149. *Crystal Structure of Enargite* (Cu_3AsS_4).

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Recently, the crystal structures of copper sulphides such as covellite (CuS), wolfsbergite (CuSbS_2), emplectite (CuBiS_2), chalcopyrite (CuFeS_2) and sylvanite (Cu_3VS_4), have been worked out by different authors. Among these minerals, sylvanite has been grouped in the mineral family to which enargite belongs, because of the similarity in their chemical compositions. However they are different in crystallographic nature, as sylvanite belongs the cubic system of the space group T_d^1 , determined by Pauling and Hultgren, and enargite belongs to the orthorhombic system of the space group V_h^{12} , determined by the present author.

Symmetry:—According to the morphological studies already made, enargite belongs to the orthorhombic holohedral class, the axial ratio being given as $a:b:c=0.8694:1:0.8308$ by Groth and Mieleitner. The Laue photograph taken from (001) shows no objection to taking the crystal as possessing the symmetry of the orthorhombic holohedral class. It is noteworthy that the photograph indicates a pseudohexagonal symmetry, of which a brief discussion has already been written in Japanese.

Unit cell:—From three reflection photographs taken by rotation of three mineral rods parallel to [001], [010] and [100] respectively, immersing in the beam of the CuK ray, the distances of the layer lines were measured, and the results are

$$a_0=6.39 \pm 0.05 \text{Å}, \quad b_0=3.68 \pm 0.03 \text{Å}, \quad c_0=6.15 \pm 0.05 \text{Å}.$$

The axial ratio obtained from the above figures is $a:b:c=1.734:1:1.674$, which are double the values of a and c given by the goniometric method.

The chemical composition of the crystal was carefully analyzed by S. Tsurumi at our Institute under the direction of Prof. Kôzu. His final result can be written as $(\text{CuFeMn})_{3.01}(\text{AsSb})_{1.00}\text{S}_{4.06}$. Using this result in the well known formula, $n=\rho \times V/M \times 1.66 \times 10^{-24}$, where $\rho=4.44$, $V=144.42 \text{Å}^3$, and $M=393.88$, n is $0.987(\sim 1)$, that is, one molecule given by the chemical formula Cu_3AsS_4 is contained in a unit cell.

Space group:—Examining the indices of all the reflections obtained by the rotation method, no special case was found in the reflections from the pyramidal faces (hkl), indicating that the simple orthorhombic lattice can exist in the crystal.

In (okl), (hol) and (hko), the reflections can be observed, when $k+l$ in (okl) is even, h and l in (hol) are even and odd, and $h+k$ in (hko) is even.

In (hoo), (oko) and (ool), the reflections can be observed only, when h , k and l are even respectively.

The space group belonging to the orthorhombic holohedral class, in which the above relations are satisfied, must be V_h^{12} . In this case, the co-ordinates of the space group retain the relation with the crystallographic axes such as $X=a$, $Y=c$ and $Z=b$.

Determination of the crystal structure:—As the one equivalent position can not exist in the space group V_h^{12} , the eight atoms of 3Cu, As and 4S must be distributed in one of the two manners such as 2Cu, 2(CuAs), 4S, in which 2(CuAs) are placed in the two equivalent positions, or 4(CuAs), 4S, in which 4(CuAs) are placed in the four equivalent positions. From the calculation of the amplitude contribution, using the atomic scattering factors given by Pauling and Sherman, it is known that the configuration of 2Cu, 2(CuAs), 4S is impossible in this case. For the configuration of 4(CuAs) and 4S three different manners may occur, but only one is possible in this case when all (CuAs) and S are placed on the reflection planes of symmetry, whose orientations are given as $(010)_0$ and $(010)_{\frac{1}{2}}$ referred to the crystallographic axes a , b and c .

