The Crystal Structure of hcc-CuAsSe

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The crystal structure of synthetic copper arsenic selenide CuAsSe, has been determined by a three-dimensional single-crystal X-ray examination using film data. The crystals, of orthorhombic space group *Pbcn*, have $Z = 24$ in a unit cell of dimensions $a = 11.75 \pm 0.02$, $b = 6.79 \pm 0.01$, and $c = 19.21 \pm 0.03$ Å. The structure was solved by Patterson projection and electron density methods and isotropically refined to $R = 0.125$ for 300 observed reflections. The structure of CuAsSe is related to the *B*6 structure of 6*H* ZnS as CuAsS is to the *B*3 structure of zincblende. Alternately in Jagodzinski nomenclature CuAsSe has hcc packing rather than ccc packing of CuAsS.

Introduction

Various inorganic materials such as SiC, ZnS, CdI_2, and TaS_2 exhibit polytypism and this fact has been exploited to probe the influence of structure on physical properties (*1*).

There is a large class of structures that are obtained from the basic zincblende and wurtzite structures by either statistical or regular replacement of zinc by two or more kinds of atom. Polytypism has been reported for these derivative structures (*2*). A rather different structure is that of CuAsS, which is derived from the zincblende structure by replacement of both the zinc and sulfur atoms by equal numbers of three kinds of atoms. We have searched for the occurrence of polytypes of this structure by partial or complete replacement of the sulfur in CuAsS with selenium.

The crystal structure of lautite, CuAsS, was determined independently by Craig and Stevenson (*3*) and by Marumo and Nowacki (*4*). The latter authors refined the

structure in the centrosymmetric space group *Pnma*, but the former authors showed that a significantly better fit to their data was obtained by refinement in space group *Pna*2_1. All three kinds of atoms (Cu, As, S) occupy the equipoints of a zincblende (or diamond) lattice in such a way that each Cu is surrounded by 1 As + 3 S, each As by 1 Cu + 2 As + 1 S, and each S by 1 As + 3 Cu. There is a simple relationship between the lengths of the three axes of CuAsS, namely, $2^{1/2}/3a \approx 2^{1/2}c \approx b \approx a(\text{ZnS})$.

Kamsu Kom (*5*) in a brief report of the preparation of CuAsSe, AgAsS, and AgAsSe concluded that these three compounds are isostructural with lautite CuAsS on the basis of visual estimates of intensities of the lines of an X-ray powder diffraction pattern.

I have synthesized CuAsSe but have not obtained crystals with the simple lautite structure. Instead, the crystals have a structure which bears a simple polytype relationship to the lautite structure.

209

Experimental

CuAsSe was synthesized by direct combination of the elements in stoichiometric proparations in an evacuated glass ampoule. Single crystals were grown by vacuum sublimation and examined by X-ray diffraction. Unit cell dimensions were obtained from precession photographs about all three axes, for a needle-shaped crystal of dimensions $0.3 \times 0.1 \times 0.1$ mm. The needle axis is the b axis of the crystal and there were well-developed pinacoid faces (100) and domes (101). Crystal data: CuAsSe, $M = 217.42$, orthorhombic, $a = 11.75 \pm 0.02$, $b = 6.79 \pm 0.01$, $c = 19.21 \pm 0.03$ Å, $U = 1525$ Å, $Z = 24$, $Dm = 5.50$ g cm^{-3}, $Dc = 5.68$ g cm^{-3} $F(000) = 2304$, Mo$K\alpha$ radiation, $\lambda = 0.7107$ Å, $\mu = 37.5$ cm^{-1}.

Precession data were taken with Zr-filtered Mo radiation for layers $h0l$-$h2l$, $hk0$-$hk3$, and $0kl$. 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. In addition to the systematic absences for space group $Pbcn$ ($0kl$ for k odd, $h0l$ for l odd and $hk0$ for $h + k$ odd), it was found that a large proportion of other reflections were systematically very weak. For example, hkl reflections for h not equal to $3n$ are weak, and $00l$ reflections for l not equal to $6n$ were not observed. Out of a total of 860 reflections that were spot-judged, some 560 were below the limit of detection.

