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## The Crystal Structure of Enargite, $Cu_3AsS_4$ .

By

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(With 1 figure.)

### Introduction.

The mineral enargite,  $Cu_3AsS_4$ , is described as forming orthorhombic crystals, with the axial ratios  $0.8694 : 1 : 0.8308$ , according to Spencer. The only previous X-ray study known to us is that of de Jong<sup>1</sup>), who prepared powder photographs of enargite and of famatinite, essentially  $Cu_3SbS_4$ , which seem to show the two substances to be isomorphous; no attempt to determine the structure from the data was reported.

In the course of our series of investigations of the sulfide minerals, we have determined the structure of enargite, with the use of data from Laue and oscillation photographs from crystals from the Philippine Islands. The structure found for enargite is closely related to that of wurtzite, the hexagonal form of zinc sulfide. This work is described in the following sections<sup>2</sup>).

### The Unit of Structure and Space-group Symmetry.

Using crystals tabular on  $a$ , about  $1 \times 1 \times 0.5$  mm in size, oscillation photographs were taken of the  $K$ -radiation of molybdenum filtered through zirconia. The angle of oscillation was  $30^\circ$  or  $45^\circ$ . Photographs obtained from (100) with [001], (100) with [010], (010) with [001], (001) with [100], and (001) with [010] as oscillation axis led to the values

$$a_0 = 6.46 \text{ \AA} \quad b_0 = 7.43 \text{ \AA} \quad c_0 = 6.18 \text{ \AA}$$

1) W. F. de Jong, Z. Krist. **68**, 522. 1928.

2) Our investigation, begun in March, 1931, was abandoned for some time because of the pressure of other work and because of our temporary inability to account for the presence of certain reflections on Laue photographs (discussed in the next section).

for the fundamental translations. In each case the probable error is about  $\pm 0.02 \text{ \AA}$ , as shown by the agreement among values calculated from layer-line separations and from angles of reflection in the equator.

On assigning indices to spots on Laue photographs made with the incident beam nearly parallel to  $[100]$ , and calculating values of  $n\lambda$  on the basis of this unit, it was found that most of the reflections gave  $n\lambda$  values greater than the short wave-length limit  $0.24 \text{ \AA}$  for the radiation used. On each photograph, however, there were a few faint spots with very large indices, leading to  $n\lambda$ -values as small as  $0.076$ . Examples of such reflections are the following, from Laue photograph No. 4:  $(1.10.12)$ ,  $n\lambda = 0.076 \text{ \AA}$ ;  $(3.\overline{18}.8)$ ,  $0.086$ ;  $(7.38.12)$ ,  $0.088$ ;  $(7.26.16)$ ,  $0.088$ ;  $(7.22.20)$ ,  $0.120$ ;  $(11.\overline{34}.20)$ ,  $0.087$ ; etc. These reflections, if due to the main crystal under investigation, would require  $a_0$  to be four times as great and  $b_0$  twice as great as indicated by the spectral data. It was observed, however, that most of these reflections did not appear on a similar Laue photograph made with a different crystal of enargite. This suggests that these reflections are due to small individuals attached to the main crystal in such a way that the axes are definitely oriented relative to those of the main crystal, as would result from twinning. Enargite is actually reported to form twins with  $\{320\}$  as twinning form. Inasmuch as the axial lengths are pseudo-hexagonal ( $2a : b = 1.739 : 1$ ), this corresponds to rotation of approximately  $120^\circ$  or  $240^\circ$  about the  $c$ -axis. The transformations from indices relative to the axes of the main crystal to those of the twins are

$$\begin{array}{ll} 120^\circ \text{ rotation} & 240^\circ \text{ rotation} \\ h' = -h/2 - 3k/4 & h'' = -h/2 + 3k/4 \\ k' = h - k/2 & k'' = -h - k/2 \\ l' = l & l'' = l. \end{array}$$

