

## The Crystal Structure of $\text{CuAsSe}_{0.8}\text{S}_{0.2}$ and Related Compounds

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The structure of  $\text{CuAsSe}_x\text{S}_{1-x}$  in the composition range  $0.5 < x < 0.9$  has been determined by single-crystal X-ray and electron diffraction and high-resolution electron microscopy.  $\text{CuAsSe}_{0.8}\text{S}_{0.2}$  is found to be orthorhombic with space group *Pbcn* and unit cell dimensions  $a = 11.66 \pm 0.02 \text{ \AA}$ ,  $b = 6.73 \pm 0.01 \text{ \AA}$ , and  $c = 25.41 \pm 0.03 \text{ \AA}$ . The structure was inferred by comparing the electron and X-ray diffraction patterns with those from  $\text{CuAsSe}$ , and was isotropically refined to  $R = 0.16$  for 287 observed X-ray reflections. High-resolution electron microscopy was used to confirm the structure by matching observed and calculated images and to show the presence of stacking faults in the crystals. The atomic positions of  $\text{CuAsSe}_{0.8}\text{S}_{0.2}$  are related to the *8H-ZnS* polytype structure. In Jagodzinski nomenclature it has *hccchccc* stacking. Powder X-ray and single crystal electron diffraction patterns of  $\text{CuAsSe}_{0.75}\text{S}_{0.25}$  and  $\text{CuAsSe}_{0.9}\text{S}_{0.1}$  were consistent with the same structure-type. Single-crystal X-ray diffraction of  $\text{CuAsSe}_{0.6}\text{S}_{0.4}$  showed it to be isostructural with  $\text{CuAsS}$  with orthorhombic space group *Pnam* and unit cell dimensions  $a = 11.59 \pm 0.02 \text{ \AA}$ ,  $b = 5.56 \pm 0.01 \text{ \AA}$ , and  $c = 3.827 \pm 0.005 \text{ \AA}$ . The same structure-type was found for  $\text{CuAsSe}_{0.5}\text{S}_{0.5}$  and  $\text{CuAsSe}_{0.67}\text{S}_{0.33}$  using X-ray powder diffraction.

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### Introduction

The crystal structure of the mineral lautite,  $\text{CuAsS}$ , is related to the *3C* form of  $\text{ZnS}$ , both the Zn and S atoms being replaced by equal numbers of three kinds of atoms (1, 2). The Se analog of lautite,  $\text{CuAsSe}$  has a structure related to the *6H* form of  $\text{ZnS}$  (3). Alternately using Strukturbericht and Jagodzinski notation,  $\text{CuAsS}$  is related to the *B3* structure with *ccc* stacking and  $\text{CuAsSe}$  to the *B6* structure with *hchcc* stacking along the *c*-axis. High-resolution micrographs obtained with a JEOL 200 CX electron microscope have been found to give direct confirmation of the stacking sequence in this tetrahedrally bonded structure (4). The X-ray powder

diffraction pattern of  $\text{CuAsSe}_{0.8}\text{S}_{0.2}$  could not be indexed in terms of *ccc* or *hcc* stacking and it was suggested that a different type of stacking might be present (3). The present paper describes the preparation of  $\text{CuAsSe}_{1-x}\text{S}_x$  in the composition range  $0.5 < x < 0.9$  and its structure determination using X-ray and electron diffraction and high-resolution electron microscopy. For  $0.5 < x < 0.67$  the  $\text{CuAsS}$ -type structure was observed, whereas for  $0.75 < x < 0.9$  a new polytype with *hccchccc* stacking was found by single crystal X-ray and electron diffraction and confirmed by high-resolution electron microscopy.

### Experimental

#### Sample Preparation

Mixed chalcogenides  $\text{CuAsSe}_x\text{S}_{1-x}$  in the composition range  $0.5 < x < 0.9$  were pre-

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pared by direct combination of the elements in stoichiometric proportions in evacuated glass ampoules. Samples were annealed for a minimum of 48 hr just below the solidus curve to promote crystal growth and homogenization. Single crystals were obtained by sublimation of  $\text{CuAsSe}_{0.6}\text{S}_{0.4}$  and  $\text{CuAsSe}_{0.8}\text{S}_{0.2}$  samples and these were examined by X-ray diffraction. For  $x = 0.5, 0.67, 0.75,$  and  $0.9$  only very small crystals were obtained and these were examined by X-ray powder diffraction. All specimens were studied by electron diffraction and high-resolution electron microscopy.