Structure Solution and Refinement

The $hk0$ precession photograph showed very strong reflections corresponding to a pseudo hexagonal lattice $a = 3.91$ Å. This is equal to the c lattice spacing divided by $2\sqrt{6}$ and suggested that the CuAsSe structure was related to the carborundum II, $B6$, structure rather than to the zincblende $B3$, structure. This hypothesis was supported by the observation that $00l$ reflections were only observed for $l = 6n$, as has been found for $6H$-ZnS (6). A two-dimensional Patterson projection along the a axis showed large peaks at positions expected if the structure is constructed on the $6H$-ZnS lattice. Phases of the intense reflections were estimated using a trial lattice based on this lattice. The positions of the atoms were determined from a Fourier synthesis and the copper atoms identified from peak heights. Arsenic and selenium have nearly the same number of electrons and so chemical considerations assisted by use of atomic models were used to distinguish them. We took the simplest assumption, namely, that CuAsSe consists of layers of atoms identical to those in CuAsS excepting that S atoms are replaced by Se atoms. These layers are then packed up the c axis of CuAsSe in a cubic, cubic, hexagonal stacking pattern as shown in the figures. This assignment of arsenic and selenium peaks leads to bond lengths, and angles and coordination of atoms comparable to those in CuAsS after making allowance for the atomic radii of Se being 0.1 Å greater than that of S. The structure obtained was refined by difference Fourier synthesis. Least squares refinement of the data using one isotropic temperature factor ($B = 0.344$ Å^2) for all nine atoms gave $R = 0.125$ for 298 observed reflections. Reflections 600, 606, 330 were omitted from this refinement as they were considered to suffer from extinction. Allowing different isotropic or anisotropic temperature factors for the nine atoms gave only a slight reduction in R.

All atoms are in the general positions $8(d)$ of space group $Pbcn$. The final positional parameters of all nine atoms in the asymmetric unit of the unit cell are listed in Table I and the interatomic distances and bond angles are listed in Table II. A table of observed and calculated structure factors

TABLE I

POSITIONAL PARAMETERS WITH STANDARD DEVIATIONS IN PARENTHESES FOR THE INDIVIDUAL ATOMS IN CuAsSe

	x	y	z
As(1)	0.0156(9)	0.0108(16)	0.1806(7)
As(2)	0.9832(9)	0.3580(18)	0.1459(7)
As(3)	0.0176(10)	0.3230(20)	0.0170(9)
Se(1)	0.3355(10)	0.9773(12)	0.1803(5)
Se(2)	0.6635(11)	0.3701(15)	0.1545(6)
Se(3)	0.3354(12)	0.3100(16)	0.0144(7)
Cu(1)	0.6685(17)	0.0364(16)	0.1965(6)
Cu(2)	0.3343(14)	0.3151(16)	0.1402(6)
Cu(3)	0.6735(18)	0.3644(17)	0.0307(6)

has been deposited with the ASIS National Auxiliary Publications Service.[1]

Description of the Structure and Discussion

A projection of the CuAsSe structure is shown in Fig. 1, and a perspective view of successive hexagonal and cubic packed layers up the c axis of CuAsSe is shown in Fig. 2. Planes of arsenic atoms at approximately $x = 0$ and $\frac{1}{2}$ interleave planes of copper plus selenium atoms at approximately $x = \frac{1}{8}$, $\frac{1}{3}$, $\frac{2}{3}$, and $\frac{3}{8}$. The chain of arsenic–arsenic bonds at $x = 0$ is indicated by unbroken lines and the copper–selenium–copper bonds at $x = \frac{1}{8}$ are indicated by dotted lines in Fig. 1. The cubic (c) or hexagonal (h) stacking up the c axis is indicated at the side of the diagrams.

Whereas CuAsS has a structure related to the $3C$ form of zinc sulfide, ZnS, CuAsSe has a structure related to the $6H$ form of ZnS. Alternatively, using Strukturbericht notation, CuAsS is related to the $B3$ structure with ccc stacking up the c axis and CuAsSe to the $B6$ structure with hcc stacking up the c axis.

