indices $h+k+l = 4n \pm 2$ is caused by the marked asymmetry of thermal oscillations of the Cu(As) atoms. From our experimental data, however, it is not possible to choose between these suggested alternatives.

The approximation to a simple integral ratio of the volumes of the cubic and hexagonal cells ($V_{\text{cub}}/V_{\text{hex}} = 187/280 \approx 2/3$) makes it possible to determine the number of molecules per unit hexagonal cell: $Z = 3$. The observed extinctions, $h-k+l = 3n$, indicate that the structure is rhombohedral in form. The possible Fedorov groups are $R\bar{3}$, $R\bar{3}$, $R32$, $R3m$, and $R\bar{3}m$. In addition, the simple relationship between the lattice constants should be noted: $a_h \approx a_c/\sqrt{2}$; $c_h \approx 2a_c\sqrt{3}$. It can be assumed that transition from the cubic to the rhombohedral structure is associated with disorder in the Cu and As atom arrangement. From the diffraction photographs produced by multiple exposure of the textured films the intensities of all 94 observed reflections were evaluated. The intensities of the

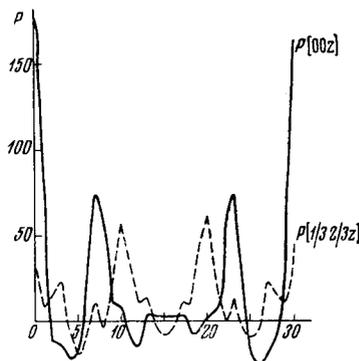


Fig. 3. One-dimensional cross section of the series $P[00z]$ and $P[1/3 2/3 z]$.

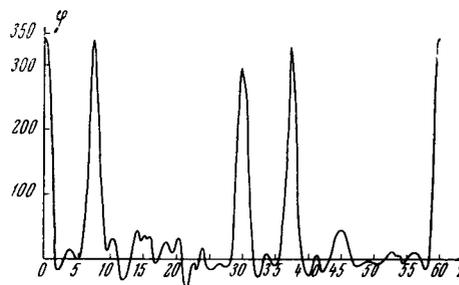


Fig. 4. One-dimensional cross section of the potential of $\varphi[00z]$.

²The density of the CuAsSe_2 mix was determined by A. Mal'gasov.

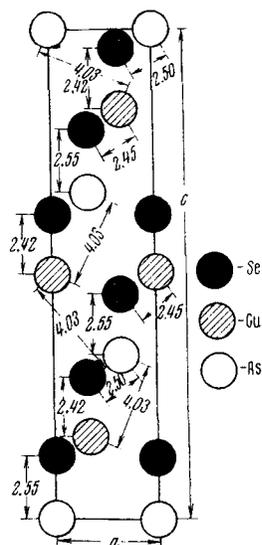


Fig. 5. Projection of the ordered structure of CuAsSe_2 on the plane (xz) .

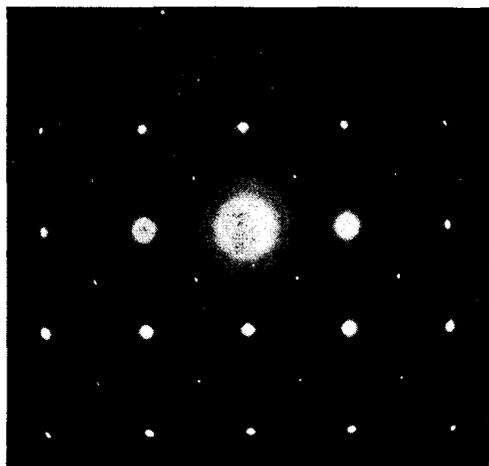


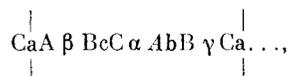
Fig. 6. Point electron diffraction photograph of the cubic phase of CuAsSe_2 .