In each case  $n\lambda$  is unchanged unless  $(h' k' l')$  or  $(h'' k'' l'')$  simplify through division by a common factor,  $n\lambda$  then being multiplied by this factor. On applying these equations, we found that all of the reflections could be accounted for as arising from one of the three individuals on the basis of the original unit of structure. For example,  $(7.38.12)$  at  $0.088 \text{ \AA}$  on rotation through  $120^\circ$  becomes  $(\overline{8}\overline{3}3)$  at  $0.352 \text{ \AA}$ . We accordingly accept this unit as the true unit of structure. The density calculated for  $2Cu_3AsS_4$  is  $4.39 \text{ g/cm}^3$ , in good agreement with the directly determined values  $4.35$  to  $4.51$  (which may be large because of the presence of antimony).

Taking cognizance of the possibility of reflections from twins, it was found that pyramid planes of all types gave first-order reflections, requir-

ing the simple orthorhombic lattice. Moreover, first-order reflections of all types were observed from the prism planes ( $h0l$ ) and ( $hk0$ ), whereas no reflections of the type ( $0kl$ ) with  $k + l$  odd were observed. If these absences result from the symmetry of the crystal, the space group is  $V_h^{13} - Pnmm$  or  $C_{2v}^7 - Pnm$ .

### The Atomic Arrangement.

The possibility that the atomic arrangement is closely similar to that of wurtzite suggests itself at once, for the values found for  $a_0$ ,  $b_0$ , and  $c_0$  are only 2 or 3% less than those for a double orthohexagonal unit of wurtzite,  $\sqrt{3}a = 6.65 \text{ \AA}$ ,  $2a = 7.68 \text{ \AA}$ ,  $c = 6.28 \text{ \AA}$ . This conception is supported by the appearance of oscillation photographs with  $[010]$  as oscillation axis, on which the odd layer lines are very weak, indicating a pseudo-unit with half the value of  $b_0$ .

The atomic arrangement shown in Figure 1 results from replacing one fourth of the zinc atoms in wurtzite by arsenic and the remaining three-fourths by copper atoms, in such a way as to give discrete  $AsS_4$  groups. The distribution of symmetry elements for this structure corresponds to the space group  $C_{2v}^7 - Pnm$ , in agreement with the X-ray data. The morphological evidence available led crystallographers to assign enargite to the orthorhombic bipyramidal crystal class; however, our results show that its crystal class is the orthorhombic pyramidal,  $C_{2v}$ .

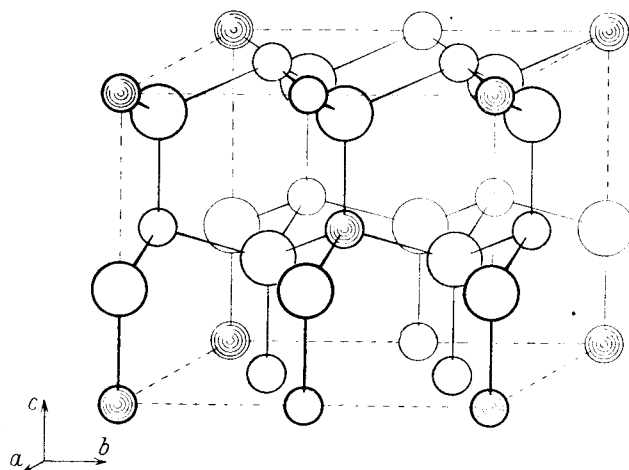


Fig. 1. The structure of enargite, showing the contents of a unit cube shifted  $\frac{a_0}{6}$  from that used in the text. The large circles represent sulfur atoms, the small open circles copper atoms, and the small shaded circles arsenic atoms.

