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The crystal structure of tetrahedrite, $Cu_{12}Sb_4S_{13}$

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With 5 figures

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Auszug

Der Tetraedrit, $Cu_{12}Sb_4S_{13}$, bildet eine merkwürdige Überstruktur des Zinkblendetyps. Diese Struktur wurde von PAULING und NEUMAN 1934 aus einer beschränkten Anzahl von Interferenzen gefolgert. Sie wird nach der Methode der kleinsten Quadrate verfeinert, wobei der R-Wert von 27,9% auf 3,9% sinkt; die absolute Konfiguration konnte ermittelt werden.

Der Tetraedrit enthält zwei verschiedene Koordinationen der Cu-Atome. Die Atome der einen Art sind von vier S-Atomen im Abstand von 2,342 Å nahezu regelmäßig tetraedrisch umgeben. Die anderen Cu-Atome haben eine ganz ungewöhnliche Dreieckskoordination mit einem Cu—S-Abstand von 2,234 Å und zwei Abständen von 2,272 Å. Diese Gruppe ist eben; ihr Cu-Atom weist eine starke Wärmebewegung auf. Das Sb-Atom ist an drei S-Atome im Abstand von 2,446 Å gebunden; die Winkel zwischen den Bindungsrichtungen sind 95° 8′. Außerdem wird das Sb-Atom von sechs weiteren S-Atomen in Van-der-Waals-Abständen von 4,033 Å umgeben.

Die komplizierte Art der Komplex-Verknüpfungen wird ausführlich diskutiert.

Abstract

Tetrahedrite, $Cu_{12}Sb_4S_{13}$, has a curious superstructure based on the sphalerite arrangement. This structure was proposed by PAULING and NEUMAN in 1934 on the basis of a limited number of measured intensities. Least-squares refinement in this study reduced an initial disagreement index of 27.9% to 3.9% and thus confirmed the correctness of the structure. The absolute configuration of the structure was established.

Tetrahedrite contains two sorts of copper atoms. A first type is coordinated by four sulfur atoms at 2.342 Å which form a nearly regular tetrahedron. The

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second type of copper atom is in an unusual triangular coordination, being bonded only to one sulfur atom at 2.234 Å and two at 2.272 Å. This group is planar, and the copper atom has a highly anisotropic thermal motion. The antimony atom is bonded to three sulfur atoms at 2.446 Å, which form bond angles of 95°8′, but has six additional sulfur neighbors at the van der Waals distance of 4.033 Å. The polyhedra are linked in a complex manner which is discussed in detail.

Introduction

Tetrahedrite is a member of a common group of sulfosalts which have composition $X_{12}Z_4S_{13}$. A complete series of solid solutions extends between $Z = Sb$ (tetrahedrite) and $Z = As$ (tennantite). The metal atom X is primarily Cu, although atoms such as Zn, Fe, Ag, Hg, Pb, Ni or Co often replace Cu in amounts up to $16\,^0/_0$.

The general nature of the crystal structure of tetrahedrite was determined by MACHATSCHKI (1928*a*, 1928*b*). The ideal composition, however, was assumed to be Cu_3SbS_3. PAULING and NEUMAN (1934) reappraised the reliable chemical analyses of tetrahedrite, and concluded that a formula $Cu_{12}Sb_4S_{13}$ was in closer accord with the analyses. They proposed an atomic arrangement which was a curious derivative of a sphalerite-type substructure.

The Pauling and Neuman structure, however, was guessed from a large number of possible arrangements permitted by the probable tetrahedrite space-group. The structure was determined through the measurement of only 18 intensities, of which 7 were not detectable. All were zero-level reflections, so that the structure was essentially solved in projection. Furthermore, the 7 unobserved intensities accounted for two-thirds of the superstructure reflections which were investigated. It is these intensities which are most sensitive to the exact nature of the departures from an ideal sphalerite-like arrangement.

For these reasons, there has been a question as to whether the vacant sulfur sites in the sphalerite-like arrangement are ordered (e.g. WELLS, 1962). Many references continue to assign the composition Cu_3SbS_3 to tetrahedrite.

It was therefore felt that the Pauling and Neuman structure might prove to be incorrect or, at any rate, require significant parameter adjustments upon refinement. A previous note (WUENSCH, 1963*a*) has reported that the structure has been confirmed. The present paper describes the results of additional least-squares refinement, and presents a more detailed discussion of the structure.

Selection of material

The superstructure intensities present in diffraction patterns obtained from minerals of the tetrahedrite series are partially due to the fact that an ordered arrangement of Cu and Sb or As atoms occupy the metal-atom sites of a sphalerite-like arrangement. The mineral investigated by PAULING and NEUMAN was binnite, a variety of tennantite. The difference in scattering power between Cu and As is only 4 electrons. More of the weak superstructure intensities should be detectable with tetrahedrite since the difference in scattering power between Cu and Sb is 22 electrons.

Tetrahedrite from Horhausen, Westerwald, Germany, was therefore selected for study. Chemical analyses of material from this locality have been given by PRIOR and SPENCER (1899), and KRETSCHMER (1911). These results are given in Table 1. The composition of these crystals is unusual in that Z is almost entirely Sb, and X is primarily Cu.

