

## The Production of a CuSe Alloy and its Structure Determination by Electron Microscopy

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Single crystals of a CuSe alloy have been produced by a new technique. It is found that this alloy exists in two modifications which can be described as the  $2H$  and  $12H$  structures. Evidence and arguments have been presented to show that the  $12H$  structure stabilizes owing to shear produced in the basic  $2H$  structure. Detailed atomic positions of both basic and modified structures have been worked out. Good agreement has been obtained between the theoretical and experimental values of the intensities.

### Introduction

The intermetallic compound CuSe was first prepared by Earley (1949) who showed that its properties and X-ray diffraction pattern were the same as those of the naturally occurring mineral, klockmannite. It was found to have the hexagonal structure with  $a = 3.93$  kX,  $c = 17.22$  kX and  $c/a = 4.38$ . The hydrosynthetic crystal showed perfect cleavage along (00.1). The single crystal rotation studies showed that there was a superstructure with twelvefold modulation of the  $a$  axis. A powder pattern was also taken and was indexed successfully with the aid of the above cell dimensions. The calculated and observed densities are consistent with the fact that there are six molecules in one unit cell.

It is difficult to prepare single crystals of the compound which are large enough to be mounted in the X-ray goniometer (Berry, 1954). Further, the single crystals from the mineral are not easily available. Berry (1954) therefore, used Earley's (1949) data to determine the possible atomic positions of Cu and Se atoms in the unit cell. Berry's (1954) work, however, showed poor agreement between the calculated and observed X-ray intensities. This fact has also been emphasized by Taylor & Underwood (1960).

A preliminary report by Taylor & Underwood (1960) suggests that the true hexagonal cell of CuSe has  $a = \sqrt{13}a' = 14.26$  and  $c = 17.25$  Å where  $a' = 3.954$  Å and the number of atoms per unit cell is 78. They believe that the apparent hexagonal super cell  $a'' = 13a' = 51.40$  Å is a result of twinning in the structure. No detailed observations were reported by Taylor & Underwood (1960) to establish their view, but recently Elliot, Bickenell & Collinge (1969) have claimed that they could find evidence of twinning in electron diffraction photographs.

Lippmann (1962) has used Taylor & Underwood's result and transformed Berry's (1954) atom positions to the super cell thus showing that the space group is not  $P6_3/mmc$  but  $P6_3/m$  (Pearson, 1967).

In view of the fact that all the previous studies were

based on the experimental data of a single author, we felt that it would be of interest to study the alloy afresh and review the results in the light of the earlier observations.

Production of alloys of the CuSe system with a Se content above 30 at. % presents its own difficulties (Hansen, 1958). When an attempt is made to melt both elements simultaneously in an open crucible, selenium evaporates completely before the melting point of copper is reached. A method of producing alloys developed in this laboratory (Arunsingh & Dayal, 1969*a, b, c*) does not suffer from this handicap. However, this method is not likely to yield any new information, since the alloy is produced in the form of a powder. The method of pulse annealing which has also been used in this laboratory (Arunsingh, Srivastava & Dayal, 1970) is free from this disadvantage and can produce single-crystal alloy films. It is quite suitable in such cases and can produce single crystals which can be studied by electron microscopy and electron diffraction for microstructure and atomic structure of the alloy. This method is quite quick compared with the method adopted by Sato, Toth & Honjo (1967) and has an added advantage that it can be used for producing alloys of metals whose melting points are widely different.

The above mentioned method has been adopted by us in the present studies. We report that CuSe belongs to the hexagonal system with  $a = 3.94$  and  $c = 2.88$  Å and can be described as a  $2H$  structure. This phase is nucleated in the initial inter-diffusion process, but as the crystallites are allowed to grow, a  $12H$  modulated structure is formed with  $a = 3.94$  and  $c = 17.28$  Å, which are the same values as observed by Earley (1949) for his sample. The detailed structures of both basic and  $12H$  modifications have also been worked out. The agreement between the observed intensities and those calculated on the basis of the atomic coordinates of the proposed structure is found to be good.

### Experimental procedure

Copper and selenium of 99.99% purity were co-deposited in the thickness range of 200 to 500 Å in equi-

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atomic proportion by the vacuum evaporation method on a thin Formvar substrate at a pressure of  $10^{-5}$  torr without breaking the vacuum. In this method selenium was the first to be deposited and was followed by copper. For the reasons discussed at length in our earlier paper (Arunsingh *et al.*, 1970), this order of deposition is necessary for the alloy production. The specimen was transferred on a Cu grid in the usual manner and then investigated in the electron microscope.