#### Single Crystal X-Ray Diffraction

Precession data of  $\text{CuAsSe}_{0.6}\text{S}_{0.4}$  were taken with Zr-filtered Mo radiation for layers  $hk0, hk1, h0l, h1l,$  and  $hkk$ . Intensities estimated visually by comparison with a calibrated series of spots were corrected for Lorentz and polarization effects, and scaled using reflections common to different layers. No corrections were applied for absorption. Out of a total of 207 possible reflections, 78 were below the limit of detection. Systematic absences were in accord with the space groups  $Pnam$  or  $Pna2_1$ .

Precession data of  $\text{CuAsSe}_{0.8}\text{S}_{0.2}$  were taken with Zr-filtered Mo radiation for layers  $0kl-4kl$  and  $6kl$ . Visually estimated intensities were corrected for Lorentz and polarization effects but not for absorption. Out of a total of 818 possible reflections, 531 were below the limits of detection. Systematic absences were in accord with the space group  $Pbcn$ . Unit cell dimensions of both types of crystals were obtained from the precession photographs.

*Crystal data.*  $\text{CuAsSe}_{0.6}\text{S}_{0.4}$ ,  $M = 198.67$ , orthorhombic,  $a = 11.59 \pm 0.02 \text{ \AA}$ ,  $b = 5.56 \pm 0.01 \text{ \AA}$ ,  $c = 3.827 \pm 0.005 \text{ \AA}$ ,  $U = 246.6 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 5.35 \text{ g} \cdot \text{cm}^{-3}$ ,  $F(000) = 355.2$ ,  $\text{MoK}\alpha$  radiation,  $\lambda = 0.7107 \text{ \AA}$ .

*Crystal data.*  $\text{CuAsSe}_{0.8}\text{S}_{0.2}$ ,  $M = 208.05$ , orthorhombic  $a = 11.66 \pm 0.02 \text{ \AA}$ ,  $b = 6.73 \pm 0.01 \text{ \AA}$ ,  $c = 25.41 \pm 0.03 \text{ \AA}$ ,  $U = 1994 \text{ \AA}^3$ ,

$Z = 32$ ,  $D_c = 5.54 \text{ g} \cdot \text{cm}^{-3}$ ,  $F(000) = 2957$ ,  $\text{MoK}\alpha$  radiation,  $\lambda = 0.7107 \text{ \AA}$ .

The single crystals were not chemically analyzed but the position of the strong sublattice peaks of a powder diffractogram of the bulk sample were in accord with the lattice parameters obtained from the single crystals confirming they were of the same stoichiometry.

#### Electron Diffraction and High-Resolution Electron Microscopy

Specimens suitable for electron microscopy were prepared by crushing the samples in an agate mortar. The thin crystals were placed on holey carbon films and examined in a JEOL 200 CX high-resolution electron microscope. The instrument was equipped with a  $\text{LaB}_6$  filament, a double-gap condenser, and a high-resolution goniometer stage which allowed the crystals to be tilted  $\pm 10^\circ$  about two orthogonal axes. The specimens were placed very low in the objective lens to reduce spherical aberration. The value of the spherical aberration coefficient,  $C_s$ , was determined by optical diffractograms as  $0.94 \text{ mm}$  (5), and this value was confirmed by image matching known structures with large unit cells. The chromatic aberration constant,  $C_c$  has previously been determined by the same image matching technique and found to be consistent with  $1.2 \text{ mm}$ . However, in the present work it was found that the effect of chromatic aberration could be described by an effective objective aperture with radius  $2 \text{ \AA}$ . The half-angle of the incident beam divergence was  $8 \times 10^{-4} \text{ rad}$  or less. All the images were taken at a nominal magnification of 850,000.

#### Structure Solution and Refinement

##### *Structure of $\text{CuAsSe}_{0.6}\text{S}_{0.4}$*

The systematic absences of reflections from single-crystal X-ray diffraction photographs of  $\text{CuAsSe}_{0.6}\text{S}_{0.4}$  indicated it belongs