Table 1. *Chemical analyses of Horhausen tetrahedrite*

	Weight percent		
	PRIOR and SPENCER (1899)	KRETSCHMER (1911)	Ideal $Cu_{12}Sb_4S_{13}$
Cu	41.55%	37.75%	45.77%
Zn	2.63	6.51	—
Fe	1.02	1.10	—
Pb	.62	.71	—
Ag	—	.11	—
Sb	28.32	28.66	29.22
Bi	.83	.53	—
S	24.33	24.61	25.01
Σ	99.30	99.98	100.00
Density	4.969 g/cm³	5.079 g/cm³	—

Specimens suitable for x-ray analysis were obtained from an excellently developed tetrahedral crystal (Harvard catalogue number 82560) with a shiny, metallic luster. Several fragments from the crystal were ground into spheres using a method similar to that described by BOND (1951). The crystal selected for final study and for the subsequent collection of intensities had a radius of 0.114 mm and was spherical to within ± 1.7% ($\mu_l R = 7.39$ for Cu$K\alpha$ radiation[2]).

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[2] An average of the two values obtained from the exact compositions and densities of Table 1.

X-ray examination and unit-cell contents

Precession photographs of the spherical specimen described above displayed symmetry $m3m$. The only reflections exhibiting systematic absences were those for which $h+k+l \neq 2n$. The diffraction symbol for tetrahedrite is therefore $m3mI$---. This permits $Im3m$, $I43$ and $I\bar{4}3m$ as possible space groups. The tetrahedron is the predominant form of the mineral and this morphology requires $I\bar{4}3m$ as the correct space group. This result is in accord with previous investigations.

The lattice constant was obtained from a precision back-reflection Weissenberg photograph (BUERGER, 1942). The extrapolated value for a, obtained with the aid of the IBM 7090 least-squares program LCLSQ (BURNHAM, 1961), was 10.3908 ± .0006 Å. The analyses and densities given in Table 1 provide unit-cell contents of

$$2\underset{\overline{11.59}}{\left|\begin{array}{l}\mathrm{Cu}_{10.56}\\ \mathrm{Zn}_{0.67}\\ \mathrm{Fe}_{0.31}\\ \mathrm{Pb}_{0.05}\end{array}\right|}\underset{\overline{4.01}}{\left|\begin{array}{l}\mathrm{Sb}_{3.94}\\ \mathrm{Bi}_{0.07}\end{array}\right|}\mathrm{S}_{12.83}\qquad\qquad 2\underset{\overline{12.32}}{\left|\begin{array}{l}\mathrm{Cu}_{10.19}\\ \mathrm{Zn}_{1.71}\\ \mathrm{Fe}_{0.34}\\ \mathrm{Pb}_{0.06}\\ \mathrm{Ag}_{0.02}\end{array}\right|}\underset{\overline{4.08}}{\left|\begin{array}{l}\mathrm{Sb}_{4.04}\\ \mathrm{Bi}_{0.04}\end{array}\right|}\mathrm{S}_{13.17}$$

for the Prior and Spencer, and Kretschmer analyses, respectively. These results neatly bracket the ideal composition $\mathrm{Cu}_{12}\mathrm{Sb}_4\mathrm{S}_{13}$.

Collection of intensities

An equi-inclination counter diffractometer, employing a proportional counter as detector, was used to record the intensities. The associated electronics included pulse-height analysis circuitory. Instrumental settings were computed with the IBM 7090 program DFSET (PREWITT, 1960). Integrated intensities were determined by recording the background intensity at both ± 3° φ from the diffraction maximum, and the total number of counts accumulated as the crystal was rotated through 6°φ. The maximum peak intensity recorded was limited to 2000 counts per second by means of Al attenuating foils introduced before the counter. The integrated intensities were corrected for background, Lorentz and polarization factors, and appropriate spherical absorption factors (BOND, 1959) with the aid of the data-reduction programs DTRDA and DTRDB (BURNHAM, 1961).

Of 153 independent reflections contained within the Cu$K\alpha$ sphere, 136 were accessible with the diffractometer which was employed. Of these, only two were undetectable. This provided 8 reflections per parameter for a least-squares refinement employing anisotropic temperature-factor coefficients. The results of reproducibility and symmetry tests which were performed on a representative sample of the intensities (WUENSCH, 1963*b*), indicated that the set of structure factors which was obtained was reliable to ± 3%.

Refinement of the structure

The structure proposed by PAULING and NEUMAN contains 5 atoms per asymmetric unit. The parameters reported for these atoms[3] are given in Table 2. The disagreement index, $R = \Sigma||F_{\text{obs}}| - |F_{\text{cal}}||/\Sigma|F_{\text{obs}}|$, for this model was 27.9% for the complete three-dimensional collection of structure factors, and 26.1% for the zero-level reflections corresponding to those measured by PAULING and NEUMAN. This relatively low value for R indicated that the structure was probably correct, and that least-squares refinement would improve the agreement between F_{obs} and F_{cal}.

