

(Contribution from Gates Chemical Laboratory, California Institute of Technology,  
No. 383.)

## The Crystal Structure of Binnite, $(\text{Cu}, \text{Fe})_{12}\text{As}_4\text{S}_{13}$ , and the Chemical Composition and Structure of Minerals of the Tetrahedrite Group.

By

Linus Pauling and E. W. Neuman in Pasadena.

(With 4 figure.)

### Introduction.

Binnite, a well-crystallized variety of tennantite found in the Binnenthal, Wallis, Switzerland, belongs to the tetrahedrite group of minerals. X-ray studies of tetrahedrite have been reported by Palacios<sup>1</sup>), de Jong<sup>2</sup>), and Machatschki<sup>3</sup>). Our investigation confirms the results of Machatschki in most respects.

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

The X-ray data used by us were obtained from oscillation and Laue photographs prepared from an excellent crystal from the Binnenthal kindly provided by Professor Charles Palache of Harvard University. The angles of reflection of planes reflecting in the equator on an oscillation photograph from (100) with [001] as axis of rotation, using molybdenum radiation filtered through zirconia, lead to  $a_0 = 10.19 \pm 0.020 \text{ \AA}$  (Table I). The less accurate value  $a_0 = 10.25 \text{ \AA}$  is given by the distance between layer lines. The cubic unit with  $a_0 = 10.19 \text{ \AA}$  accounts completely for all reflections observed on two completely analyzed Laue photographs (with the incident beam making angles of  $1^\circ$  and  $7^\circ$  with the direction [100]), and may hence be accepted with confidence as the true unit of structure.

---

1) J. Palacios, An. Soc. Espan. Fis. Quim. **52**, 246. 1927.

2) W. F. de Jong, Dissertation, Delft, 1928. Our acquaintance with this work and that of Palacios is limited to the Strukturbericht abstract.

3) F. Machatschki, Norsk. Geol. Tidsskr. **10**, 23. 1928; Z. Krist. **68**, 204. 1928.

Table I. The determination of  $a_0$  from oscillation data.

$(h k l)$	X-ray line <sup>1)</sup>	$a_0$	$(h k l)$	X-ray line <sup>1)</sup>	$a_0$
400	$\alpha_1$	10.212 Å	800	$\alpha_2$	10.160 Å
400	$\alpha_2$	10.192 Å	10.2.0	$\alpha_2$	10.229 Å
510	$\alpha_2$	10.173 Å	12.0.0	$\alpha_2$	10.213 Å
710	$\alpha_1$	10.175 Å	16.0.0	$\alpha_1$	10.202 Å
710	$\alpha_2$	10.147 Å	16.0.0	$\alpha_2$	10.189 Å
800	$\alpha_1$	10.168 Å			
		Average			10.187 Å

A symmetrical Laue photograph through (100) was found to show a four-fold axis and four planes of symmetry, requiring the space group to be isomorphous with one of the point groups  $T_d$ ,  $O$ , and  $O_h$ . No odd-order reflections from planes with  $h + k + l$  odd were observed on any oscillation or Laue photograph, showing the lattice to be the body-centered one,  $F_c''$ . Of the possible space groups  $T_d^3$ ,  $T_d^6$ ,  $O^5$ ,  $O^8$ ,  $O_h^9$ , and  $O_h^{10}$ , three are definitely eliminated by observed reflections.  $T_d^6$  and  $O_h^{10}$  permit no reflections of the type  $(hhl)$  with  $\frac{1}{2}(2h + l)$  odd; they are consequently eliminated by the appearance on Laue photographs of many first-order reflections from planes of this type, including (118), (1. 1. 12), (3. 3. 16), (338), etc.  $O^8$  requires that  $(h00)$  reflect only in the fourth, eighth, etc., orders, and is eliminated by the observation on an oscillation photograph of a very weak but unmistakable reflection in the sixth order, (600). Of the remaining space groups,  $T_d^3$ ,  $O^5$ , and  $O_h^9$ , the first is shown to be correct by the tetrahedral face-development of the minerals of the tetrahedrite group.

The space group  $T_d^3$  was found also by Machatschki, who further reported the value  $a_0 = 10.189$  Å for tennantite from Redruth, Cornwall, and 10.205 Å for binnite. The lattice constants of antimony-rich tetrahedrites are considerably larger, ranging up to 10.55 Å.