TABLE I  
TEMPERATURE FACTORS AND POSITIONAL  
PARAMETERS WITH STANDARD DEVIATIONS IN  
PARENTHESES FOR THE INDIVIDUAL ATOMS IN  
 $\text{CuAsSe}_{0.6}\text{S}_{0.4}$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
As	0.4844(17)	0.1436(13)	0.25	0.6
Se,S	0.1667(9)	0.1728(17)	0.25	1.4
Cu	0.3274(9)	0.4269(17)	0.25	1.6

to space group  $Pnam$  or  $Pna2_1$ . A comparison of diffraction intensities with CuAsS data indicates that CuAsS and  $\text{CuAsSe}_{0.6}\text{S}_{0.4}$  are probably isostructural. The space group chosen for CuAsS in (1) is  $Pna2_1$  with two atoms, As and S, on a mirror plane and the Cu atom displaced from a mirror plane by 0.04 Å. However, analysis of the structure factors in that reference shows that no significant alteration is produced in the reliability index if the Cu atom is also placed on the mirror plane. Therefore in the refinement of the  $\text{CuAsSe}_{0.6}\text{S}_{0.4}$  structure all atoms were assumed to be in positions  $4c$  ( $x, y, \frac{1}{2}$ ) of space group  $Pnam$  and the  $x$  and  $y$  parameters reported for CuAsS were taken as initial values. The S and Se atoms were assumed to be distributed randomly over the chalcogen sites. A least-square refinement led to a reliability index  $R$  of 0.11 for 129 observed  $hkl$  reflections using isotropic temperature factors. No significant alteration in the reliability index resulted when the Cu atom was moved off the mirror plane at  $z = 0.25$  to  $z = 0.26$ . The positional parameters are listed in Table I and selected bond distances and angles in Table II with the corresponding mean values for CuAsS listed for comparison. The bond distances to the chalcogen are slightly greater for the Se-substituted compound in accord with the larger tetrahedral covalent radius of Se (1.14 Å) compared to S (1.04 Å) (6).

Due to the similarity of atomic numbers

of Cu, As, and Se the allotment of lattice sites to Cu and As atoms and of Cu, As, and Se atoms in the structure solutions of CuAsS (1) and CuAsSe (3), respectively, was based not solely on peak heights from a Fourier map, but also by appealing to chemical considerations such as bond distances and angles and coordinations of the different atoms. The substitution of S by Se results in a proportionate increase in electron density at the proposed S site which confirmed the correctness of the structures proposed for CuAsS and CuAsSe. The structures of CuAsS and CuAsSe are shown schematically in the Figs. 1a and b, respectively.

#### Structure of $\text{CuAsSe}_{0.8}\text{S}_{0.2}$

The structure of  $\text{CuAsSe}_{0.8}\text{S}_{0.2}$  was solved by a combination of X-ray and electron diffraction and high-resolution electron microscopy. Figure 2 shows a high-resolution electron micrograph and diffraction pattern viewed down the  $a$ -axis. From the position of the white dots in the image, the stacking sequence could be pro-

TABLE II  
BOND DISTANCES (Å) AND ANGLES (°) FOR  
 $\text{CuAsSe}_{0.6}\text{S}_{0.4}$  AND CuAsS

	$\text{CuAsSe}_{0.6}\text{S}_{0.4}$	CuAsS
Cu-tetrahedron		
Cu-(S,Se)	2.338(17)	2.238
Cu-(S,Se)	2.353(8)	2.322
Cu-As	2.407(13)	2.416
(Se,S)-Cu-(Se,S)	112.0(3)	112.5
(Se,S)-Cu-(Se,S)	108.8(5)	109.8
As-Cu-(S,Se)	101.9(4)	101.0
As-Cu-(S,Se)	111.0(3)	110.5
As-tetrahedron		
As-Cu	2.407(13)	2.416
As-As	2.518(10)	2.490
As-(S,Se)	2.347(12)	2.252
As-As-As	98.9(4)	97.7
As-As-Cu	121.6(3)	121.1
As-As-(Se,S)	98.4(3)	99.3
Cu-As-(Se,S)	113.3(4)	114.2