The refinement was performed with the full-matrix, least-squares program SFLSQ3 (PREWITT, 1962). All atoms were assumed to be un-ionized. Form factors given by FREEMAN and WATSON, THOMAS and UMEDA, and DAWSON were employed for Cu, Sb, and S, respectively[4]. Use of only a single factor to scale F_{cal} to F_{obs} was justified, since the symmetry tests which had been performed on the reflections (WUENSCH 1963*b*) indicated that the degree of agreement between equivalent structure factors occuring on different levels was the same as that between equivalent structure factors occuring within the same level.

The refinement was carried out in six stages, as indicated in Table 3. The stages differed in the weighting scheme employed. All reflections were assigned equal weights in the initial stage. The scale factor and atomic positions, and then temperature-factor coefficients, were alternately varied to convergence, until no further refinement ensued. The value of R was then computed as a function of F_{obs}, and its behavior approximated by a collection of functions, each of which was valid over a limited range of values of F_{obs}. The weighting scheme adopted

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[3] PAULING and NEUMAN, as has been noted, actually investigated the structure of tennantite. On the basis of MACHATSCHKI's work, however, parameters were also proposed for tetrahedrite. These parameters, which were considered highly reliable, are the values given in Table 2.

[4] International tables for x-ray crystallography, Vol. III. (Kynoch Press, Birmingham, 1962) 201—212.

Table 2. *Positional parameters for tetrahedrite*

Atom	Equipoint		Parameter	PAULING and NEUMAN (1934)		Present study	
					Distortion from sphalerite arrangement		Distortion from sphalerite arrangement
Cu(1)	12*d*	$\bar{4}$	*x*	$\frac{1}{4}$	0	$\frac{1}{4}$	0
		$\frac{1}{4}\,\frac{1}{2}\,0$	*y*	$\frac{1}{2}$	0	$\frac{1}{2}$	0
			z	0	0	0	0
Cu(2)	12*e*	*mm*	*x*	.225	—.025	.2150 ± .0005	—.0350
		*x*00	*y*	0	0	0	0
			z	0	0	0	0
S(1)	24*g*	*m*	*x*	.122	—.003	.1152 ± .0003	—.0098
		xxz	*y*	.122	—.003	.1152 ± .0003	—.0098
			z	.363	—.012	.3609 ± .0005	—.0141
S(2)	2*a*	$\bar{4}3m$	*x*	0	—	0	—
		000	*y*	0	—	0	—
			z	0	—	0	—
Sb	8*c*	3*m*	*x*	.278	+.028	.2682 ± .0001	+.0182
		xxx	*y*	.278	+.028	.2682 ± .0001	+.0182
			z	.278	+.028	.2682 ± .0001	+.0182

Table 3. *Stages in the refinement of tetrahedrite*

Stage	Weighting scheme		Parameters varied and number of cycles required to attain convergence		R	Weighted R
	Ranges of F_{obs}	Weight	Scale factor and atomic positions	Temperature factors		
0	—	—	—	—	27.9	—
1	—	1.0 (equal weights)	4	3		
			1		10.4	9.7
2	> 70	1.0	1	1		
	70 — 0	$13.6/54.4 - 0.592\,F_{obs}$	1		9.3	7.8
3	> 225	1.0		2		
	225 — 160	$6.0/36.0 - 0.125\,F_{obs}$	1	0	9.0	6.5
	160 — 110	$6.0/0.16\,F_{obs} - 11.6$		2[a]	6.8	5.3
	110 — 75	1.0				
	75 — 0	$6.0/80.0 - F_{obs}$				
4	> 256	1.0	2	0		
	256 — 151	$1.5/24.2 - 0.088\,F_{obs}$	0		6.7	3.5
	151 — 52	$1.5/4.9 + 0.003\,(106 - F_{obs})^2$	2[b]	3		
	52 — 0	$1.5/52.0 - 0.72\,F_{obs}$	2	2	4.9	2.4
5	> 500	1.0				
	500 — 145	$1/9.45 - 0.017\,F_{obs}$	1	0		
	145 — 120	$1/0.12\,F_{obs} - 10.4$	0	0	4.8	2.4
	120 — 0	$F_{obs}/590.4 - 0.92\,F_{obs}$				
6	> 500	1.0	1	1		
	500 — 145	$(9.45 - 0.017\,F_{obs})^{1/2}$	1	1		
	145 — 120	$(0.12\,F_{obs} - 10.4)^{1/2}$	1	0		
	120 — 0	$[(590.4 - 0.92\,F_{obs})/F_{obs}]^{1/2}$	0	0	3.9	4.7

[a] Anisotropic temperature-factor coefficients introduced in these, and subsequent cycles.
Anomalous-scattering corrections introduced for all atoms in these, and subsequent cycles.

for the next stage was one for which the product of weight and R was constant for all F_{obs}. This scheme assigns the highest reliability to those reflections which have the lowest R. The introduction of each new weighting scheme naturally improved the value of the weighted R, $[\Sigma w(|F_{\mathrm{obs}}|-|F_{\mathrm{cal}}|)^2/\Sigma wF_{\mathrm{obs}}{}^2)^{1/2}$, since increased weight was assigned to those reflections for which the agreement between F_{obs} and F_{cal} had been improved. It is noteworthy, however, that the introduction of an improved weighting scheme invariably improved the value of R as well.