#### The Chemical Formula of Minerals of the Tetrahedrite Group.

Using the reported values of the density and  $a_0 = 10.19$  Å, the numbers of atoms in the unit of binnite according to Prior's analyses (the most recent and without doubt the most accurate that have been carried out on this substance) are given in Table II. These support the ideal formula  $Cu_3AsS_3$  used by Machatschki rather than  $Cu_3AsS_4$  suggested by de Jong. However, there is a notable excess of sulfur, amounting in the case of Analysis 75 to nearly two atoms. In default

1)  $MoK_{\alpha_1} = 0.7078$  Å;  $MoK_{\alpha_2} = 0.7124$  Å.

Table II. Numbers of atoms in unit of binnite, according to Prior's analyses<sup>1)</sup>.

Analysis No.	Density	<i>Cu</i>	<i>Fe</i>	<i>Ag</i>	<i>Cu + Fe + Ag</i>	<i>As</i>	<i>S</i>
75	4.62	23.18	0.59	0.51	24.28	7.50	25.43
76	4.598	20.43	1.94	1.30	23.67	(8.05)	24.69

of more reliable analyses of binnite, we have reconsidered the best analyses of the tetrahedrite minerals in general; namely, those resulting from the beautiful work of Kretschmer<sup>2)</sup>. Because of the variability of density and lattice constant, we have calculated relative numbers of atoms on the basis  $As + Sb = 1.00$ . The symbol *Cu* in Table III represents  $Cu + Ag$ ;  $Zn$ ,  $Zn + Fe$ ; and *Sb*,  $As + Sb + Bi$ . It is seen that the ratio  $(Cu + Zn)/Sb$  lies very close to 3.00, the root-mean-square deviation being only 0.032 (excluding Analyses 8 and 15). However, the ratio  $S/Sb$  deviates pronouncedly from 3.00. The next possible value for this ratio, in view of the body-centered lattice, is  $26/8 = 3.25$ . The

Table III. Recalculation of Kretschmer's analyses of tetrahedrite minerals.

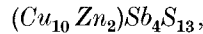
Origin	<i>Cu</i>	<i>Zn</i>	<i>Cu + Zn</i>	<i>S</i>
1. Horhausen . . . . .	2.47	0.51	2.98	3.19
2. Hornachuelos . . . . .	2.52	.49	3.00	3.28
3. Huanchaca . . . . .	2.59	.43	3.02	3.25
4. Schemnitz . . . . .	2.48	.52	3.00	3.25
5. Dillenburg . . . . .	2.47	.51	2.98	3.20
6. Kapnik . . . . .	2.58	.48	3.06	3.32
7. Siebenbürgen . . . . .	2.46	.55	3.01	3.34
*8. Müsen . . . . .	2.13	.71	2.84	2.94
9. Kotterbach . . . . .	2.60	.40	3.00	3.15
10. Brixlegg . . . . .	2.56	.49	3.05	3.27
11. Algier . . . . .	2.59	.39	2.98	3.20
12. Santiago . . . . .	2.57	.46	3.03	3.29
13. Guanajuato . . . . .	2.58	.49	3.07	3.29
14. Kupferberg . . . . .	2.82	.18	3.00	3.11
*15. Redruth . . . . .	3.43	.13	3.56	3.39
* 8'. —	2.32	.68	3.00	3.20
* 15'. —	3.04	.00	3.04	3.00

\* 8' and 15' are 8 and 15 as corrected by Kretschmer for  $NiSb$  and  $Cu_3FeS_3$ , respectively.

1) Quoted by Hintze, Handbuch der Mineralogie.

2) A. Kretschmer, Z. Krist. 48, 484. 1911.

observed figures approximate this value closely, the mean of all but 8 and 15 being 3.24, and the root-mean-square deviation from 3.25 being 0.066. We consequently feel that we are justified in adopting as the ideal formula for the tetrahedrite minerals the expression



with  $Cu = Cu' + Ag'$ ,  $Zn = Zn'' + Fe''$  and perhaps  $Cu''$ ,  $Sb = As''' + Sb''' + Bi'''$ , two molecules of this composition being contained in the unit of structure. The parenthesis indicates that the  $Cu$  and  $Zn$  atoms are distributed among twelve equivalent positions.

Essentially this formula has been suggested before. Tschermak in 1894 wrote  $Cu_{10}Zn_2Sb_4S_{13}$ , and Kretschmer adopted the more general expression  $(Cu_xZn_y)SbS_{3+y/2}$ , with  $x + y = 3$ . Machatschki pointed out the existence of excess sulfur over that required by the formula  $Cu_3SbS_3$ , but preferred to retain this expression as the ideal formula, and to consider the excess sulfur as due to solid solutions of a type discussed later.

In view of the concordance of Kretschmer's analyses, we believe that the wide fluctuations shown by earlier analyses are to be attributed in the main to experimental error, and that actually the composition of the minerals of the tetrahedrite group does not depart greatly from that expressed by our ideal formula<sup>1</sup>).

