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Refinement of the crystal structure of binnite[1], $Cu_{12}As_4S_{13}$

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Auszug

Die Kristallstruktur von Binnit, $Cu_{12}As_4S_{13}$, wurde verfeinert, um einen Vergleich mit Tetraedrit, $Cu_{12}Sb_4S_{13}$, zu ermöglichen und um gleichzeitig die Resultate einer mit photographisch erhaltenen Daten ausgeführten Verfeinerung mit denen einer Verfeinerung, deren Daten mittels Zählrohr erhalten waren, vergleichen zu können. Ein Zuverlässigkeitsindex von 23,9% für das von Pauling und Neuman 1934 vorgeschlagene Modell wurde auf 7,2% reduziert. Es wurde bemerkt, daß etwas As durch Sb ersetzt sein muß. Der Besetzungsfaktor dieser Punktlage wurde verfeinert und erwies sich in ausgezeichneter Übereinstimmung mit den Resultaten einer spektrographischen Analyse. Die Resultate der Verfeinerung mit den photographisch erhaltenen Daten sind durchaus mit den zählrohrgoniometrisch erhaltenen Daten vergleichbar, aber die Standardabweichungen der Parameter, Bindungslängen und Bindungswinkel sind ungefähr um 50% größer.

Binnit enthält zwei Arten von Cu-Atomen. Die erste ist tetraedrisch durch vier S-Atome im Abstand 2,337 Å umgeben; die zweite planar-dreieckig von zwei S-Atomen im Abstand 2,258 Å und einem S-Atom im Abstand 2,204 Å. Das As-Atom ist an drei S-Atome im Abstand 2,246 Å mit Bindungswinkeln von 98°22′ gebunden. Sowohl Binnit wie Tetraedrit sind Überstrukturen des Zinkblendetyps. Im allgemeinen sind die Abweichungen von dieser Idealstruktur beim Binnit weniger ausgesprochen als beim Tetraedrit.

Abstract

The crystal structure of binnite, $Cu_{12}As_4S_{13}$ has been refined to permit comparison with tetrahedrite $Cu_{12}Sb_4S_{13}$, and to compare the results of refinement of photographically recorded data with those obtained with counter data. A disagreement index of 23.9% for a model proposed by Pauling and Neuman in 1934 has been reduced to 7.2%. Substitution of Sb for As was noted; the

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occupancy of this site was refined and a value in excellent agreement with the results of a spectroscopic analysis was obtained. The results of refinement with the present photographically recorded data are comparable to those obtained with counter data, but the standard deviations of the parameters, bond lengths, and bond angles are approximately 50% greater.

Binnite contains two varieties of copper atoms. A first type is tetrahedrally coordinated by four sulfur atoms at 2.337 Å. A second type is triangularly coordinated by two sulfur atoms at 2.258 Å and one at 2.204 Å. The arsenic atom is bonded to three sulfur atoms at 2.246 Å which form bond angles of 98°22′. Both binnite and tetrahedrite are superstructures based on a sphalerite-like arrangement of atoms. The displacements from this idealized arrangement are generally less pronounced in binnite than in tetrahedrite.

Introduction

Tennantite, $Cu_{12}As_4S_{13}$, is the arsenic end-member of a widely occurring group of sulfosalts. A complete series of solid solutions extends to tetrahedrite, $Cu_{12}Sb_4S_{13}$. Substitution for the Cu atoms may also occur. Atoms such as Zn, Fe, and Ag have been reported in amounts up to 18 weight per cent in tetrahedrite and up to 14 weight per cent in tennantite.

The crystal structures and chemical formulae of these phases were investigated by MACHATSCHKI (1928*a*, 1928*b*). PAULING and NEUMAN (1934) conducted a more detailed analysis of binnite, a variety of tennantite. They proposed a crystal structure which was an unusual superstructure based upon a sphalerite-like arrangement of atoms. Although the structure analysis of PAULING and NEUMAN was based on but a limited amount of data, the structure was confirmed for tetrahedrite by WUENSCH (1963, 1964).

The atoms in tetrahedrite were found to be appreciably displaced from the locations corresponding to an ideal sphalerite arrangement. The present determination of the crystal structure of binnite was undertaken to permit comparison of the details of these distortions in the As and Sb phases. Furthermore, the diffracted intensities for tetrahedrite were determined with the aid of a counter diffractometer. A photographic technique was employed in the present study. It was felt that a comparison of the results of least-squares refinement of similar structures for which data had been obtained by two different techniques would also be of interest.