The value of R decreased less markedly with each introduction of a new weighting scheme toward the final stages. When the structure had essentially converged, a final stage of refinement was performed in which weights proportional to $R^{1/2}$ were assigned to each reflection. The final weighting scheme rapidly effected small adjustments in the converged structure which were necessary to improve the agreement for those reflections which had previously been assigned low weights All of the shifts which occurred were of the order of the estimated standard deviations, with the exception of the parameter x for Cu(2). This parameter previously had interacted strongly with the scale factor. The weighting scheme of the final stage, however, reduced the correlation coefficient (GELLER, 1961) from 0.44 to 0.10.

The final value for R was 3.9%; the weighted R was 2.4% and 4.7% for the weighting schemes in which weights were assigned proportional to $1/R$ and $R^{1/2}$, respectively.

Results of the refinement

The values obtained for the atomic coordinates, and their estimated standard deviations, are presented in Table 2, where they may be compared with the values given by PAULING and NEUMAN. The departure of these coordinates from an ideal sphalerite-like arrangement of atoms is also given. In comparison with the Pauling and Neuman structure, Cu(2) and S(1) are more displaced from a sphalerite arrangement, while Sb is less displaced. The anisotropic temperature-factor coefficients are presented in Table 4. The symmetry restrictions on the coefficients were obtained according to the method of LEVY (1956). Table 4 also includes an "equivalent" isotropic temperature factor for each atom, computed according to the relation

$$B = \tfrac{4}{3} \sum_i \sum_j \beta_{ij} \, (\mathbf{a}_i \cdot \mathbf{a}_j)$$

Table 4. *Anisotropic temperature-factor coefficients for tetrahedrite*

Atom	Symmetry restrictions	Independent values of β_{ij}	Equivalent isotropic temperature-factor
Cu(1)	$\beta_{22} = \beta_{33}$ $\beta_{12} = \beta_{23} = \beta_{31} = 0$	$\beta_{11} = .0028 \pm .0003$ $\beta_{22} = .0027 \pm .0002$	1.19 Å^2
Cu(2)	$\beta_{22} = \beta_{33}$ $\beta_{12} = \beta_{31} = 0$	$\beta_{11} = .0032 \pm .0005$ $\beta_{22} = .0130 \pm .0006$ $\beta_{23} = -.0094 \pm .0014$	4.19
S(1)	$\beta_{11} = \beta_{22}$ $\beta_{23} = \beta_{31}$	$\beta_{11} = .0030 \pm .0003$ $\beta_{33} = .0026 \pm .0004$ $\beta_{12} = -.0008 \pm .0004$ $\beta_{23} = -.0001 \pm .0003$	1.23
S(2)	$\beta_{11} = \beta_{22} = \beta_{33}$ $\beta_{12} = \beta_{23} = \beta_{31} = 0$	$\beta_{11} = .0027 \pm .0006$	1.14
Sb	$\beta_{11} = \beta_{22} = \beta_{33}$ $\beta_{12} = \beta_{23} = \beta_{31}$	$\beta_{11} = .0026 \pm .0001$ $\beta_{12} = -.0003 \pm .0001$	1.11

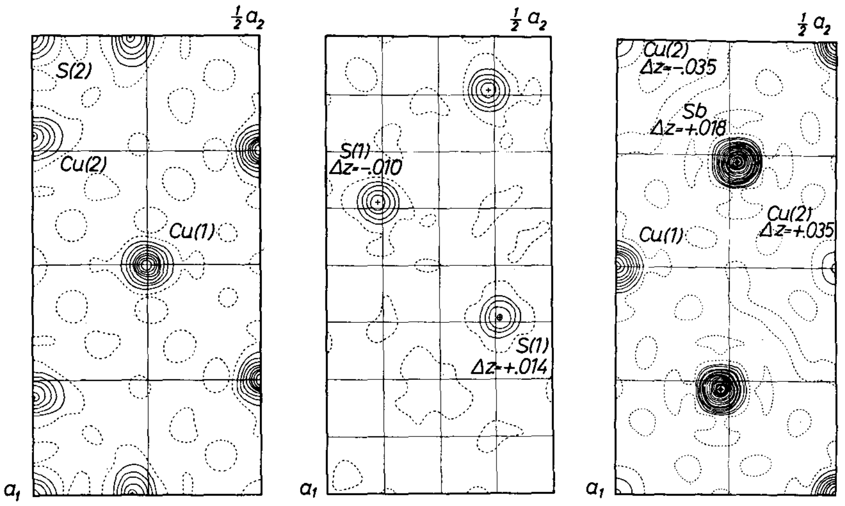
Table 5. *Comparison of observed and calculated structure factors*