### The Atomic Arrangement.

Accepting our ideal formula, we must place 2  $(Cu, Fe)_{12}As_4S_{13}$  in positions provided by  $T_d^3$ . These positions, in Wyckoff's tabulation, are

2 a.	000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ .	12 a.	$u00$ , etc.
6 e.	$0\frac{1}{2}0$ , etc.	24 f.	$u0\frac{1}{2}$ , etc.
8 a.	$uuu$ , $u\bar{u}\bar{u}$ , etc.	24 g.	$uvw$ , $u\bar{v}\bar{v}$ , etc.
12 h.	$\frac{1}{2}0\frac{1}{4}$ , $0\frac{1}{4}\frac{1}{2}$ , etc.	48.	$xyz$ , etc.

Because of the large number of structures involving several parameters, a rigorous derivation of the atomic arrangement would be difficult. However, it was evident from the oscillation photographs that the

1) A similar conclusion was reached from the consideration of selected chemical analyses by E. T. Wherry and W. F. Foshag (J. Wash. Acad. Sci., 11, 4, 1921), who wrote "... Tschermak's [formula] is here adopted; the more complex formulas of Prior and Spencer and of Kretschmer do not appear to be justified by the evidence". A. N. Winchell (Amer. Mineral., 11, 181, 1926), on the other hand, has emphasized the deviations of the analyses from Tschermak's formula.

structure is closely related to that sphalerite, inasmuch as the strongest reflections which occur are those with  $h + k + l = 0 \pmod{8}$  and with  $h/2 = k/2 = l/2 \pmod{2}$ . As pointed out by Machatschki, a structure of this type is the following:

- 8  $As$  in 8  $a$  with  $u_{As} \cong 0.250$ ;
- 12  $Cu_I$  in 12  $h$ ;
- 12  $Cu_{II}$  in 12  $a$  with  $u_{Cu} \cong 0.250$ ;
- 24  $S_I$  in 24  $g$  with  $u_S \cong 0.125$  and  $v_S \cong 0.375$ ;
- 2  $S_{II}$  in 2  $a$ .

On calculating intensities of reflection for these parameter values, it was found that the general agreement with observation for all except the very weak reflections was excellent, as is shown by the data in Table IV for useful reflections from  $45^\circ$  oscillation photographs from (100) with

Table IV. Observed and calculated intensities of reflection on oscillation photograph from (100) with [001] as axis.

Equator					
(200)	0.0 <sup>a</sup>				
0.00 <sup>b</sup>	0.00 <sup>c</sup>				
(400)	25	(402)	0.0	(404)	50
21.0	23.5	0.01	0.00	62.5	56.8
(600)	0.2	(602)	0.6	(604)	0.0
0.00	0.17	0.11	0.39	0.00	0.00
(800)	30	(802)	0.3	(804)	4
33.8	28.4	0.01	0.17	5.9	4.5
(10.0.0)	0.0	(10.0.2)	0.5	(10.0.4)	0.0
0.1	0.03	0.09	0.36	0.01	0.09
(12.0.0)	1.0	(12.0.2)	0.0	(12.0.4)	6
1.3	1.1	0.00	0.09	8.4	5.6
(14.0.0)	0.0				
0.00	0.14				
(16.0.0)	1.5				
2.3	1.6				

a Observed intensity.

b Intensity calculated for ideal parameter values.

c Intensity calculated for final parameter values.

[001] as axis of oscillation. The observed relative intensities were estimated by the comparison of several photographs taken under identical conditions except for variation in the time of exposure. The calculated intensities are those given by the intensity formula

$$I = \frac{1 + \cos^2 2\vartheta}{2 \sin 2\vartheta} h \omega |F|^2 \cdot e^{-2B(\sin \vartheta, \lambda)^2}$$

in which  $\omega$  is the Ott factor for varying time of reflection. Pauling-Sherman  $f_0$ -values for neutral atoms were used, and an estimated value of 1.00 was adopted for the coefficient  $B$  in the temperature factor. The factor  $h$  is required by the experimental method, involving reflection from the face of a small strongly-absorbing crystal bathed in the X-ray beam. Because of lack of knowledge of the effect of absorption for them, reflections from planes whose traces with the developed face (100) were not horizontal were not used in the parameter determination.