The ideal atomic arrangement is the following, based on the sets of equivalent positions for  $C_{2v}^7$ :

- 2a.  $u0v$ ,  $\bar{u}\frac{1}{2}\frac{1}{2} + v$ ;    4b.  $xyz$ ,  $x\frac{1}{2} - y\frac{1}{2} + z$ ,  $x\frac{1}{2} + y\frac{1}{2} + z$ ,  $x\bar{y}z$ ;  
 2  $As$  in 2a with  $u_{As} \cong 0.833$ ,  $v_{As} \cong 0.000$ ;  
 2  $Cu_I$  in 2a with  $u_{Cu} \cong 0.167$ ,  $v_{Cu} \cong 0.500$ ;  
 4  $Cu_{II}$  in 4b with  $x_{Cu} \cong 0.333$ ,  $y_{Cu} \cong 0.250$ ,  $z_{Cu} = 0.000$ ;  
 2  $S_I$  in 2a with  $u_I \cong 0.833$ ,  $v_I \cong 0.375$ ;  
 2  $S_{II}$  in 2a with  $u_{II} \cong 0.167$ ,  $v_{II} \cong 0.875$ ;  
 4  $S_{III}$  in 4b with  $x_S \cong 0.333$ ,  $y_S \cong 0.250$ ,  $z_S \cong 0.375$ .

Intensities of reflections were calculated for these parameter values for planes reflecting on oscillation photographs (Table I) by use of the equation

$$I = C \cdot \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} (h \text{ or } l) \omega |F|^2 e^{-2B(\sin \theta, \lambda)^2}.$$

Here  $\omega$  is the Ott factor for varying time of reflection, and  $h$  or  $l$  a factor required by the experimental method of reflection from the small developed face (100) or (001) of the absorbing crystal bathed in the incident radiation. Pauling-Sherman  $f_0$ -values were used, and an estimated value of 1.00 for the coefficient  $B$  in the temperature factor. The constant  $C$  was given the value  $1/18000$  in Tables I and II, and  $1/40000$  in Table III. It was found that the general agreement with the observed intensities (estimated by the visual intercomparison of several similar photographs with varying exposure times) is good for all except the weak reflections. (The estimated intensities are accurate to only about 50%, inasmuch as the crystals used were small and imperfect.) This shows that the atomic arrangement is only slightly different from the assumed one. We accordingly considered the effect of varying the thirteen parameters by small amounts, and ultimately selected as the best values of the parameters the following set:

$$\begin{aligned} u_{As} &= 0.820, & v_{As} &= 0.000; \\ u_{Cu} &= 0.165, & v_{Cu} &= 0.500; \\ x_{Cu} &= 0.333, & y_{Cu} &= 0.245, & z_{Cu} &= 0.990; \\ u_I &= 0.830, & v_I &= 0.360; \\ u_{II} &= 0.140, & v_{II} &= 0.875; \\ x_S &= 0.330, & y_S &= 0.255, & z_S &= 0.367. \end{aligned}$$

Inasmuch as our survey of the region has not been complete, these parameters may not be exactly right; however, an arbitrary change of 0.005 in one or two of the parameters somewhat impairs the agreement in the

Table I. Data from oscillation photographs 4, 5, 6. (100), [010] as oscillation axis<sup>1</sup>).

		(440) 2	(540) <i>a</i>	(640) 6															
		2.8	2.1	0.00	0.01	5.8	4.9												
		(330) 0.3	(430) 0.1	(530) <i>a</i>	(630) 0.2														
		0.00	0.18	0.01	0.11	0.01	0.01	0.00	0.25										
	(220) <i>a</i>	(320) 20	(420) 0.1	(520) 3	(620) <i>a</i>														
	0.00	0.00	25	24	0.00	0.23	3.3	2.6	0.01	0.00									
	(210) <i>a</i>	(310) 0.3	(410) 0.3	(510) <i>a</i>	(610) 0.3														
	0.00	0.02	0.00	0.24	0.01	0.18	0.01	0.01	0.00	0.28									
(100) <i>a</i>	(200) 10	(300) <i>a</i>	(400) 4	(500) <i>a</i>	(600) 9	(700) <i>a</i>	(800) 1												
0.01	0.01	13	12	0.01	0.00	5.0	4.0	0.01	0.00	9.3	7.5	0.00	0.02	1.1	0.7				

Table II. Data from oscillation photographs 1, 2, 3. (100), [001] as oscillation axis<sup>2</sup>).