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
2 0 0	123.4	110.6	10 6 0	49.5	51.5	9 8 1	29.5	26.3	9 4 3	49.9	50.7
4 0 0	416.7	419.1	7 7 0	10.7	13.4	2 2 2	670.3	692.7	11 4 3	38.9	38.7
6 0 0	49.0	53.4	9 7 0	96.8	96.3	4 2 2	114.0	111.6	6 5 3	160.7	161.2
8 0 0	407.5	404.7	8 8 0	208.0	204.3	6 2 2	399.8	394.9	8 5 3	88.5	87.1
10 0 0	42.7	36.2	10 8 0	21.3	26.3	8 2 2	30.7	25.5	10 5 3	74.8	79.2
12 0 0	31.5	29.9	9 9 0	107.6	115.2	10 2 2	164.2	162.6	7 6 3	80.9	80.3
1 1 0	37.4	24.4	2 1 1	49.3	41.6	12 2 2	18.5	21.5	9 6 3	57.0	57.9
3 1 0	38.2	22.9	4 1 1	155.2	150.3	3 3 2	85.6	89.4	8 7 3	106.2	105.9
5 1 0	92.9	92.4	6 1 1	197.8	198.1	5 3 2	86.0	80.4	10 7 3	60.0	62.8
7 1 0	102.0	99.0	8 1 1	103.2	99.8	7 3 2	65.5	60.7	9 8 3	51.2	55.9
9 1 0	45.8	45.6	10 1 1	110.3	112.1	9 3 2	109.6	107.1	4 4 4	251.7	241.7
11 1 0	20.6	13.1	12 1 1	135.3	140.6	11 3 2	40.5	40.1	6 4 4	42.3	40.7
2 2 0	175.3	160.4	3 2 1	101.9	91.5	4 4 2	93.3	83.1	8 4 4	293.1	289.1
4 2 0	108.5	101.8	5 2 1	129.8	130.5	6 4 2	79.4	75.1	10 4 4	21.5	24.6
6 2 0	121.2	119.1	7 2 1	15.4	12.2	8 4 2	54.6	52.0	5 5 4	109.8	109.0
8 2 0	57.9	55.5	9 2 1	40.9	39.7	10 4 2	42.4	43.8	7 5 4	104.3	103.3
10 2 0	51.1	49.3	11 2 1	32.3	33.6	12 4 2	2.8*	6.4	9 5 4	89.0	92.5
12 2 0	17.2	10.5	4 3 1	125.0	118.4	5 5 2	31.9	26.1	11 5 4	41.5	43.9
3 3 0	87.1	91.1	6 3 1	95.5	93.9	7 5 2	97.5	97.5	6 6 4	71.6	74.1
5 3 0	50.2	47.6	8 3 1	171.0	170.8	9 5 2	31.1	31.6	8 6 4	4.8*	12.6
7 3 0	21.7	17.1	10 3 1	160.2	164.6	11 5 2	67.4	72.6	10 6 4	23.8	27.0
9 3 0	25.0	22.7	12 3 1	88.6	95.1	6 6 2	276.8	267.5	7 7 4	62.9	62.2
11 3 0	9.3	12.1	5 4 1	70.8	65.0	8 6 2	28.9	28.3	9 7 4	51.6	55.0
4 4 0	636.6	652.2	7 4 1	91.7	89.6	10 6 2	107.2	107.2	8 8 4	66.8	73.8
6 4 0	32.9	29.3	9 4 1	50.2	49.3	7 7 2	93.9	93.8	6 5 5	122.9	125.3
8 4 0	127.9	132.1	11 4 1	61.7	59.7	9 7 2	94.3	95.6	8 5 5	67.0	66.2
10 4 0	10.6	11.4	6 5 1	85.5	87.5	8 8 2	30.7	26.2	10 5 5	63.3	64.6
12 4 0	127.1	132.5	8 5 1	122.8	122.3	4 3 3	135.3	132.4	7 6 5	58.3	63.0
5 5 0	139.2	128.3	10 5 1	139.8	142.1	6 3 3	111.7	106.9	9 6 5	23.9	22.1
7 5 0	53.4	48.7	7 6 1	89.1	90.1	8 3 3	107.8	107.1	8 7 5	75.7	81.6
9 5 0	70.2	69.9	9 6 1	96.2	94.9	10 3 3	91.5	93.5	6 6 6	155.6	155.4
11 5 0	96.0	93.9	11 6 1	24.7	24.9	12 3 3	120.1	128.8	8 6 6	25.8	29.2
6 6 0	75.3	72.0	8 7 1	94.2	93.0	5 4 3	81.9	76.1	7 7 6	47.4	46.1
8 6 0	23.0	26.3	10 7 1	54.4	59.0	7 4 3	63.3	60.7	8 7 7	21.8	22.8

* unobservable intensity

(HAMILTON, 1959). This relation provides the isotropic temperature factor which corresponds to the same mean-square thermal displacement as that predicted by the anisotropic coefficients. The observed and calculated structure factors are compared in Table 5.