X-ray examination and chemical composition of material

The tennantite selected for study was a well-crystallized variety known as binnite which occurs at the Lengenbach, Canton Wallis, Switzerland. Excellent crystals were obtained from Specimen L 2120 from the collection of the Mineralogical Institute of the University of Bern. Weissenberg patterns displayed symmetry $m3m$ and systematic absences for reflections with $h + k + l \neq 2n$. The diffraction symbol for binnite is therefore $m3mI{-}{-}{-}$. This permits $Im3m$, $I43$ and $I\bar{4}3m$ as possible space groups. Since the morphology of all sulfosalts of this family displays symmetry $\bar{4}3m$, $I\bar{4}3m$ may be selected as the correct space group.

The lattice constant was obtained by extrapolation of values obtained from a Fe$K\alpha$ powder pattern obtained with an evacuated camera of the Bradley type. The value of a which was obtained was 10.232 ± .005 Å. This lattice constant is somewhat larger than the values reported for pure tennantite (PALACHE *et al.*, 1944) which are of the order of 10.19 Å. It was therefore suspected that a small amount of Sb might be present in the specimen of binnite which was examined, since tetrahedrite was found to have a lattice constant of 10.3908 Å. The composition of fragments of the crystal used in the present work was therefore determined by electron-microbeam-probe analysis, and by a spectroscopic analysis. The results obtained are summarized in Table 1, in which they are compared with previously reported analyses

Table 1. *Chemical analyses of binnite*

	Present study		PRIOR and SPENCER (1899)	PRIOR (1916)	Ideal $Cu_{12}As_4S_{13}$
	Electron microprobe analysis*	Spectroscopic analysis**			
Cu	40.7 ± 1.5 wt%	48.2 wt%	49.83 wt%	42.03 wt%	51.55 wt%
Zn	5.2 ± 0.2	5.64	—	7.76	
Fe	2.6 ± 0.1	—	1.11	0.62	
Ag	—	1.91	1.87	1.24	
Pb	—	—	0.17	—	
As	20.0 ± 0.8	14.6	19.04	19.80	20.26
Sb	—	3.58	—	—	
S	32.5 ± 1.0	(26.06)	27.60	28.08	28.19
Σ	101.0	99.99	99.62	99.53	100.00
Density			4.62	4.61 (g/cm³)	

* Analyst: C. BAHEZRE, Bureau de Recherches Géologiques et Minières, Paris.

** Analyst: ST. GRAESER, Mineralogisch-Petrographisches Institut der Universität Bern; S as balance.

occupancy of this site was refined and a value in excellent agreement with the results of a spectroscopic analysis was obtained. The results of refinement with the present photographically recorded data are comparable to those obtained with counter data, but the standard deviations of the parameters, bond lengths, and bond angles are approximately 50% greater.

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Table 1. *Chemical analyses of binnite*

	Present study		Prior and Spencer (1899)	Prior (1916)	Ideal $Cu_{12}As_4S_{13}$
	Electron microprobe analysis*	Spectroscopic analysis**			
Cu	40.7 ± 1.5 wt%	48.2 wt%	49.83 wt%	42.03 wt%	51.55 wt%
Zn	5.2 ± 0.2	5.64	—	7.76	
Fe	2.6 ± 0.1	—	1.11	0.62	
Ag	—	1.91	1.87	1.24	
Pb	—	—	0.17	—	
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* Analyst: C. Bahezre, Bureau de Recherches Géologiques et Minières, Paris.

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of binnite (Prior and Spencer, 1899; Prior, 1916). The analyses correspond to unit-cell contents of

$$2\left|\begin{array}{c}\mathrm{Cu}_{9.54}\\ \mathrm{Zn}_{1.18}\\ \mathrm{Fe}_{0.69}\\ \hline 11.41\end{array}\right|\mathrm{As}_{3.97}\mathrm{S}_{15.09}\quad\text{(microprobe analysis)}$$

$$2\left|\begin{array}{c}\mathrm{Cu}_{11.30}\\ \mathrm{Zn}_{1.29}\\ \mathrm{Ag}_{0.26}\\ \hline 12.85\end{array}\right|\left|\begin{array}{c}\mathrm{As}_{2.90}\\ \mathrm{Sb}_{0.44}\\ \hline 3.34\end{array}\right|\mathrm{S}_{12.08}\quad\text{(spectroscopic analysis)}$$