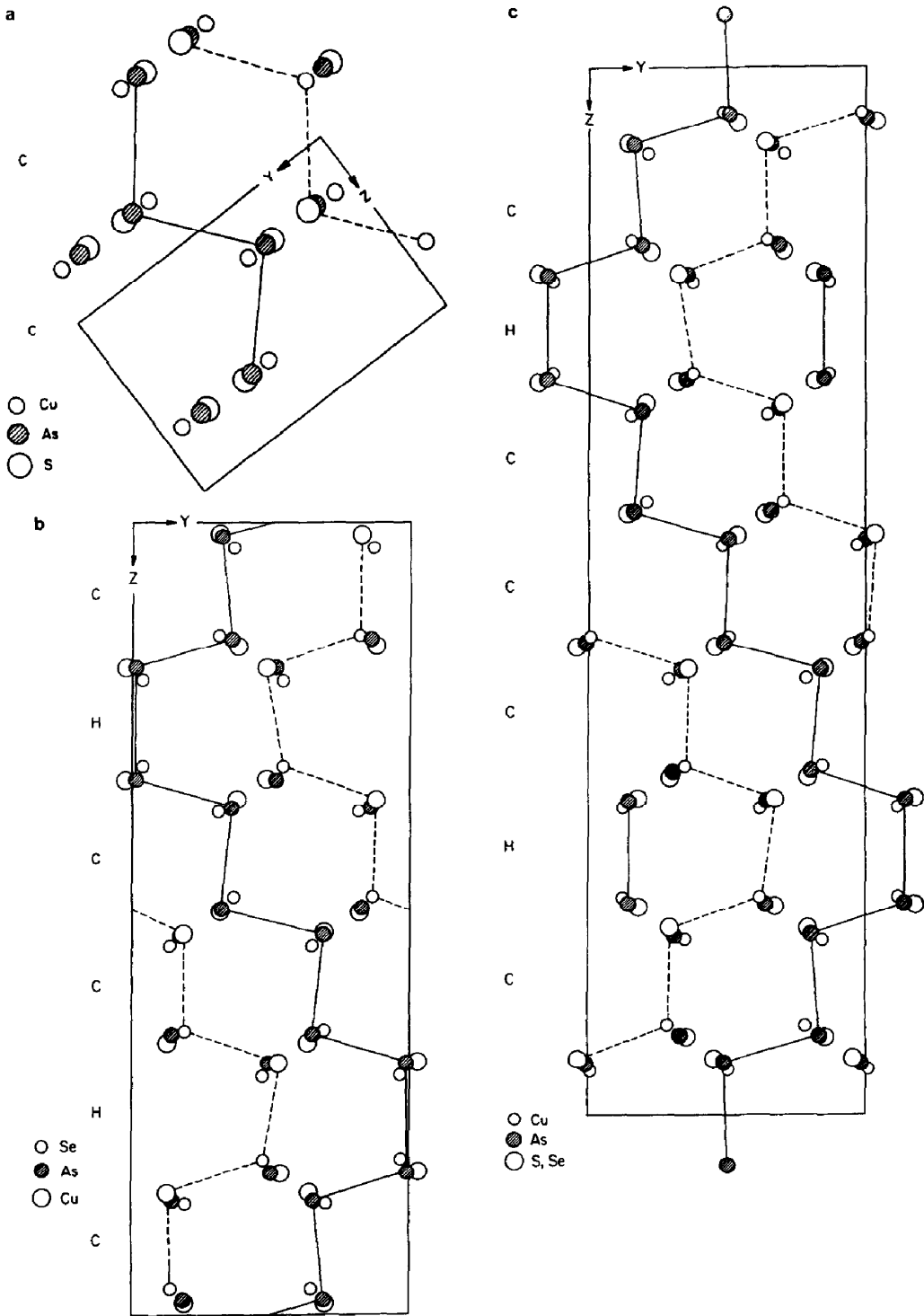


FIG. 1. The [100] projections of the unit cells of (a)  $\text{CuAsS}$ , (b)  $\text{CuAsSe}$ , and (c)  $\text{CuAsSe}_{0.8}\text{S}_{0.2}$ .

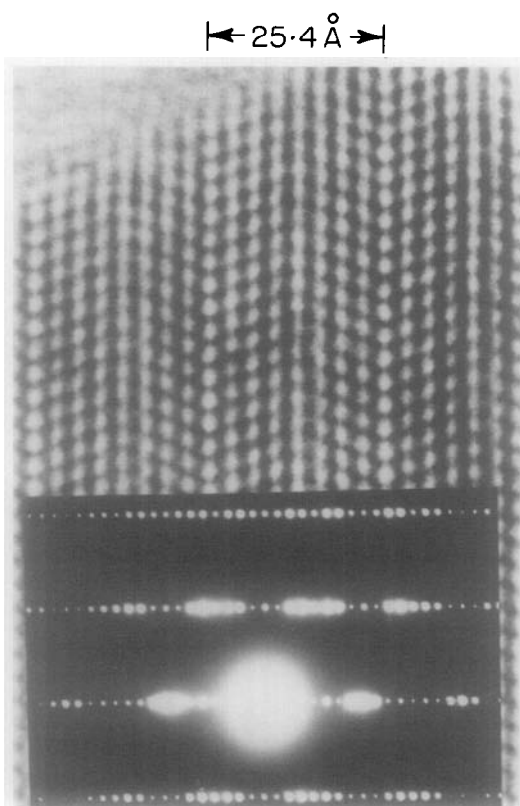


FIG. 2. Experimental high-resolution electron image (top) and selected area diffraction pattern (bottom) of  $\text{CuAsSe}_{0.8}\text{S}_{0.2}$  viewed down  $[100]$ .