Figure 1 presents electron-density sections at $z = 0, \frac{1}{8}$, and $\frac{1}{4}$. All atoms in the asymmetric unit lie in or near one of these sections. One half of the unit cell is shown for each section. The remainder of the cell is related to the portion shown by diagonal symmetry planes.



a) $z=0$ b) $z=\frac{1}{8}$ c) $z=\frac{1}{4}$

Fig. 1. Electron-density sections for tetrahedrite. Contours at equal, but arbitrary, intervals; zero contour dotted. All atoms would lie in the sections, and on the subnets shown in an undistorted sphalerite-like arrangment

Small peaks surround each of the peaks which represent an atom location. These peaks occur at the same distance from each atom location, and did not appear in difference syntheses. They undoubtedly are due to series-termination effects.

Subnets given by $\frac{1}{4}\,a$ or $\frac{1}{8}\,a$, as required, have been shown in these maps. All atoms in an ideal sphalerite-like arrangement would lie exactly in the sections and would occur at one of the lattice points of the subnet. The displacements, Δz, of each atom from the plane of the section, and the positions of the peaks relative to the neighboring grid points, provide a picture of the magnitude of the distortions from a sphalerite-like arrangement. The S atom required for completion of the sphalerite arrangement would be located at $\frac{1}{8}$ $\frac{1}{8}$ in the section

$z = \frac{1}{8}$. There is no evidence for electron density in this site, as had been proposed by MACHATSCHKI (1928*b*) and by PAULING and NEUMAN to explain variations in sulfur content in the mineral.

During stages 4 and 5 of the refinement, in which corrections for anomalous dispersion were introduced, parallel refinement was carried out for both the structure given above and its inverse. The value of R for the latter arrangement remained about 3 % higher at all stages. The absolute configuration of the structure was therefore established with certainty. Unfortunately, since the crystal employed in the collection of intensities had been ground to a spherical shape, no relation between the structure and its morphology can be given.

Discussion of the structure

The arrangement of atoms in the structure is most readily visualized by considering the linkage of polyhedra formed by the metal atoms about the sulfur atoms. S(2) is coordinated by six Cu(2) at 2.234 Å. These Cu atoms form a regular octahedron. Each S(1) is tetrahedrally coordinated by two Cu(1) at 2.342 Å, one Cu(2) at 2.272 Å and one Sb at 2.446 Å. The bond angles in the tetrahedron, Fig. 2*a*, range from 100°45′ to 117°14′. This is an appreciable distortion from the angles of 109°28′ which would be found in a regular tetrahedron.

The linkage of these polyhedra is indicated in Fig. 3, in which one quarter of the unit cell is shown. The octahedra are located at the origin and the body-centered position. Each tetrahedron shares a corner with such an octahedron. The remaining three corners of each tetrahedron share corners with two other tetrahedra in a sphalerite-like arrangement. The Sb atoms, indicated in Fig. 3 by small circles, are located at those corners of the tetrahedra which lie closest to the octahedra. A large void exists in the structure at the site where the S atom is missing from the completed sphalerite arrangement. This is apparent at the left-hand corner of the cell in Fig. 3.

Consideration of the arrangement of the polyhedra formed by the metal atoms about sulfur facillitates visualization of the structure and its relation to sphalerite. This representation, however, obscures several curious features about the structure, and the reasons for this arrangement. Fig. 2*b* illustrates the arrangement of sulfur atoms about the metal atoms of the structure. Cu(1) is tetrahedrally coordinated by S(1) at 2.342 Å. The bond angles of this tetrahedron are all equal to 110°58′. This is but a slight distortion from a regular tetrahedron. Cu(2) is trigonally coordinated by two S(1) at 2.272 Å and one S(2) atom at 2.234 Å. This group of four atoms lies in a symmetry plane and is therefore planar. Three S(1) atoms are located about a 3-fold axis at 2.446 Å from Sb. The S(1)—Sb—S(1) bond angle is 95°8′.

These polyhedra are linked in a complex fashion. Six CuS_3 triangles share a corner at the origin, Fig. 4a, to form a six-bladed "spinner". Since the triangles lie in the (110) symmetry planes of the cell, there are four locations on the "spinner" at which the corners of three different triangles are in close proximity. The base of a SbS_3 pyramid links these three corners, as shown in Fig. 5.