		(303)	(403)	(503)	(603)	(703)	(803)												
		<i>a</i>	0.03	6	7.5	<i>a</i>	0.07	<i>a</i>	0.01	<i>a</i>	0.05	1.5	1.2						
	(202)	(302)	(402)	(502)	(602)	(702)	(802)												
4	3.3	<i>a</i>	0.04	2	2.0	<i>a</i>	0.16	5	3.7	<i>a</i>	0.03	0.5	0.45						
	(201)	(301)	(401)	(501)	(601)	(701)	(801)												
6	11	<i>a</i>	0.01	4	4.5	<i>a</i>	0.01	<i>a</i>	0.14	<i>a</i>	0.10	0.5	0.31						
(100)	(200)	(300)	(400)	(500)	(600)	(700)	(800)												
<i>a</i>	0.01	10	12	<i>a</i>	0.00	4	4.0	<i>a</i>	0.00	9	7.5	<i>a</i>	0.00	1	0.7				

Table III. Data from oscillation photograph 7. (001), [100] as oscillation axis.

				(405)	(406)														
				2	1.8	<i>a</i>	0.2												
				(304)	(305)	(306)													
				<i>a</i>	0.05	<i>a</i>	0.00	<i>a</i>	0.03										
				(203)	(204)	(205)	(206)												
				7	6.5	0.2	0.4	3	2.3	0.4	0.5								
				(102)	(103)	(104)	(105)	(106)											
				<i>a</i>	0.00	<i>a</i>	0.02	<i>a</i>	0.01	<i>a</i>	0.05	<i>a</i>	0.03						
(001)	(002)	(003)	(004)	(005)	(006)	(007)	(008)												
<i>a</i>	0.00	10	11	<i>a</i>	0.00	1	1.4	<i>a</i>	0.00	2	2.0	<i>a</i>	0.00	1.5	1.1				

1) In each case, the number to the right of the indices ( $h k l$ ) represents the observed intensity,  $a$  signifying absent. Of the two numbers below, that to the left is the intensity calculated for the ideal set of parameter values, and that to the right for the final set.

2) The left of each pair of numbers below the indices ( $h k l$ ) in this table and Table III represents the observed intensity, the right the intensity calculated for the final set of parameter values.

intensities shown in Tables I, II, and III, and we believe it improbable that the values given are in error by more than about  $\pm 0.005$ .

#### Description of the Structure.

The structure found for enargite is very closely similar to that of wurtzite, each arsenic or copper atom being surrounded by four sulfur atoms at the corners of a nearly regular tetrahedron, and each sulfur atom being similarly surrounded by a tetrahedron of one arsenic atom and three copper atoms. The  $AsS_4$  groups are discrete, sharing no sulfur atoms with one another, so that the substance may be described as cuprous sulfoarsenate. The  $As-S$  distances lie between 2.21 and 2.24 Å, in excellent agreement with the sum of the tetrahedral radii<sup>1)</sup> for arsenic and sulfur, 2.22 Å. The  $Cu-S$  distances lie between 2.31 and 2.33 Å, in good agreement with the values  $2.32 \pm 0.03$  Å in chalcopyrite,  $2.285 \pm 0.014$  Å in sulvanite, and  $2.29 \pm 0.05$  Å in binnite.

#### Summary.

Enargite is shown to have an orthorhombic unit of structure with  $a_0 = 6.46$  Å,  $b_0 = 7.43$  Å,  $c_0 = 6.18$  Å (in each case  $\pm 0.02$  Å), containing  $2Cu_3AsS_4$ . The atomic arrangement, based on the space group  $C_{2v}^i-Pnm$ , is closely similar to that of wurtzite, each arsenic atom and each copper atom being tetrahedrally surrounded by four sulfur atoms at  $2.22 \pm 0.03$  Å and  $2.32 \pm 0.03$  Å, respectively. The parameter values describing the atomic arrangement are given above.

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1) L. Pauling and M. L. Huggins, Z. Krist. **87**, 205. 1934.

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