while the Prior and Spencer, and Prior analyses provide

$$2\left|\begin{array}{c}\mathrm{Cu}_{11.69}\\ \mathrm{Fe}_{0.30}\\ \mathrm{Ag}_{0.26}\\ \mathrm{Pb}_{0.01}\\ \hline 12.26\end{array}\right|\mathrm{As}_{3.79}\mathrm{S}_{12.83}\qquad 2\left|\begin{array}{c}\mathrm{Cu}_{9.84}\\ \mathrm{Zn}_{1.77}\\ \mathrm{Fe}_{0.17}\\ \mathrm{Ag}_{0.17}\\ \hline 11.95\end{array}\right|\mathrm{As}_{3.93}\mathrm{S}_{13.02}$$

respectively. The results of the standard chemical analysis, which are more accurate than those of the present work, provide cell contents which are in excellent agreement with the ideal composition $\mathrm{Cu}_{12}\mathrm{As}_4\mathrm{S}_{13}$. It is important to note, however, that the ratio of As to Sb obtained from the spectroscopic analysis indicates that the relative occupancy of this site is $\mathrm{As}_{.87}\mathrm{Sb}_{.13}$ for the binnite employed in this study.

Collection of intensities

A fragment of the binnite crystal was ground into a sphere of 0.149 ± .003 mm radius ($\mu r = 5.60$ for Cu$K\alpha$ radiation). The diffracted intensities were recorded by the multiple-film technique using an integrating equi-inclination Weissenberg camera. The integrated intensities were measured with the aid of a double-beam recording microdensitometer. The intensities were corrected for appropriate spherical absorption factors, and Lorentz and polarization factors with programs written for the Bull-Gamma computer by Y. Iitaka (unpublished).

Of the 150 independent reflections contained within the Cu$K\alpha$ sphere, a total of 144 were measured. Of these, nine were too weak to be detectable. This provided slightly less than six reflections per parameter for a least-squares refinement employing separate scale-factors for the individual levels, and anisotropic temperature-factor coefficients.

Refinement of the structure

The parameters reported for binnite by PAULING and NEUMAN are listed in Table 2. The disagreement index, $R = \Sigma||F_{\text{obs}}| - |F_{\text{cal}}||/\Sigma|F_{\text{obs}}|$, for this model was 19.3% for the 16 zero-level reflections corresponding to those measured by PAULING and NEUMAN, and 23.9% for the complete three-dimensional collection of structure factors.

Least-squares refinement was performed with the full-matrix program SFLSQ3 written for IBM 7090 computer by PREWITT (1962). Un-ionized form factors given by FREEMAN and WATSON, and DAWSON[3] were employed for Cu and As, and S, respectively. The nine undetectable intensities were assigned values of zero; they were included in the evaluation of R, but not in the calculation of the parameter shifts.

All reflections were assigned equal weights in the initial stages of the refinement. Corrections for anomalous scattering were made for all atoms. The scale factors and atomic positions, and then isotropic temperature factors were alternately varied until the parameters had converged. At this stage R for all reflections had decreased to 12.0%.

The value of R was then computed as a function of $|F_{\text{obs}}|$. It was found that the value of R was independent of F_{obs} for the larger structure factors, but increased rapidly for smaller values. This dependence could be expressed by a relation of the form $R = (a/F_{\text{obs}}) - b$, where a and b are constants. The relative values of a and b were such that a/F_{obs} was 2 to 5 times as great as b over most of the range of applicability of this relation. The weighting scheme adopted in subsequent cycles of refinement was one for which the product of weight and R was constant for all values of F_{obs}. This scheme assumes that the most reliable structure factors are the ones which display the best agreement between F_{obs} and F_{cal}. Further refinement did not change the manner in which R varied with F_{obs}.

Additional cycles of refinement in which anisotropic temperature-factor coefficients were introduced reduced R to 9.1% for all data and 7.9% when the unobserved reflections were omitted. The diagonal coefficients $\beta_{11} = \beta_{22} = \beta_{33}$ for As, however, had attained the rather low value of .0014. It was suspected that this might reflect a compen-

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

sation for the extra electron density in this site which would result if some As had been replaced by Sb. A difference map prepared at this stage did indeed show additional electron density in the site and thus confirmed this suspicion.