Initial recording of the powder pattern showed face-centred cubic lines corresponding to copper. The pattern of selenium did not appear because it has an amorphous character in thin film form. The film couple was then pulse-annealed with a focused electron beam in the electron microscope. This process is known (Arunsingh *et al.*, 1970) to produce single-crystal alloy films through interdiffusion. The changed powder pattern is shown in Fig. 1 which can be completely indexed in terms of a hexagonal unit cell with  $a=3.94$  and  $c=2.88$  Å. The individual crystallites in this case were small so the single-crystal pattern could not be recorded.

Further pulse annealing led to grain growth and the formation of single-crystal regions with sizes greater than a few microns. In the micrograph we could definitely locate two types of regions. One such region which shows no features is presented in Fig. 2. The diffraction pattern obtained from such a region is shown in Fig. 3. This has a hexagonal symmetry and the orientation is (00.1). In the second type of nucleated region there are numerous stacking fault fringes and thin platelets. Typical transmission electron micrographs exhibiting this feature are shown in Figs. 4 and 5. The diffraction photographs from these faulted regions are shown in Figs. 6 and 7 and these exhibit a modulated structure. Attempts were also made to record diffraction patterns from the unfaulted crystal as shown in Fig. 2, by tilting it through a small angle. Except in a few cases the tilted unfaulted crystal always produced additional spots besides those arranged on a sixfold grid. These additional spots can be easily seen in Fig. 8 and show that even in unfaulted crystals there is a faulted modulated structure parallel to the  $c$  axis. A large number of observations were taken and the same results could be repeated. Further heating of the unfaulted crystal did not produce any change, whereas faulted crystals tended to become more faulted.

Attempts were made to index the diffraction patterns and it was found that the indexing could be done successfully if the structure corresponded to the hexagonal phase of the CuSe system. It thus became evident that the pattern shown in Fig. 3 represented the basal plane projection of the hexagonal CuSe phase with  $a=3.94$  Å. Since modulations are introduced along the  $c$  axis, which in this case is perpendicular to the film, *i.e.* parallel to the electron beam, their projections cannot be recorded. We have already seen that a small tilting of this region away from this orientation did produce additional spots characteristic of the modulation along

the  $c$  axis. All the crystals having their  $c$  axes perpendicular to the electron beam showed faulted structure and gave rise to the sixfold modulated diffraction spots (Figs. 6 and 7). We are thus led to believe that the CuSe alloy exists in two forms: the basic hexagonal structure with  $a=3.94$ ,  $c=2.88$  Å and the sixfold modulated  $12H$  structure with  $a=3.94$  and  $c=17.28$  Å.

### Crystal structure analysis

Since we have obtained two types of projections of the reciprocal lattice, it is possible to find the structure and compare the intensity between the calculated and the observed values. As the range of the angles in which we are interested is very small, the polarization factor has not been taken into account. To take into account the variation of the atomic scattering factor with  $\theta$  approximately we have multiplied it by the value of  $\lambda/\sin \theta$  for the plane under consideration. Following the usual procedure (Henry, Lipson & Wooster, 1951) one can write down the expression for intensity as

$$I \propto (A_{\text{Cu}}f_{\text{Cu}} + A_{\text{Se}}f_{\text{Se}})^2 + (B_{\text{Cu}}f_{\text{Cu}} + B_{\text{Se}}f_{\text{Se}})^2$$

where

$$A_{\text{Cu}} = \sum_{\text{Cu}} \cos 2\pi(hz + ky + lz)$$

$$B_{\text{Cu}} = \sum_{\text{Cu}} \sin 2\pi(hx + ky + lz),$$

with a similar expression for Se atoms. Here  $x, y, z$  are atomic coordinates and  $h, k$  and  $l$  are indices of the plane whose reflexion we are considering.  $f_{\text{Cu}}$  and  $f_{\text{Se}}$  are the atomic scattering factors of Cu and Se atoms. For the purpose of the present calculations we have replaced them by the atomic numbers of these elements.