$hk0$ reflections were measured microphotometrically and were used as density standards for the visual evaluation of the intensities of the remaining reflections. A one-dimensional cross section of the Φ^2 series along $[00Z]$ showed that the peaks on it lie at the points $z_1 = 0.000$, $z_2 = 0.125$, $z_3 = 0.375$, $z_4 = 0.500$. By analyzing the geometry of the Φ^2 series $P[00z]$ and $P[\frac{1}{3}\frac{2}{3}z]$ (Fig. 3), and by considering the crystal chemistry, a model of a structure belonging to the Fedorov groups $R\bar{3}m$ and $R\bar{3}m$ can be constructed. Since the attempts to refine the structural model based on the $R\bar{3}m$ did not allow the R factor to be reduced below 40% this variant

was abandoned. On examination of the structure belonging to the $R3m$ group we were satisfied that our model conformed more readily to the symmetry of this group. The 12 atoms in the cell were therefore arranged as follows: $3\text{Cu}-3(a)$, $z_1 = 0.500$; $3\text{As}-3(a)$, $z_2 = 0.000$; $3\text{Se}_I-3(a)$, $z_3 = 0.125$; $3\text{Se}_{II}-3(a)$, $z_4 = 0.625$.

On the basis of this model we calculated the values of the structural amplitudes, allowing for the temperature factor ($B = 0.5 \text{ \AA}^2$). We determined the signs of the structural amplitudes and constructed a one-dimensional cross section of the three-dimensional $\varphi[00z]$ series in order to determine more exactly the coordinates of the atoms in the structure. The peak heights in the cross section (Fig. 4) showed immediately the correctness of the selected model. The coordinates of the atoms were hardly changed. The final coordinates of the atoms in the ordered phase of CuAsSe_2 are as follows: $z_{\text{Cu}} = 0.500$; $z_{\text{As}} = 0.000$; $z_{\text{Se}_I} = 0.129$; $z_{\text{Se}_{II}} = 0.622$. The divergence factor R was 18.7%.

The cubic packing of the selenium atoms, ABCABC, is the basis of the crystal structure of the ordered phase of the CuAsSe_2 , in which all the tetrahedral cavities are occupied by Cu and As atoms:



where a, b, c are the Cu atoms and α , β , γ are the As atoms (Fig. 5). The shortest interatomic distances are as follows: Cu-Se 2.42 and 2.45; As-Se 2.50 and 2.55; Cu-Cu 4.05; As-As 4.05; Cu-As 4.03; Se-Se 3.94 and 4.16 \AA . A comparison of these distances with the corresponding distances in the structures of Cu_2Se [1] and As_2Se_3 [2] shows that they are in good agreement, and that the bonds between the Cu-Se and As-Se are largely covalent in character. Thus, in both the ordered and disordered structures of CuAsSe_2 the atoms retain a tetrahedral coordination and the ordering is accompanied only by the appropriate redistribution of the Cu and As atoms in the cubic close packing of the Se atoms. The latter form the rigid framework for the structure undergoing the phase transition.

It is interesting to compare the phase transition in CuAsSe_2 with that in ZnS, CuI [3], and AgI [4]. In the last of these three structures we have a transition from one ordered phase of the sphalerite type to another. Here the tetrahedral coordination of the atoms is retained as in CuAsSe_2 , but the cubic close packing is changed. In wurtzite there is two-fold hexagonal packing of the S atoms, but in CuI

and AgI there is a sixfold packing of the I atoms (ABABAB and ABCABC respectively) with the metal atoms occupying half of the tetrahedral cavities.

It has been noted above that when a mix of CuAsSe_2 is deposited onto a hot NaCl crystal substrate, films are produced having the structure of a mosaic single crystal. Electron diffraction photographs of such films taken perpendicularly to the film have a four-fold axis of symmetry (Fig. 6). Interpretation of these patterns showed that they could be indexed on the basis of the cubic cell of the disordered CuAsSe_2 phase. In this case the crystallites are oriented with the (100) planes parallel to the NaCl cube edge.

The authors would like to thank Professor Z. G. Pinsker for his valuable comments.

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