It would have been possible to modify the least-squares program to permit refinement of a mixed As—Sb occupancy subject to the constraint that the sum of the fractional amounts of each atom totaled unity. Instead, however, it was noted that the form factors for Sb and As could both be represented to an accuracy of about 10% by the product of the number of electrons per atom and the same scattering power per electron, $\hat{f}$. Since it was anticipated that the amount of Sb present would be relatively small, it was felt that this represented a satisfactory approximation. The values for $\hat{f}$ obtained from As were therefore employed as the form factor for this site and, starting with the assumption of no Sb in the site, the number of electrons present was refined along with the other parameters. The value of R was decreased by only 0.3% through this procedure, but, more significantly, the anisotropic temperature-factor coefficients increased to a more reasonable value, and the anomaly in the difference map was removed. The final value for R was 8.3% for all data and 7.2% if the nine unobservable structure factors were excluded.

Results of the refinement

The positional parameters obtained for binnite are listed in Table 2 where they may be compared with the parameters reported for binnite by PAULING and NEUMAN (1934) and the parameters obtained for tetrahedrite by WUENSCH (1964). Also given are the displacements of the atoms from the positions which they would occupy in an ideal sphalerite-like arrangement of atoms. It may be seen that the structure of binnite is, in general, slightly less distorted than that of tetrahedrite.

The value obtained for the number of electrons contained in the As site was 35.72 ± 0.56. This corresponds to an occupancy of $As_{.85}Sb_{.15}$ which is in excellent agreement with the value $As_{.87}Sb_{.13}$ which was obtained from spectroscopic analysis of the crystal which was used.

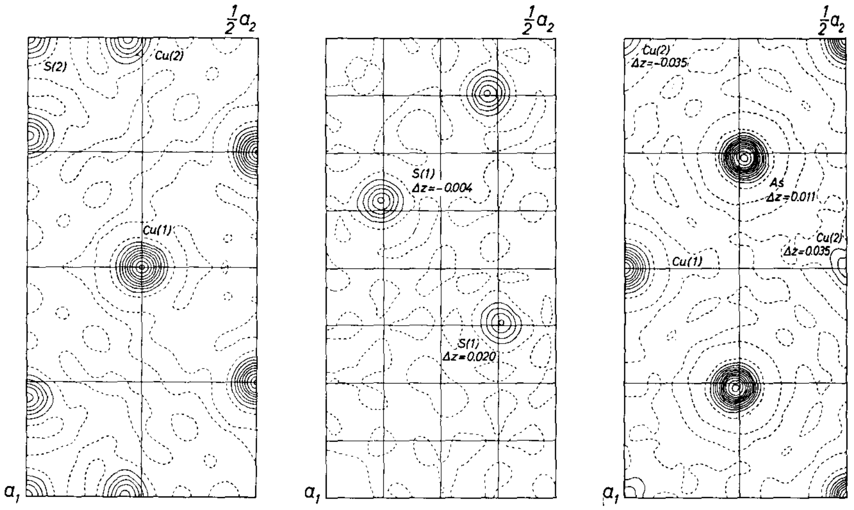
The anisotropic temperature-factor coefficients obtained for binnite are compared in Table 3 with those which were obtained for tetrahedrite. Also listed is the "equivalent" isotropic temperature factor

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

Table 2. *Comparison of atomic positions for binnite and tetrahedrite*

Atom	Equipoint	Parameter	Binnite, PAULING and NEUMAN (1934)		Binnite, present study		Tetrahedrite, WUENSCH (1964)	
				Distortion from sphalerite arrangement		Distortion from sphalerite arrangement		Distortion from sphalerite arrangement
Cu(1)	12 *d*	*x*	1/4	0	1/4	0	1/4	0
	$\frac{1}{4}\frac{1}{2}0$	*y*	1/2	0	1/2	0	1/2	0
		z	0	0	0	0	0	0
Cu(2)	12 *e*	*x*	.225	− .025	.2154 ± .0008	− .0346	.2150 ± .0005	− .0350
	x 00	*y*	0	0	0	0	0	0
		z	0	0	0	0	0	0
S(1)	24 *g*	*x*	.122	− .003	.1206 ± .0005	− .0044	.1152 ± .0003	− .0098
	xxz	*y*	.122	− .003	.1206 ± .0005	− .0044	.1152 ± .0003	− .0098
		z	.363	− .012	.3555 ± .0007	− .0195	.3609 ± .0005	− .0141
S(2)	2 *a*	*x*	0	—	0	—	0	—
	000	*y*	0	—	0	—	0	—
		z	0	—	0	—	0	—
$As_{.85}Sb_{.15}$ or Sb	8 *c*	*x*	.255	+ .005	.2605 ± .0004	+ .0105	.2682 ± .0001	+ .0182
	xxx	*y*	.255	+ .005	.2605 ± .0004	+ .0105	.2682 ± .0001	+ .0182
		z	.255	+ .005	.2605 ± .0004	+ .0105	.2682 ± .0001	+ .0182