The coordination of the three kinds of atoms (Cu,As,Se) is exactly analogous to the coordination in lautite (3), in that each Cu is surrounded by 1 As + 3 Se, each As

TABLE II

DISTANCES AND ANGLES WITH STANDARD DEVIATIONS IN PARENTHESES

As(1)– As(1)	2.69(3)	Se(1)– Cu(1)	2.40(2)
As(1)– As(2)	2.47(2)	Se(1)– Cu(2)	2.41(2)
As(2)– As(3)	2.52(2)	Se(1)– Cu(2)	2.40(2)
As(3)– As(3)	2.52(3)	Se(2)– Cu(1)	2.40(2)
As(1)– Se(2)	2.36(2)	Se(2)– Cu(1)	2.41(2)
As(2)– Se(1)	2.37(2)	Se(2)– Cu(3)	2.38(2)
As(3)– Se(3)	2.40(2)	Se(3)– Cu(2)	2.41(2)
As(1)– Cu(2)	2.34(2)	Se(3)– Cu(3)	2.37(2)
As(2)– Cu(1)	2.36(2)	Se(3)– Cu(3)	2.40(2)
As(3)– Cu(3)	2.41(2)		

Angles (deg)

As(1)–As(1)– As(2)	104.2(4)	As(2)–Se(1)– Cu(1)	110.5(6)
As(1)–As(2)– As(3)	98.6(5)	As(2)–Se(1)– Cu(2)	103.9(6)
As(2)–As(3)– As(3)	97.9(8)	As(2)–Se(1)– Cu(2)	120.0(5)
As(1)–As(1)– Se(2)	95.1(5)	As(1)–Se(2)– Cu(1)	109.3(7)
As(2)–As(1)– Se(2)	101.0(6)	As(1)–Se(2)– Cu(1)	117.9(6)
As(1)–As(2)– Se(1)	96.4(5)	As(1)–Se(2)– Cu(3)	105.2(7)
As(3)–As(2)– Se(1)	99.3(6)	As(3)–Se(3)– Cu(2)	105.1(6)
As(2)–As(3)– Se(3)	98.0(4)	As(3)–Se(3)– Cu(3)	107.3(5)
As(3)–As(3)– Se(3)	98.4(7)	As(3)–Se(3)– Cu(3)	115.6(6)
As(1)–As(1)– Cu(2)	115.5(6)	Cu(1)–Se(1)– Se(2)	99.0(4)
As(2)–As(1)– Cu(2)	124.5(7)	Cu(1)–Se(1)– Cu(2)	112.0(6)
As(1)–As(2)– Cu(1)	119.4(6)	Cu(2)–Se(1)– Cu(2)	109.1(6)
As(3)–As(2)– Cu(1)	125.0(5)	Cu(1)–Se(2)– Cu(1)	107.9(6)
As(2)–As(3)– Cu(3)	123.1(6)	Cu(1)–Se(2)– Cu(3)	108.6(5)
As(3)–As(3)– Cu(3)	121.9(9)	Cu(1)–Se(2)– Cu(3)	107.6(9)
Se(2)–As(1)– Cu(2)	111.8(7)	Cu(2)–Se(3)– Cu(3)	110.6(6)
Se(1)–As(2)– Cu(1)	112.8(7)	Cu(2)–Se(3)– Cu(3)	111.3(8)
Se(3)–As(3)– Cu(3)	112.6(6)	Cu(3)–Se(3)– Cu(3)	106.9(6)
As(2)–Cu(1)–Se(1)	107.8(7)	Se(1)– Cu(1)–Se(2)	119.2(6)
As(2)–Cu(1)–Se(2)	109.0(7)	Se(1)– Cu(1)–Se(2)	105.6(7)
As(2)–Cu(1)–Se(2)	103.9(5)	Se(2)– Cu(1)–Se(2)	110.4(7)
As(1)–Cu(2)–Se(1)	115.3(7)	Se(1)– Cu(2)–Se(1)	109.7(6)
As(1)–Cu(2)–Se(1)	105.1(5)	Se(1)– Cu(2)–Se(3)	107.8(5)
As(1)–Cu(2)–Se(3)	109.6(7)	Se(1)– Cu(2)–Se(3)	109.3(7)
As(3)–Cu(3)–Se(2)	110.5(8)	Se(2)– Cu(3)–Se(3)	110.3(6)
As(3)–Cu(3)–Se(3)	108.5(6)	Se(2)– Cu(3)–Se(3)	114.0(9)
As(3)–Cu(3)–Se(3)	101.8(5)	Se(3)– Cu(3)–Se(3)	111.2(7)