To determine the structure one must know the number of atoms per unit cell. The consideration of atomic radii along with observations of Earley (1949) led us to the conclusion that there should be six molecules of CuSe in the modified structure. Further it was noticed that the 30.0 spots were outstandingly strong; this suggested that some of the atoms must be located at  $\frac{1}{3}, \frac{2}{3}, z$  or  $\frac{1}{3}, \frac{1}{3}, z$  the former being the special position of the close packed structure. The appearance of (00.1) spots gave the clue that  $z$  should not be  $\frac{1}{2}$ . Taking all these factors into account many trial calculations were made and finally we found that the positions given in Table 1 for the basic structure and in Table 2 for the modified structure gave the best fit with the intensity sequence. For the case of basic structure, qualitative agreement between the observed intensities (see Fig. 1) and the calculated intensities was found. However, since the dominant grain orientation for the basic  $2H$  structure was (00.1), the diffraction lines with  $l=0$  exhibited spottiness and were weak. Therefore it was not possible to obtain a quantitative match between observed and calculated intensities for all the diffraction lines. The calculated and observed ' $d$ ' values for the basic structure are presented in Table 3. Similarly for the modified structure the calculated and ob-

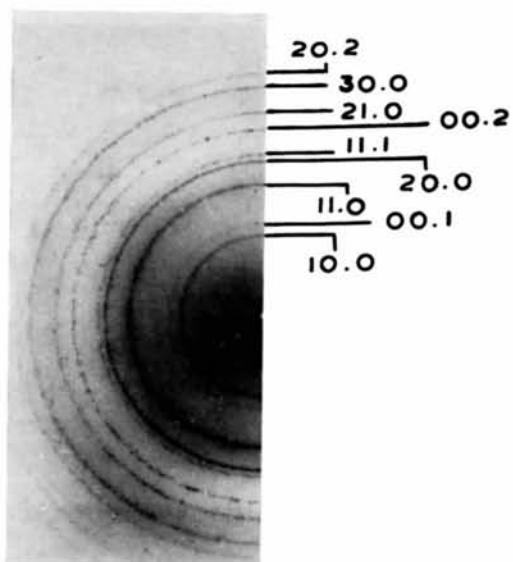


Fig. 1. The powder pattern recorded in initial stages of pulse annealing.

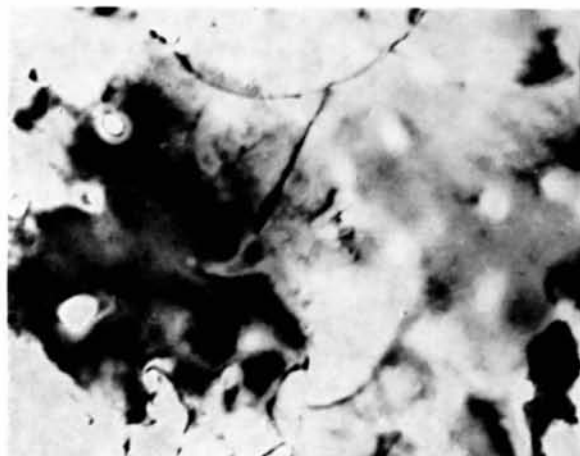


Fig. 2. Featureless region which gave the basal plane pattern of Fig. 3 (Magnification 40,000).

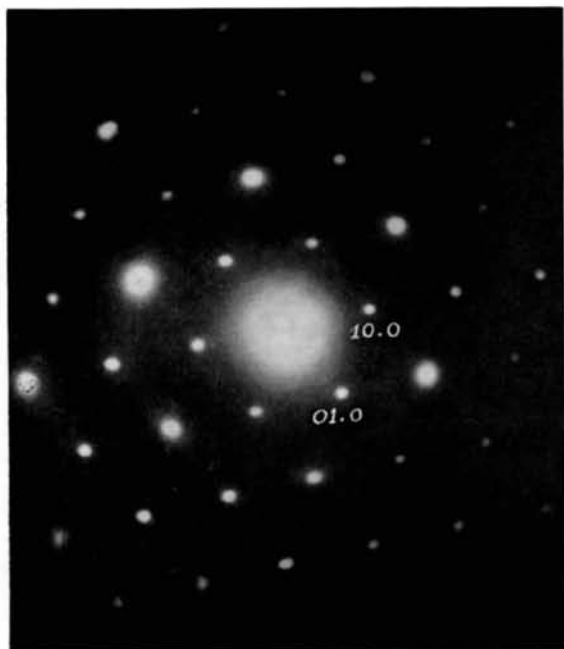


Fig. 3. Single-crystal pattern corresponding to the micrograph of Fig. 2.



Fig. 4. Faulted region, which gave the sixfold modulated pattern as shown in Fig. 6 (Magnification 80,000).

served intensity sequences for the single-crystal pattern for 10.*l* and 11.*l* are given in Table 4.