equivalent. Both models provided identical values of R. The effect of the anomalous dispersion correction was compensated for by slight parameter shifts, all of which were within the standard deviations of either model. The model reported above was selected, somewhat arbitrarily, on the basis of a slightly better agreement between F_{obs} and F_{cal} for the weaker reflections. Observed and calculated structure factors for the parameters listed in Tables 2 and 3 are compared in Table 4.



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

Fig. 1. Electron-density sections for binnite. 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 arrangement

There are several reasons for the failure to distinguish the absolute configuration of the structure. The data of the present study are undoubtedly less accurate than those which were obtained by counter methods for tetrahedrite. Furthermore, the introduction of separate scale factors for the different levels provides additional parameters in the refinement which may compensate for the slight difference between the two configurations. On the other hand, it should be noted that the atoms requiring the largest correction for anomalous dispersion are the Sb and As atoms. The correction for Sb is much larger than that required for As. The difference between the two configurations will therefore be much less pronounced for binnite than in the case of tetrahedrite.

Fig. 1 presents electron-density sections for the structure 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 presented in each section. The remainder of the cell is related to the portion indicated by diagonal symmetry planes. Subnets with $a' = \frac{1}{4}a$ or $\frac{1}{8}a$, as required, have been indicated in these maps. The displacement of the atoms from their neighboring sublattice point and from the plane of the section provides a picture of the magnitude of the distortion from the ideal sphalerite arrangement. As with tetrahedrite, marked series-termination effects are evident, particularly about the As site.

Discussion of the structure

The general arrangement of the atoms in binnite is the same as that in tetrahedrite. There are two types of sulfur atoms. The coordination polyhedra formed about these atoms by the metal atoms in the structure are compared with the corresponding polyhedra in tetrahedrite in Fig. 2. S(2) is coordinated by six Cu(2) which form

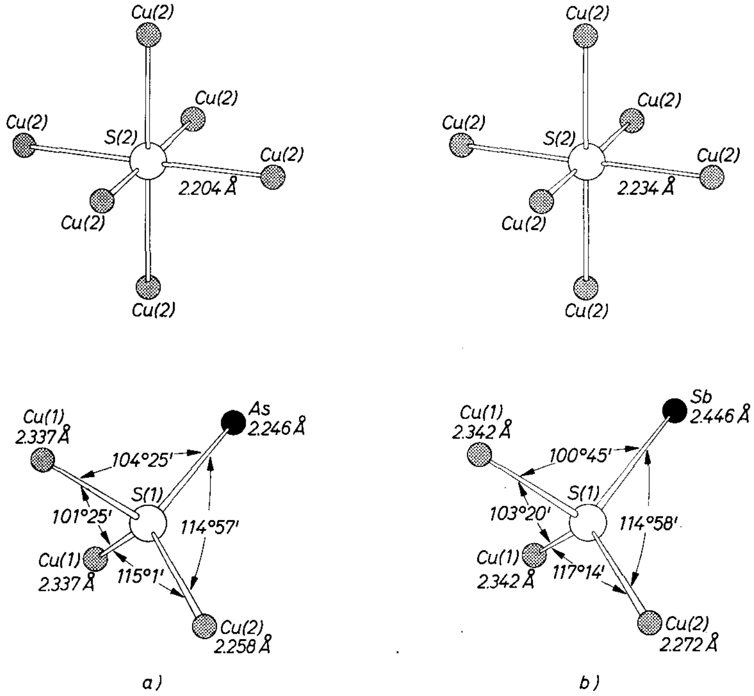


Fig. 2. Coordination polyhedra formed by the metal atoms about the sulfur atoms. *a)* Binnite, $Cu_{12}As_4S_{13}$. *b)* Tetrahedrite, $Cu_{12}Sb_4S_{13}$

a regular octahedron. In binnite this bond length is 2.204 Å, somewhat shorter than the distance obtained for tetrahedrite. S(1) is coordinated by two Cu(1) neighbors at a distance of 2.337 Å, one Cu(2) at 2.258 Å, and one As at 2.246 Å. The symmetry of the tetrahedron is *m*; the symmetry plane contains As, Cu(2), and S(1). The bond angles in this tetrahedron are distorted by as much as 8° from the values of 109°28′ which would be found in a regular tetrahedron. The details of the distortions differ in binnite and tetrahedrite, but the tetrahedron is generally less distorted in binnite.