posed directly. Subsequent image calculations showed that each white dot corresponds to a tunnel in the structure. High-resolution micrographs of the  $[\bar{1}30]$  crystal orientation showed very similar images to those for the  $[100]$  setting. One example is shown in Fig. 3. The stacking sequence could be proposed directly from the position of the dots in the image. The  $[100]$  and  $[\bar{1}30]$  orientations could not be distinguished by comparing the lattice images without very detailed calculations. The zero-order Laue zone of the electron diffraction patterns are also very similar for these two orientations as can be seen by comparing the Figs. 2b and 3b. However, these two orientations could easily be dis-

tinguished by comparing the first-order Laue zones.

As for  $\text{CuAsSe}$  there is a strong sublattice and a much weaker superlattice with many of the weaker reflections being below the limit of detection in X-ray precession photographs. The high-resolution images and lattice geometry suggested the structure has hccchccc type rather than the hcchcc polytype stacking of  $\text{CuAsSe}$ . A trial structure was chosen with all atoms in general 8d positions of space group  $No\ 60$ ,  $Pbcn$ . Initial position parameters of the 12 atom asymmetric unit of the trial structure had As atoms at lattice points

$$\left(\frac{1}{2}, \frac{1}{3}, \frac{13}{64}\right), \left(0, \frac{1}{6}, \frac{11}{64}\right), \left(0, \frac{1}{6}, \frac{5}{64}\right), \left(\frac{1}{2}, 0, \frac{3}{64}\right),$$

Se at lattice points

$$\left(\frac{1}{6}, \frac{1}{3}, \frac{13}{64}\right), \left(\frac{2}{3}, \frac{1}{6}, \frac{11}{64}\right), \left(\frac{1}{3}, \frac{1}{6}, \frac{5}{64}\right), \left(\frac{5}{6}, 0, \frac{3}{64}\right),$$

and Cu at lattice points

$$\left(\frac{5}{6}, \frac{1}{3}, \frac{13}{64}\right), \left(\frac{1}{3}, \frac{1}{6}, \frac{11}{64}\right), \left(\frac{2}{3}, \frac{1}{6}, \frac{5}{64}\right), \left(\frac{1}{6}, 0, \frac{3}{64}\right).$$

These initial position parameters were derived from the  $8H\text{-ZnS}$  polytype positions (7) by appropriate choice of origin and taking into account the larger unit cell and the lowered symmetry of the space group. The deviations of the atom coordinates from these ideal sites were determined experimentally from the intensities of the weak and unobserved superlattice reflections by difference Fourier and least-square structure factor refinement of X-ray single-crystal data.

The differentiation between atom types could not be based solely on the relative peak heights of Fourier maps due to the similarity of the atomic numbers of the Cu, As, and Se. Therefore atoms were allotted to lattice points on the basis of general chemical considerations and assuming that the coordination of the various atoms will be similar. Thus in  $\text{CuAsSe}_{0.8}\text{S}_{0.2}$  each As atom is coordinated to two other As atoms, one chalcogen, and one Cu atom while each Cu atom is coordinated to three chalcogen

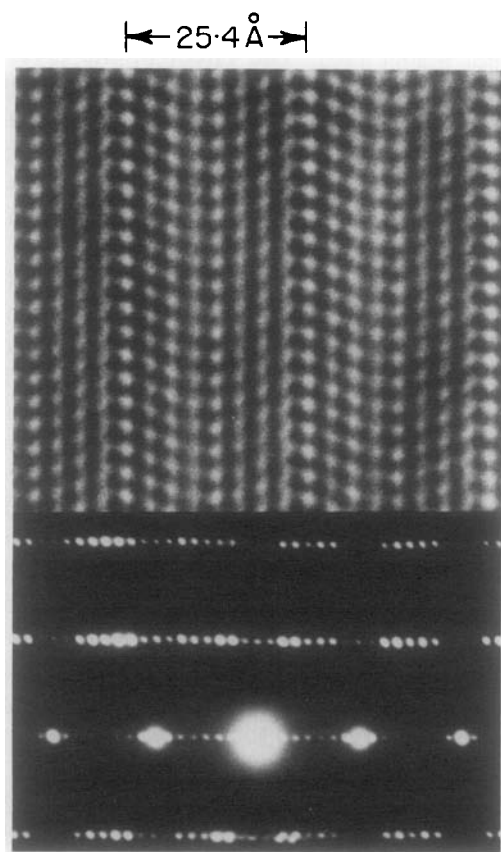


FIG. 3. Experimental high-resolution image (top) and selected area diffraction pattern (bottom) of  $\text{CuAsSe}_{0.8}\text{S}_{0.2}$  viewed down  $[130]$ .