Table 1. Atomic coordinates of basic CuSe (2H)

A	Cu	000
A'	Se	$\frac{1}{3}\frac{1}{3}\frac{1}{3}$

Table 2. Atomic coordinates of modified CuSe (12H)

	Cu		Se
A	000	A'	$\frac{1}{3}\frac{1}{3}\frac{1}{3}$
B	$\frac{1}{3}\frac{2}{3}\frac{1}{3}$	B'	$\frac{2}{3}\frac{0}{3}\frac{4}{3}$
A	$\frac{0}{3}\frac{2}{3}\frac{2}{3}$	A''	$\frac{1}{3}\frac{2}{3}\frac{7}{3}$
C	$\frac{2}{3}\frac{1}{3}\frac{6}{3}$	C'	$\frac{3}{3}\frac{1}{3}\frac{8}{3}$
B	$\frac{1}{3}\frac{2}{3}\frac{6}{3}$	B''	$\frac{0}{3}\frac{2}{3}\frac{10}{3}$
A	$\frac{1}{3}\frac{2}{3}\frac{6}{3}$	A''	$\frac{2}{3}\frac{0}{3}\frac{13}{3}$
	000		$\frac{1}{3}\frac{2}{3}\frac{8}{3}$

Table 3. Calculated and observed 'd' values in Å for the basic CuSe (2H) structure

Ring number	$d_{\text{calc}}$	$d_{\text{obs}}$	Plane
1	3.52	3.37	10.0
2	2.88	2.82	0.1
3	1.97	1.97	11.0
4	1.70	1.70	20.0
5	1.61	1.61	11.1
6	1.44	1.44	0.2
7	1.29	1.29	21.0
8	1.14	1.14	30.0
9	1.09	1.09	20.2

Table 4. Calculated and observed intensity of modified 12H structure of CuSe

Plane	$I_{\text{calc}}$	$I_{\text{obs}}$
10.1	4.4	<i>m</i>
10.2	3.0	<i>w</i>
10.3	8.9	<i>s</i>
10.4	2.2	<i>m</i>
10.5	1.4	<i>w</i>
10.6	3.0	<i>m</i>
11.1	0	<i>vw</i>
11.2	9.6	<i>s</i>
11.3	0	<i>vw</i>
11.4	9.6	<i>s</i>
11.5	0	<i>vw</i>
11.6	27	<i>vs</i>

### Discussion

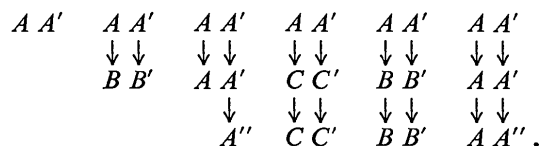
The stabilization of the ordered alloy phases is known to be due to several factors. For example Sato & Toth (1961, 1968) and Sato, Toth & Honjo (1967) have shown in a series of papers that the electron:atom ratio governs the nucleation of various stable phases. The stability of phases is governed by the interaction between the Fermi surface and Brillouin zone of the structures. In such a situation the structure is sensitive to the composition. We therefore changed the percentage of one metal component and found that it did not affect the growth of the observed phase. We believe that the occurrence of the 12H phase is not governed

by the electron: atom ratio, *i.e.* by the interaction of Brillouin zone with Fermi surface.

Several alloy phases (Bradley & Taylor, 1937; Hume-Rothery, Batterton & Reynolds, 1952) are known to occur as defect structures and their stabilization is controlled by the fact that the stable phase structures can accommodate vacant lattice sites. Unlike the aforesaid case, in such a situation the phase has vacant sites and thus less electrons. The deficit electron concentration stabilizes the phase. The defect structures can be identified in two ways. Firstly, there is a contraction in the lattice constants. Further, since more than one identical unit cell in different orientations can be derived for the defect structure, these exhibit domain structures in transmission electron micrographs. However, in the present case evidence for none of the above facts was found, so we do not think that the observed phase corresponds to a defect structure.

A variety of alloy phases are nucleated as a result of martensitic transformations. In such transformations the structure stabilizes as a result of shear in the parent lattice. The shear usually produces stacking faults and the structure can be considered to have been produced by the occurrence of a sequence of stacking faults in the parent structure (Toth & Sato, 1968; Hirabayasi, Yamaguchi, Hiraga, Ino, Sato & Toth, 1970). In such structures electron microscopy reveals the presence of stacking faults as well as martensitic structure strips and plates. The present observation revealed the presence of both these features. We therefore conclude that the modulated 12H structure is stabilized due to shear in the 2H structure and consequently we observed stacking faults.