Nonbonded Distances (Å)

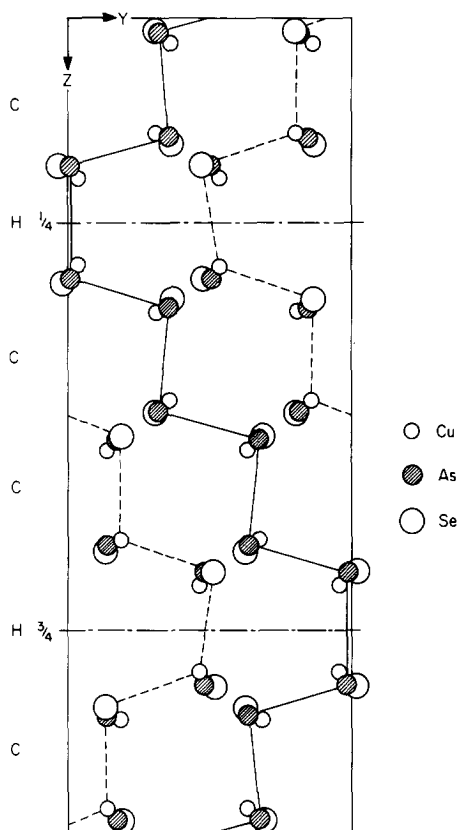| As(1)– Se(1)	3.61
Cu(1)– Cu(2)	3.66
As(2)– Se(3)	3.71

FIG. 1. Projection of the unit cell of CuAsSe along [100].

by 1 Cu + 1 Se + 2As, and each Se by 1 As + 3 Cu. The mean values for the As–Se bonds (2.38 Å), for the As–Cu bonds (2.37), the Cu–Se bonds (2.40) and the As–As bonds (2.55) agree well with the sums of the theoretical single covalent bond distances of As (1.21), Se (1.17) and Cu(I) (1.173 Å) (7). The As–Se bond distance is close to that in As_4Se_4 (2.39) (8), the As–Cu bond is close to that in CuAsS (2.42) (3) and the As–As is close to that in As_4Se_4 (2.56) (7), As_4S_5 (2.55) (9), As_4S_3 (2.47) (10), As_4S_4 (2.59) (11), and CuAsS (2.49) (3).

Comparing the bonds for hexagonal and cubic close packed layers we note no significant bond differences for Cu–Se bonds, but for As–As bonds we observe

that the As(1)–As(1) bond is significantly longer than the other As–As bonds.

The tetrahedra of atoms surrounding copper atoms are only slightly distorted in agreement with the copper being in spherically symmetric $d10$ arrangement and the degree of distortion compares well with that observed for the Cu tetrahedron in CuAsS. The tetrahedra of atoms surrounding the selenium atoms are also only slightly distorted, and the amount of distortion is similar to that around the sulfur atom in CuAsS. For the arsenic atoms there is rather more distortion of the tetrahedron of neighbors than for selenium or copper atoms. The mean values of the angles (with the corresponding angle in CuAsS (3) in parentheses) are As–As–As 100 (98), As–As–Se 98 (99), As–As–Cu 119 (121) and Cu–As–Se 112 (114). This correspondence in the distortion of the tetrahedra in CuAsS and CuAsSe is confirmation of the choice of atomic sites for As and Se.