TABLE III  
ATOMIC COORDINATES FOR IDEAL AND REFINED  
 $\text{CuAsSe}_{0.8}\text{S}_{0.2}$  STRUCTURE

	Ideal			Refined		
	x	y	z	x	y	z
As(1)	.500	.333	.203	.479(2)	.349(1)	.2010(5)
As(2)	.000	.167	.172	.989(2)	.195(1)	.1716(5)
As(3)	.000	.167	.078	.010(2)	.164(1)	.0754(5)
As(4)	.500	.000	.047	.512(2)	.015(1)	.0484(5)
Se(1)	.167	.333	.203	.162(2)	.318(1)	.1992(5)
Se(2)	.667	.167	.172	.656(2)	.205(1)	.1775(5)
Se(3)	.333	.167	.078	.343(2)	.142(1)	.0734(5)
Se(4)	.833	.000	.047	.842(2)	.034(1)	.0525(5)
Cu(1)	.833	.333	.203	.843(2)	.377(1)	.2075(5)
Cu(2)	.333	.167	.172	.342(2)	.150(1)	.1668(5)
Cu(3)	.667	.167	.078	.674(2)	.205(1)	.0844(5)
Cu(4)	.167	.000	.047	.160(2)	.975(1)	.0423(5)

and one As atom. The Se and S atoms are assumed to be distributed randomly on chalcogen sites.

Least-square refinement for all 818 reflections using one isotropic temperature factor ( $B = 0.1 \text{ \AA}^2$ ) for all 12 atoms gave  $R = 0.16$  for the 287 observed reflections. The final positional parameters of the 12 atoms in the asymmetric unit of the unit cell are listed in Table III and the interatomic distances and bond angles in Table IV. The structure of  $\text{CuAsSe}_{0.8}\text{S}_{0.2}$  is shown schematically in Fig. 1c. A Table of observed and calculated structure factors has been deposited with the ASIS National Auxiliary Publications Service.<sup>1</sup>

#### Other $\text{CuAsSe}_x\text{S}_{1-x}$

Powder X-ray patterns for  $\text{CuAsSe}_x\text{S}_{1-x}$  where  $x$  has the values 0.5 and 0.67 were indexed in terms of the  $\text{CuAsS}$  structure. For values of  $x = 0.75$  and 0.90 the powder patterns were consistent with the  $\text{CuAsSe}_{0.8}\text{S}_{0.2}$  structure. The lattice dimensions increase monotonically as S is replaced with Se (see Table V).

#### High-Resolution Imaging of $\text{CuAsSe}_{0.8}\text{S}_{0.2}$

In order to confirm the refined structure of  $\text{CuAsSe}_{0.8}\text{S}_{0.2}$  experimental high-resolution lattice images were compared with calculated ones. The lattice images were calculated using the multislice formulation of the dynamical theory for the electron scattering (8, 9). Due to the long periodicities in

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TABLE IV  
DISTANCES WITH STANDARD DEVIATIONS IN  
PARENTHESES AND ANGLES FOR  $\text{CuAsSe}_{0.8}\text{S}_{0.2}$

(a) Distances (Å)			
As(1)–As(1)	2.53(1)	Se(1)–Cu(1)	2.40(1)
As(1)–As(2)	2.47(1)	Se(1)–Cu(2)	2.38(1)
As(2)–As(3)	2.46(1)	Se(1)–Cu(2)	2.51(3)
As(3)–As(4)	2.47(1)	Se(2)–Cu(1)	2.34(1)
As(4)–As(4)	2.48(1)	Se(2)–Cu(1)	2.59(3)
As(1)–Se(2)	2.35(3)	Se(2)–Cu(3)	2.37(1)
As(2)–Se(1)	2.30(3)	Se(3)–Cu(2)	2.37(1)
As(3)–Se(4)	2.22(3)	Se(3)–Cu(4)	2.38(1)
As(4)–Se(3)	2.23(3)	Se(3)–Cu(4)	2.54(3)
As(1)–Cu(2)	2.26(3)	Se(4)–Cu(3)	2.41(3)
As(2)–Cu(1)	2.20(3)	Se(4)–Cu(3)	2.37(1)
As(3)–Cu(4)	2.32(3)	Se(4)–Cu(4)	2.40(1)
As(4)–Cu(3)	2.46(3)		
(b) Mean angles (°)			
As-tetrahedra			
As–As–As		102.5	
As–As–Cu		120.2	
As–As–(Se,S)		100.4	
Cu–As–(Se,S)		109.8	
Cu-tetrahedra			
As–Cu–(Se,S)		109.0	
(Se,S)–Cu–(Se,S)		109.8	
(Se,S)-tetrahedra			
As–(Se,S)–Cu		111	
Cu–(Se,S)–Cu		107.8	

the crystals parallel to the incident electron beam, the slice thickness in the calculations was  $\frac{1}{4}$  of the repeat distance. The calculations were carried out using a special purpose computer program of Lynch. Atomic