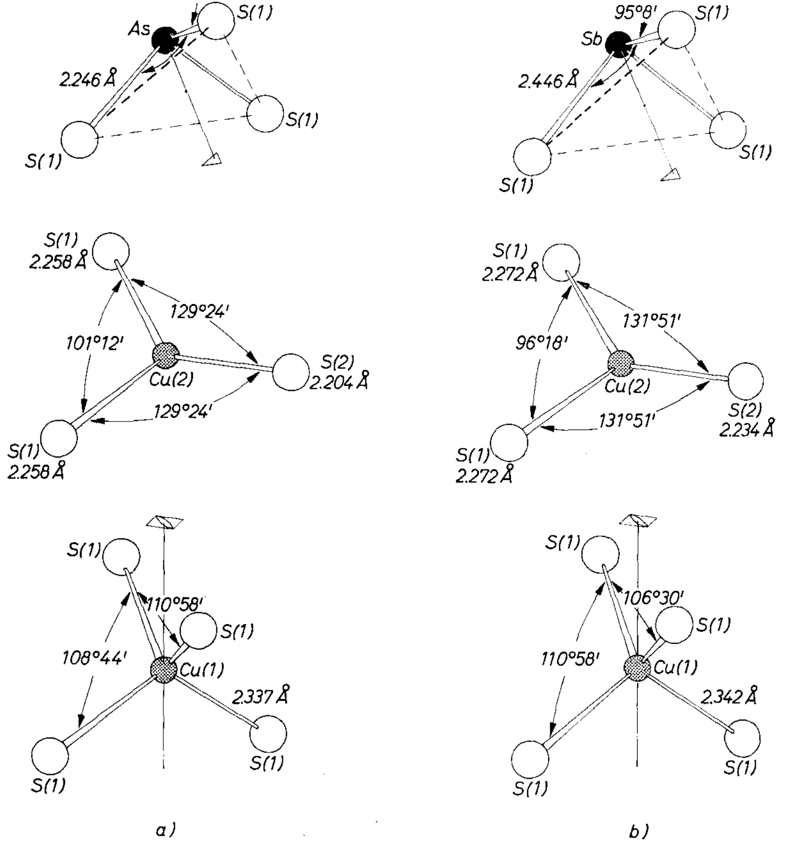


Fig. 3. Coordination polyhedra formed by the sulfur atoms about the metal atoms. *a)* Binnite, $Cu_{12}As_4S_{13}$. *b)* Tetrahedrite, $Cu_{12}Sb_4S_{13}$

The polyhedra formed by the sulfur atoms about the metal atoms in the structure are compared for binnite and tetrahedrite in Fig. 3. The arsenic atom in binnite is coordinated by three S(1) atoms at

2.246 Å and together form a trigonal pyramid. The bond angle for the As atom departs from orthogonality by an additional 3°14′ from that found for the Sb atom in tetrahedrite. There are two types of copper atoms in the structure. Cu(2) has only three sulfur neighbors: S(2) at 2.204 Å and two S(1) at 2.258 Å. This group of atoms is planar. Cu(1) is tetrahedrally coordinated by four S(1). The bond length of 2.337 Å is almost identical to the value of 2.342 Å found in tetrahedrite. [These Cu—S bond lengths are considerably larger than those found in the $Cu(2)S_3$ triangle, but this difference is partially due to the fact that the latter bond lengths have not been corrected for the highly anisotropic thermal motion of Cu(2)]. The bond angles in the Cu(1) tetrahedron are only slightly distorted from the values which would obtain in a regular tetrahedron. The bond angles in this tetrahedron are almost identical in both tetrahedrite and binnite, but with a curious interchange: the distortion in binnite corresponds to a compression of the tetrahedron along the $\bar{4}$ axis, while that in tetrahedrite corresponds to an extension. The reason for the difference is discussed below. The bond lengths and bond angles in the structures, along with their standard deviations[4], are summarized in Tables 5 and 6, respectively.