X-Ray Powder Patterns of CuAsSe and $CuAsSe_{0.8}S_{0.2}$

In Table III is listed an X-ray powder diffraction pattern of a flat plate sample prepared by powdering a single crystal of CuAsSe. The spectrum was recorded on a Rigaku Miniflex X-ray diffractometer using Ni-filtered Cu radiation. The observed peak heights I(obs) are in excellent agreement with calculated diffraction intensities, I_{hkl}.
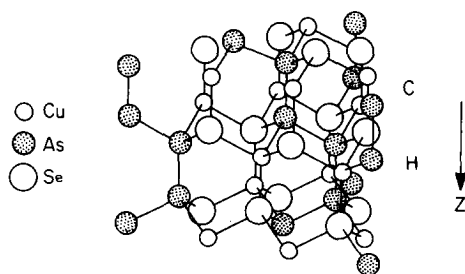

FIG. 2. Perspective view of successive hexagonal and cubic packed layers of CuAsSe.

TABLE III

X-RAY POWDER DIFFRACTION PATTERN OF CuAsSe

d (Å)	hkl	I(calc)	I(obs)
3.394	020, 310	0.3	
3.342	021, 311	38	40
3.201	006, 022, 312	100	100
2.999	313, 023	17	20
2.772	024	0.9	
2.596	412	3	4
2.544	025, 315	3	4
2.485	413	3	5
2.335	217	1	2
2.329	026	0.1	
2.134	317, 027	10	10
2.112	218	2	3
1.960	318, 028, 330, 600	89	95
1.950	331	0.9	
1.924	219	0.9	2
1.894	506	0.9	2
1.807	319, 029	20	20
1.785	431	2	3
1.746	335	0.3	
1.698	040	0.1	
1.691	041	0.9	2
1.672	141, 419, 02.10, 31.10, 606, 336, 042	38	35

TABLE IV

X-RAY POWDER PATTERN OF $CuAsSe_{0.8}S_{0.2}$ INDEXED FOR hcc AND hccc POLYTYPES

d (Å)	I(obs)	hkl (hcc)	hkl (hccc)
3.37	5	020	020
3.25	35		022, 312
3.18	100	006, 022, 312	008
3.13	25		023, 313
2.974	5	023, 313	024, 314
2.635	2		026, 316
2.028	15		02.10, 31.10
1.943	80	330, 600, 028, 318	330, 600
1.905	20	219	02.11, 31.11
1.792	5	029, 319	02.12, 31.12
1.690	5	040	02.13, 31.13
1.658	25	606, 336, 141, 419 02.10, 31.10, 042	608, 338

I_{hkl} is given by the relationship

$$I_{hkl} = MLPF_{hkl}^2$$

where M is the multiplicity factor, L the lorentz factor, P the polarization factor and F_{hkl} the structure factor of a line. I_{hkl} was calculated for all diffraction peaks of d spacing greater than 1.67 Å and all peaks for which the intensity was greater than 0.1% of the most intense peak are listed in the table. X-Ray powder patterns of well-annealed samples of CuAsSe are in good agreement with this pattern from a powdered single crystal in agreement with the sample being all of one polytype. However, for one sample preparation two extra weak peaks were observed at 3.29 and 3.148 Å that gradually disappeared on long anneal. These may arise from a second polytype of CuAsSe.

The X-ray powder diffraction of material and stoichiometry $CuAsSe_{0.8}S_{0.2}$ could be indexed only partially in terms of an hcc structure with unit cell dimensions $a = 11.66$, $b = 6.73$, and $c = 19.06$ Å but could be indexed completely in terms of an orthorhombic unit cell of dimensions $a = 11.66$, $b = 6.73$, and $c = 25.41$ Å (Table IV). The cell dimensions are compatible with the possibility that this mixed crystal has an hccc polytype structure, similar to the 8H polytypes of ZnS (12) and SiC (13).

Further work is in progress aimed at growing single crystals of compositions intermediate between CuAsS and CuAsSe to determine if fractional hexagonal packing between the zero value of ccc-CuAsS and that of one-third of hcc-CuAsSe, indeed occurs.

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