The observed strength of the reflections (602), (802), and (40.0.2) relative to (402), etc. can be accounted for only by keeping  $u_{As}$  close to 0.250 and decreasing  $u_{Cu}$  to about 0.225. The simultaneous determination of the two sulfur parameters cannot be made with much accuracy. However, inasmuch as the  $Cu_I$  atoms are surrounded tetrahedrally by four  $S_I$  atoms, each of which itself is surrounded by four metal atoms, the assumption may be made with considerable confidence that the  $Cu-S$  distance is about the same as in chalcopyrite<sup>1</sup>),  $2.32 \pm 0.03$  Å, and sylvanite<sup>2</sup>),  $2.285 \pm 0.014$  Å. This limits  $v_S$  to values near 0.360. With this limitation, it was found that satisfactory agreement between calculated and observed intensities was obtained with the parameter values  $u_{As} = 0.255$ ,  $u_{Cu} = 0.225$ ,  $u_S = 0.122$ , and  $v_S = 0.363$ . The agreement is somewhat impaired by changing these values by as much as 0.005.

### Description of the Structure.

The structure found for binnite is shown in Figure 1, the interatomic distances corresponding to the finally accepted parameter values being given in Table V. Each  $S_I$  atom is surrounded tetrahedrally by four other atoms, to which it is presumably attached by bonds which are largely covalent in character. The interatomic distances are in approximate

Table V. Interatomic distances in binnite.

Atom	Neighboring atoms	Interatomic distance <sup>3)</sup>	Atom	Neighboring atoms	Interatomic distance <sup>3)</sup>
$As$	3 $S_I$	2.21 Å	$S_I$	4 $As$	2.21 Å
$Cu_I$	4 $S_I$	2.28 Å	$S_I$	2 $Cu_I$	2.28 Å
$Cu_{II}$	2 $S_I$	2.23 Å	$S_I$	4 $Cu_{II}$	2.23 Å
$Cu_{II}$	4 $S_{II}$	2.29 Å	$S_{II}$	6 $Cu_{II}$	2.29 Å

1) L. Pauling and L. O. Brockway, Z. Krist. **82**, 488. 1932.

2) L. Pauling and R. Hultgren, Z. Krist. **84**, 204. 1933.

3) All distances are accurate to about  $\pm 0.05$  Å.

agreement with this assumption, the sum of the normal covalent radii<sup>1)</sup> for *As* and *S* being 2.25 Å, and of the tetrahedral radii<sup>2)</sup> for *Cu* and *S* 2.39 Å. The coordination number of *Cu*<sub>II</sub> is only three, so that the observed decrease in *Cu*<sub>II</sub> = *S*<sub>I</sub> distance from *Cu*<sub>I</sub> (surrounded tetrahedrally by

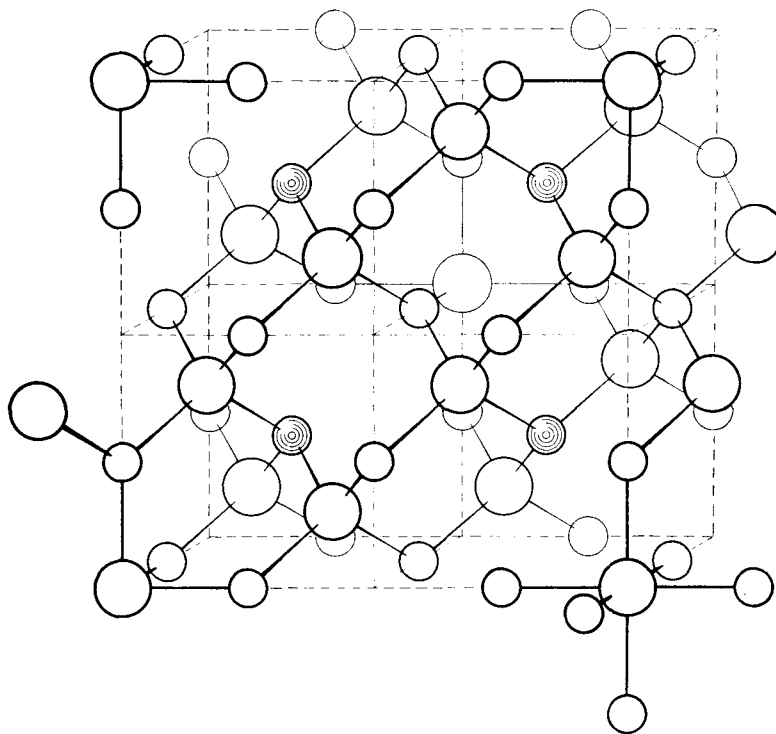


Fig. 1. Diagram showing the forward half of the unit cube of binnite. Large circles represent sulfur atoms, small open circles copper atoms, and small shaded circles arsenic atoms. Bonds between adjacent atoms are indicated. Note that there are two kinds of copper atoms and two kinds of sulfur atoms.

four sulfur atoms) is not unexpected. The atom *S*<sub>II</sub> is surrounded by six *Cu*<sub>II</sub> atoms at the corners of a regular octahedron, and, as would be anticipated, the *Cu*<sub>II</sub> — *S*<sub>II</sub> distance is somewhat larger than the *Cu*<sub>II</sub> — *S*<sub>I</sub> distance. Although rather rare, the coordination number six for sulfur is not unprecedented, being shown in the sulfides with the niccolite

1) L. Pauling, Pr. Nat. Acad. Sci. **18**, 293. 1932.