Hence the positions of 4(CuAs) and 4S can be given as:

$$\begin{aligned} &(m_1, \frac{1}{2}, p_1); (\bar{m}_1, \frac{1}{2}, \bar{p}_1); (m_1 + \frac{1}{2}, 0, \bar{p}_1 + \frac{1}{2}); (\bar{m}_1 + \frac{1}{2}, 0, p_1 + \frac{1}{2}) \quad \text{for (CuAs),} \\ &(m_2, 0, p_2); (\bar{m}_2, 0, \bar{p}_2); (m_2 + \frac{1}{2}, \frac{1}{2}, \bar{p}_2 + \frac{1}{2}); (\bar{m}_2 + \frac{1}{2}, \frac{1}{2}, p_2 + \frac{1}{2}) \quad \text{for S.} \end{aligned}$$

The amplitude contribution, F , is given by

$$\begin{aligned} F = &(-1)^k 2f_1 \cos(\theta_{m_1} h + \theta_{p_1} l) + (-1)^{k+l} 2f_1 \cos(\theta_{m_1} h - \theta_{p_1} l) \\ &+ 2f_2 \cos(\theta_{m_2} h + \theta_{p_2} l) + (-1)^{h+k+l} 2f_2 \cos(\theta_{m_2} h - \theta_{p_2} l). \end{aligned}$$

Using the above formula, the values of θ_{m_1} and θ_{p_1} and also those of θ_{m_2} and θ_{p_2} were obtained by calculation in comparison with the reflections from the faces of two sets of (002) , (004) and (006) , and (200) , (400) and (600) respectively. The results are given in Table I.

TABLE I.

	n	θ_a	θ_b	θ_c	m	p	n
Cu(As)	4	38°	82°	180°	0.106	0.228	0.500
S	4	95	72	0	0.264	0.200	0.000

Substituting these values into the co-ordinates of (CuAs) and S, expressed in the general terms given above the configuration diagrams projected on the a-c plane and the a-b plane are given in Figs. 1 and 2. The amplitude contribution F obtained by calculation based on the crystal structure derived as above, and the observed intensities of the reflections obtained by the rotation method, are given in parallel in Table II. We see that they are in fairly good agreement.

Fig. 1.

Fig. 2.

The full description of the determination of the crystal structure of this mineral and of its structural relation with the allied copper sulphide mineral will be published in the near future in the Science Reports of the Tohoku Imperial University, Series III.

The present investigation was carried out under the guidance of Prof. S. Kôzu in his laboratory and all the crystals used for the present experiments were supplied by him. The author wishes to offer his

heartly thanks to him for his kindness extended throughout this investigation.

TABLE II.

hkl	$\sin \theta$	$\frac{\sin \theta}{\lambda}$	I (Obs.)	F (Calc.)
200	0.238	0.16	W	- 20
400	0.478	0.31	W	38
600 } 305 }	0.722	0.47	M	{ - 66 - 16
020	0.416	0.27	V.S	124
040	0.438	0.55	M	78.4
002	0.248	0.16	V.V.S	-140
004	0.500	0.33	M	87
006	0.755	0.49	M	- 57.8
011	0.245	0.16	absent	0
013	0.331	0.22	absent	4
022	0.486	0.32	S	-105.3
031	0.640	0.42	absent	1
015	0.664	0.43	absent	- 8
024	0.652	0.43	M	72
033	0.732	0.48	absent	1.5
026	0.865	0.56	M	35.8
042	0.875	0.57	M	- 70
017	0.909	0.60	V.W	15
201	0.270	0.18	M	- 77
202	0.347	0.23	M	10.5
103	0.400	0.26	M	- 30
203 } 302 }	0.445	0.29	M	{ 78.8 - 1.3
402	0.539	0.35	W	38
204	0.552	0.36	V.W	5
403	0.609	0.40	M	54
105	0.637	0.42	W	29.3
502	0.652	0.42	W	14.2
205	0.671	0.44	M	- 47
420 } 510 } 130 }	0.639	0.42	M	{ 50.9 26.5 52.6
710 } 530 } 240 }	0.873	0.57	M	{ - 14 + 30.2 - 11.4
440	0.964	0.63	W	- 13