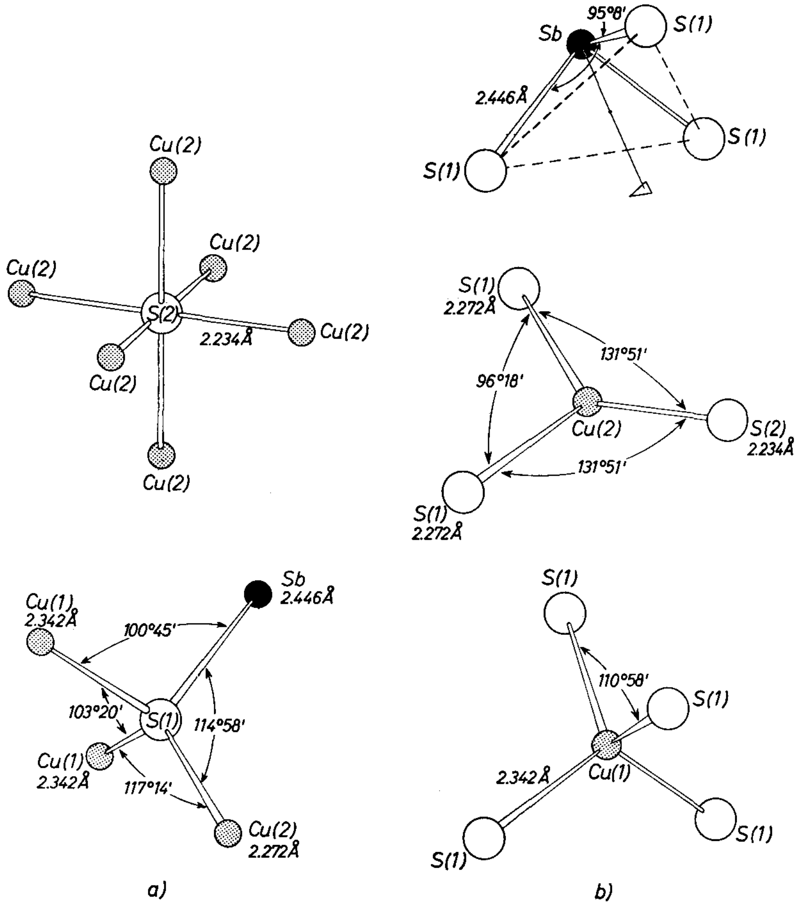


Fig. 2. Coordination polyhedra in tetrahedrite. (a) Coordination of metal atoms about the sulfur atoms. (b) Coordination of sulfur atoms about the metal atoms

Correspondingly, there are also four locations on the "spinner" at which the corners of the triangles are widely separated. An Sb atom at the apex of the pyramid associated with a neighboring spinner nests in between the triangles at this point. This Sb atom is equidistant from six S(1) atoms. The bond length is 4.033 Å. This value is almost identical with 4.05 Å, the sum of the van der Waals radii for Sb and S as given by PAULING (1960). In addition to the vertex of the SbS_3 pyramid, each corner of a triangle is further shared by vertices from two different CuS_4 tetrahedra. The corners of each tetrahedron link four different "spinners" in this fashion, Fig. 4*b*.

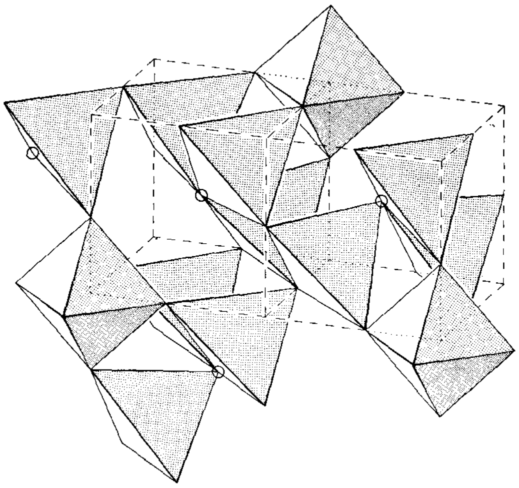


Fig. 3. Linkage of the polyhedra formed by the metal atoms coordinated about the sulfur atoms in tetrahedrite. Antimony locations are indicated by small circles. All other vertices of the polyhedra represent copper-atom locations

The bond lengths and bond angles for tetrahedrite are summarized in Tables 6 and 7. The uncertainties given for these results represent the difference between the values computed from the results of the refinement, and the maximum values obtainable when all of the standard deviations are taken in the most unfavourable combination. These uncertainties are therefore considered conservative estimates.

The temperature-factor coefficients for nearly all of the atoms represent a thermal motion which is essentially isotropic. The thermal vibration of Cu(2), however, is strongly anisotropic. Such behavior is not unexpected for an atom in planar coordination. This triangle coordination is rare for a B-subgroup metal. It is known only in the