TABLE V  
STRUCTURE TYPE, UNIT CELL DIMENSIONS, AND  
SPACE GROUP FOR  $\text{CuAsSe}_{1-x}\text{S}_x$

$x$	Structure	$a, b, c$ (Å)	S.G.
0	ccc	11.35, 5.46, 3.749	<i>Pnam</i>
0.5	ccc	11.55, 5.55, 3.810	<i>Pnam</i>
0.6	ccc	11.59, 5.56, 3.827	<i>Pnam</i>
0.67	ccc	11.61, 5.57, 3.830	<i>Pnam</i>
0.75	hccchccc	11.65, 6.72, 25.41	<i>Pbcn</i>
0.8	hccchccc	11.67, 6.74, 25.41	<i>Pbcn</i>
0.9	hccchccc	11.71, 6.76, 25.51	<i>Pbcn</i>
1.0	hcchcc	11.75, 6.79, 19.21	<i>Pbcn</i>

scattering factors were taken from Cromer and Waber (10). The effect of the divergence of the incident electron beam was taken into account by incoherent summation of images over different angles. The chromatic aberration was simulated by using an effective objective aperture with radius 2 Å.

Figure 4 shows a comparison of experimental and calculated lattice images of  $\text{CuAsS}_{0.2}\text{Se}_{0.8}$  in the [100] orientation. Image calculations were carried out for both the [100] and  $[\bar{1}30]$  zone axis orientations. Images for off-axis crystal orientations were calculated using a modified computer program. Details of these calculations will be reported elsewhere (11). The experimental images in Fig. 4a and b are very well reproduced by calculations for a crystal of thickness 174 Å at defects of focus  $-600$  and  $-900$  Å. In Fig. 4a the white dots correspond to columns of atoms whereas in Fig. 4b they correspond to tunnels in the structure.

High-resolution electron microscopy of  $\text{CuAsSe}_{1-x}\text{S}_x$  with  $0.75 < x < 0.9$  showed evidence in many samples of crystal imperfections. Even apparently well-ordered crystals showed occasional stacking sequences different from hccchccc (or 4,4 in Zhdanov notation). One example is shown in Fig. 5 where stacking sequences hccccchccc (7,4) and hccchccc (5,4) are indicated.

## Conclusion

The structure of  $\text{CuAsSe}_{1-x}\text{S}_x$  in the range  $0.5 < x < 0.9$  has been determined by a combination of single-crystal X-ray and electron diffraction and high-resolution electron microscopy. Increase in  $x$  leads to an increase in the percentage of hexagonal stacking. Thus for  $x$  values 0.5, 0.6, 0.67 only cubic stacking (ccc) is found as in  $\text{CuAsS}$  (1). For  $x$  values of 0.75, 0.8, and 0.9 the stacking is hccchccc and for  $x$  equal