If we represent the parent structure of CuSe by  $A A'$  where the prime indicates the position of Se atoms, the basis structure of 2 layers can be transformed into the derived structure of 12 layers. We present below a scheme for the derivation of the modulated structure from the basic structure:



Thus the modified structure has the form  $A A' B B' A A'' C C' B B' A A'' \dots$ . It is a shear structure and can be derived from the parent structure by shear operation. The same is evident from Fig. 9 which shows the projection of the *b* axis on the *ac* plane.

When the unfaulted crystals are tilted their micrographs also show contrast similar to those observed with faulted crystals. This observation clearly indicates that the presumed stacking faults producing modulated structures must be parallel to the basal planes. This is in agreement with the scheme proposed for the derivation of modulated structure since stacking faults parallel to the layers have been envisaged. An exact determination of the displacement vectors characterizing



Fig. 5. Faulted region which gave the sixfold modulated pattern of Fig. 7 (Magnification 40,000).

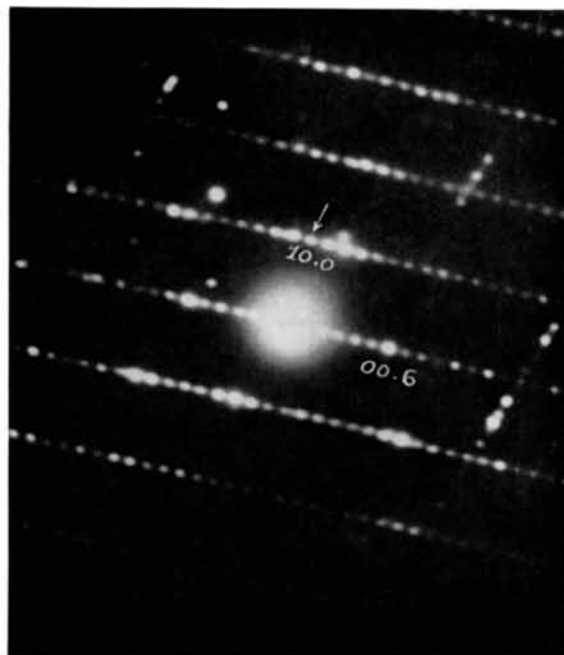


Fig. 6. Single-crystal pattern corresponding to the micrograph of Fig. 4.



Fig. 7. Single-crystal pattern corresponding to the micrograph of Fig. 5.



Fig. 8. Single-crystal pattern showing additional spots when the featureless region shown in Fig. 4 was slightly tilted.

the stacking faults through contrast pictures was, however, not possible and it seemed that more than one vector was involved, which is also evident from the proposed modulated structure sequence.

Our work supports the observation of Earley (1949) that the structure of CuSe is hexagonal with  $a=3.94$ ,  $c=17.28$  Å. However, we did not find any evidence to support Earley's (1949) conclusion that the structure is modulated along the  $a$  axis. Neither did we find any evidence of twinning as presumed by Taylor & Underwood (1960) and reported by Elliot, Bicknell & Collinge (1969). Elliot *et al.* have investigated synthetic CuSe by electron diffraction and confirmed the twinning hypothesis of Taylor & Underwood. A clear electron diffraction photograph made available to us by Professor H. Lipson shows unmistakable evidence of twinning. It is possible that the difference in results obtained by us and Elliot *et al.* is due to different methods of preparation of the CuSe specimens. This is not the singular case where difference in observed structural

features may be due to the different methods adopted for preparation of the specimen. Several such cases are known to exist (Mader, 1966). Elliot *et al.* have found that even different methods of mounting the same specimen lead to different results, regarding the presence of the superlattice and the twinning. Further investigations are needed to understand why different characteristics are shown by the synthetic specimens examined by Elliot *et al.* and the thin-film single-crystal specimens investigated by us.

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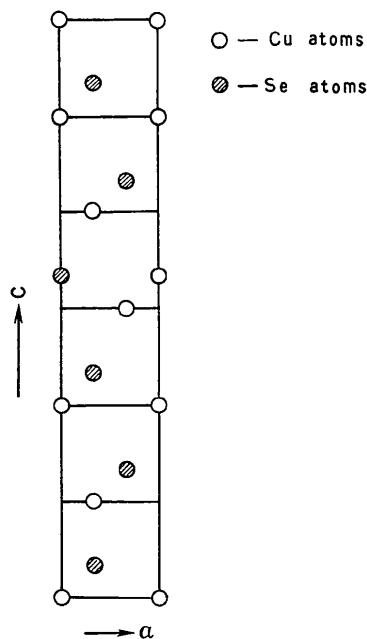


Fig. 9. Projection parallel to the  $b$  axis on the  $ac$  plane of the proposed  $12H$  structure of CuSe.