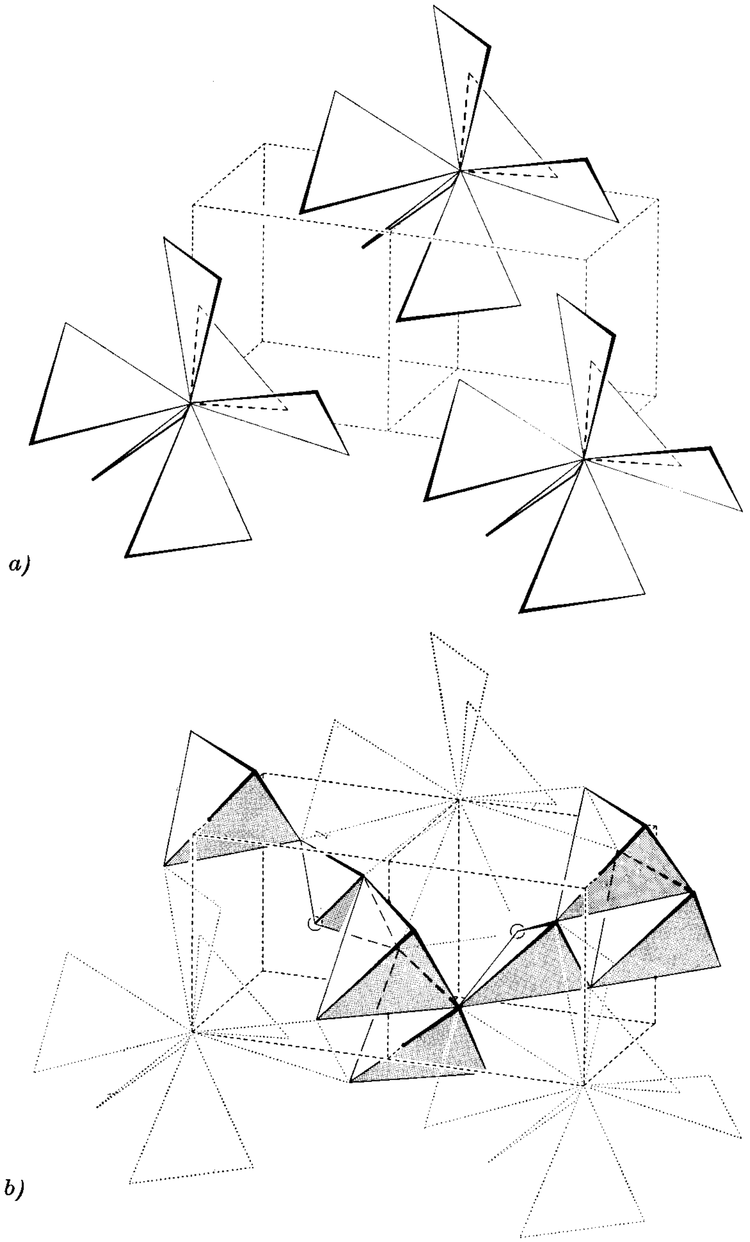


Fig. 4. Linkage of the polyhedra formed by the sulfur-atom coordination about the metal atoms in tetrahedrite. (*a*) Arrangement of "spinners" composed of six CuS_3 triangles sharing a corner. (*b*) Linkage of SbS_3 pyramids and CuS_4 tetrahedra (for clarity, the "spinners" are only lightly indicated)

additional compounds CuS (Berry, 1954), Cu_2S (Buerger and Wuensch, 1963), and CuAgS (Frueh, 1955). In inorganic compounds, this coordination appears to be unique to copper sulfides.

The coordination of Sb suggests the reason for the formation of the structure. While the Sb atoms in sulfosalts often display a range of bond lengths to neighboring S atoms, the disposition of the three short bonds in tetrahedrite suggests a strong bond involving the p^3 electrons of Sb. The failure of Sb to form a fourth bond with an S atom accounts for the atom missing from the sphalerite arrangement. It is therefore misleading to describe the tetrahedrite structure as a sphalerite derivative structure in which different metal atoms

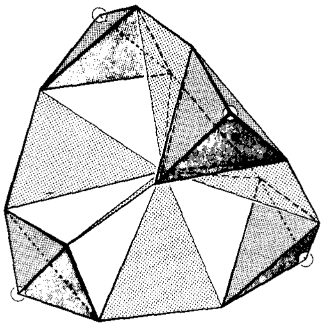


Fig. 5. Positions of the SbS_3 pyramids which link corners of three of the CuS_3 triangles in each "spinner"

Table 6. *Interatomic distances in tetrahedrite*

Atoms	Designation	Number and type of neighbor	Distance
S	S(1)	2 Cu(1)	2.342 ± .004 Å
		1 Cu(2)	2.272 ± .010
		1 Sb	2.446 ± .007
	S(2)	6 Cu(2)	2.234 ± .005
Metal	Cu(1)	4 S(1)	2.342 ± .004
	Cu(2)	2 S(1)	2.272 ± .010
		1 S(2)	2.234 ± .005
	Sb	3 S(1)	2.446 ± .007
		6 S(1)	4.033 ± .005

Table 7. *Bond angles in tetrahedrite*

Atoms	Designation	Bonds	Angle
S	S(1)	Cu(1) — S(1) — Sb	100°45′ ± 11′
		Cu(1) — S(1) — Cu(1)	103°20′ ± 13′
		Cu(2) — S(1) — Sb	114°58′ ± 19′
		Cu(1) — S(1) — Cu(2)	117°14′ ± 11′
Metal	Cu(1)	S(1) — Cu(1) — S(1)	110°58′ ± 9′
	Cu(2)	S(1) — Cu(2) — S(2)	131°51′ ± 10′
		S(1) — Cu(2) — S(1)	96°18′ ± 10′
	Sb	S(1) — Sb — S(1)	95° 8′ ± 9′

have been substituted in an ordered fashion (as, for example, in chalcopyrite, $CuFeS_2$). The SbS_3 group is really a different type of coordination polyhedron. In this connection, however, it is of interest to point out the existance of structures such as enargite, Cu_3AsS_4, in which As *does* have a tetrahedral coordination. Compared to tennantite, this requires a completely different sort of bonding for As, although the compounds are chemically similar.

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