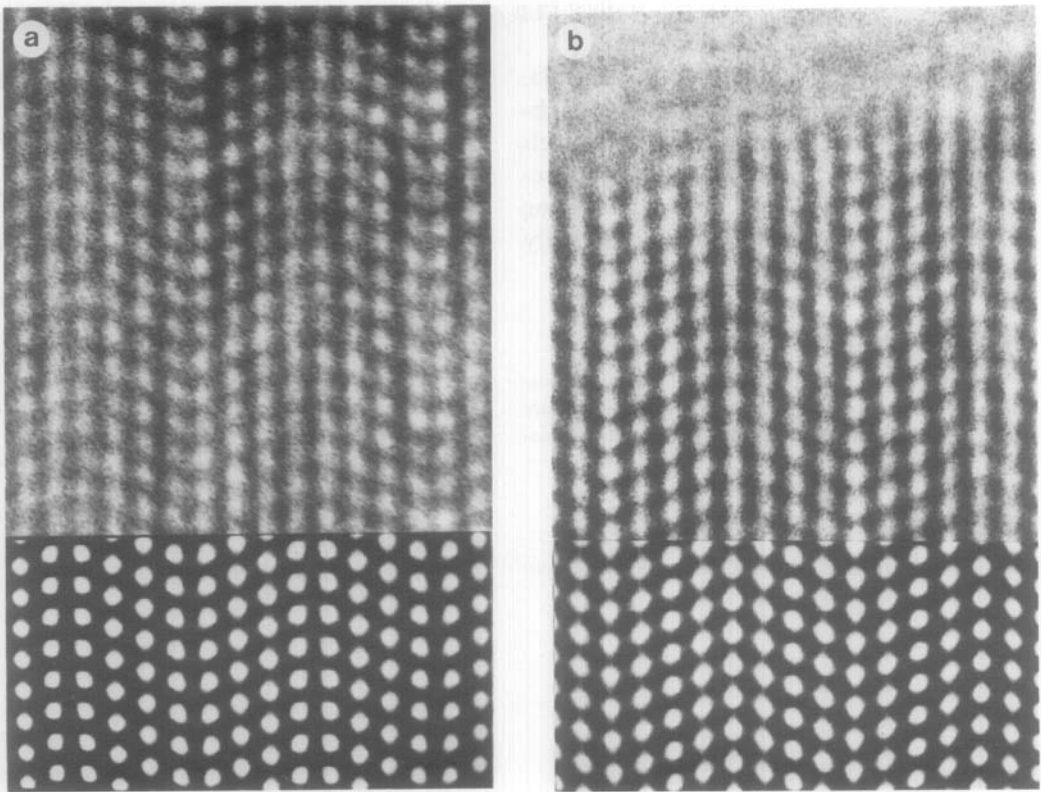


FIG. 4. Comparison of experimental and calculated lattice images of  $\text{CuAsSe}_{0.8}\text{S}_{0.2}$  in [100] orientation at defects of focus (a)  $-600 \text{ \AA}$  and (b)  $-900 \text{ \AA}$ .

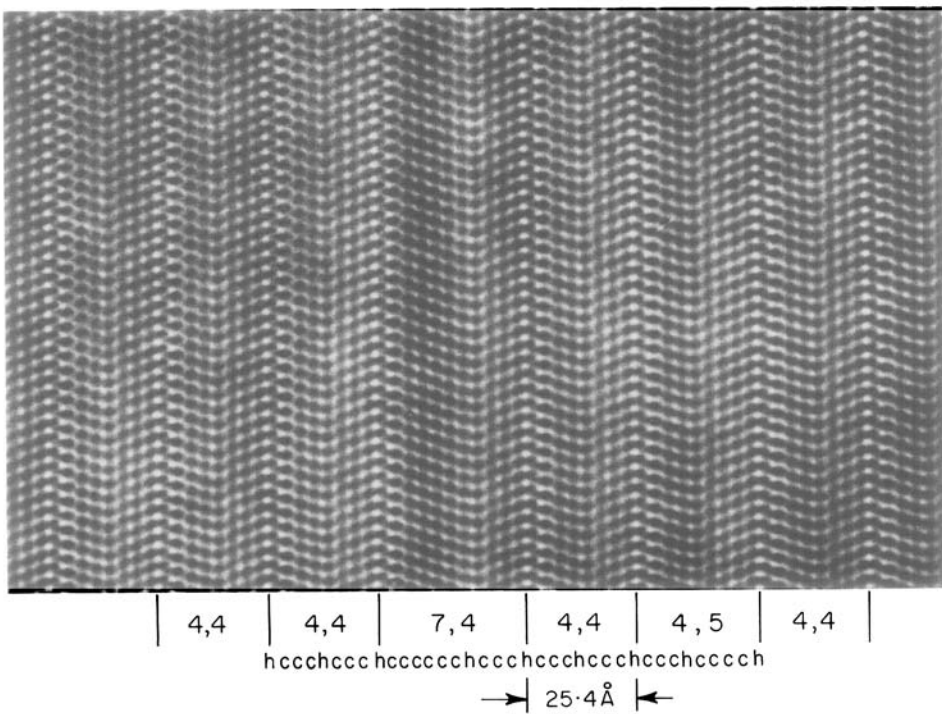


FIG. 5. Experimental lattice image of  $\text{CuAsSe}_{0.8}\text{S}_{0.2}$  in [100] orientation showing two stacking faults.



to 1 (CuAsSe) the stacking is hcchcc (3). The present work demonstrated that high-resolution electron microscopy is an excellent method for identifying polytype structures of new compounds and for observing and characterizing faults in tetrahedrally coordinated compounds.

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