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

structure,  $FeS$ ,  $CoS$ , etc. (provided that the structures assigned them are correct).

The binnite structure may be described in terms of the sphalerite structure in the following way. In a large cube containing  $32 ZnS$ , replace  $8 Zn$  (at  $\frac{1}{4} \frac{1}{4} \frac{1}{4}$ ,  $\frac{1}{4} \frac{1}{4} \frac{3}{4}$ , etc.) by  $As$  and the remaining  $24$  by  $Cu$ . Then remove  $8 S$  (at  $\frac{1}{8} \frac{1}{8} \frac{1}{8}$ , etc.), leaving  $As$  bonded to  $3 S$  only, and introduce  $2 S$  at  $0 0 0$  and  $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ , the centers of the two tetrahedra formed by the eight sulfur atoms removed.

The structure assigned by Machatschki to tetrahedrite is essentially the same as the structure of binnite (neglecting the  $S_{II}$  atoms), his suggested parameter values being  $u_{Sb} = \frac{5}{18} = 0.278$ ,  $u_{Cu} = \frac{1}{4}$ ,  $u_S = \frac{1}{8}$ ,  $v_S = \frac{3}{8}$ . Because of the large scattering power of  $Sb$  for X-rays, the value of  $u_{Sb}$  found by Machatschki must be very nearly correct, but small changes in the other parameters might well be made. It seems not unreasonable that  $u_{Cu}$ ,  $u_S$ , and  $v_S$  have about the same values in tetrahedrite as in binnite, leading to about the same  $Cu-S$  interatomic distances. The change from  $u_{As} = 0.255$  to  $u_{Sb} = 0.278$  is, however, real, resulting from the increase in covalent radius from  $1.21 \text{ \AA}$  for  $As^{III}$  to  $1.41 \text{ \AA}$  for  $Sb^{III}$ . With these parameter values and with  $a_0 = 10.30 \text{ \AA}$ , the  $Sb-S$  distance is calculated to be  $2.43 \text{ \AA}$ , in excellent agreement with the sum of the normal covalent radii,  $2.45 \text{ \AA}$ .

In his first paper, Machatschki suggested that the sulfur atoms present in excess over the number required by his ideal formula,  $Cu_3SbS_3$ , occupy the positions  $0 0 0$  and  $\frac{1}{2} \frac{1}{2} \frac{1}{2}$  at which we have located the  $S_{II}$  atoms. In his second paper, however, he considers the excess sulfur to occupy positions corresponding to the completed sphalerite arrangement ( $\frac{1}{8} \frac{1}{8} \frac{1}{8}$ , etc.). There is little chance of deciding between these alternatives by X-ray data; however, our conviction that the ideal formula is  $(Cu, Zn)_{12}Sb_4S_{13}$  requires the acceptance of the former.

We wish to thank Professor Palache for lending us an excellent crystal of binnite, and Dr. S. Weinbaum for carrying out many of the intensity calculations.

### Summary.

Using data from Laue and oscillation photographs, it is shown that the unit of structure of binnite has  $a_0 = 10.19 \pm 0.02 \text{ \AA}$ , the space group being  $T_d^3$ . The unit contains  $2(Cu, Fe)_{12}As_4S_{13}$ , with the atomic arrangement



8  $As$  in  $8a$ ,  $u_{As} = 0.255$ ;  
12  $Cu_I$  in  $12h$ ;  
12  $Cu_{II}$  in  $12a$ ,  $u_{Cu} = 0.225$ ;  
24  $S_I$  in  $24g$ ,  $u_S = 0.122$ ,  $v_S = 0.363$ ;  
2  $S_{II}$  in  $2a$ .

The parameter values are accurate to  $\pm 0.005$ . In view of the work of Machatschki, it is probable that this structure is common to all members of the tetrahedrite group, except that on replacing  $As$  by  $Sb$  the corresponding parameter changes to  $u_{Sb} = 0.278$ .

Pasadena, California, September 26, 1933.

Received November 1<sup>st</sup>, 1933.