The linkage of these polyhedra in the structure is complex and has been previously described for tetrahedrite (WUENSCH, 1964). Six CuS_3 triangles share a corner to form a six-bladed "spinner". Such spinners are located at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. There are four locations for each spinner at which vertices of three different triangles are in close approach. An AsS_3 pyramid links each of these vertices. Correspondingly, there are four locations at which six vertices of three different triangles are widely separated. The As atom vertex of a AsS_3 pyramid associated with a neighboring spinner nests in between the six vertices at these locations. In tetrahedrite the distance from the Sb atom to these second-nearest S neighbors is 4.033 Å. This distance is the sum of the van der Waals radii proposed by PAULING (1960). In binnite the corresponding As—S distance is 4.057 Å. This larger distance in binnite

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[4] The uncertainties in bond lengths and bond angles previously reported for tetrahedrite (WUENSCH, 1964) represented the difference between the values computed from the parameters obtained from the least-squares refinement, and the maximum values which were obtained when the standard deviations of the parameters were taken in their most unfavorable combination. The uncertainties reported here for both tetrahedrite and binnite are standard deviations obtained with the aid of the IBM 7090 program MGEOM (J. S. WOOD, unpublished). These values take into account correlations between symmetrically related atoms in the bond, and also correlations between parameters of the individual atoms.

Table 5. *Comparison of interatomic distances in binnite and tetrahedrite*

Atom	Designation	Number and type of neighbor	Distance	
			Binnite, present work	Tetrahedrite, WUENSCH (1964)
S	S(1)	2 Cu(1)	2.337 ± .008 Å	2.342 ± .006 Å
		1 Cu(2)	2.258 ± .009	2.272 ± .007
		1 As or Sb	2.246 ± .005	2.446 ± .003
	S(2)	6 Cu(2)	2.204 ± .008	2.234 ± .005
Metal	Cu(1)	4 S(1)	2.337 ± .008	2.342 ± .006
	Cu(2)	2 S(1)	2.258 ± .009	2.272 ± .007
		1 S(2)	2.204 ± .008	2.234 ± .005
	As or	3 S(1)	2.246 ± .005	2.446 ± .003
	Sb	6 S(1)	4.057 ± .005	4.033 ± .003

Table 6. *Comparison of bond angles in binnite and tetrahedrite*

Atom	Designation	Number and type of bond	Angle	
			Binnite, present work	Tetrahedrite, WUENSCH (1964)
S	S(1)	2 Cu(1)–S(1)–As or Sb	104°25′ ± 17′	100°45′ ± 11′
		1 Cu(1)–S(1)–Cu(1)	101°25′ ± 19′	103°20′ ± 13′
		1 Cu(2)–S(1)–As or Sb	114°57′ ± 22′	114°58′ ± 14′
		2 Cu(1)–S(1)–Cu(2)	115°1′ ± 24′	117°14′ ± 14′
Metal	Cu(1)	4 S(1)–Cu(1)–S(1)	108°44′ ± 15′	110°58′ ± 12′
		2 S(1)–Cu(1)–S(1)	110°58′ ± 18′	106°30′ ± 12′
	Cu(2)	2 S(1)–Cu(2)–S(2)	129°24′ ± 9′	131°51′ ± 8′
		1 S(1)–Cu(2)–S(1)	101°12′ ± 28′	96°18′ ± 19′
	As or Sb	3 S(1)–As–S(1)	98°22′ ± 28′	95° 8′ ± 16′

is somewhat surprising in view of the smaller lattice constant of this mineral, and the smaller size of the As atom. The As atom therefore cannot be considered as being in van der Waals contact with the S atoms of a neighboring "spinner".

Each of the S(1) vertices of the CuS_3 triangle is joined to the base of an AsS_3 pyramid. These vertices are further joined to the vertices of two different CuS_4 tetrahedra. Each such tetrahedron shares vertices with four different spinners. This linkage connects neighboring spinners and, in binnite, prevents the further collapse of the structure which would bring the As atom and its second-nearest sulfur neighbors in contact.

Table 7. *Comparison of sulfur-sulfur contact distances in metal-atom coordination polyhedra in binnite and tetrahedrite*

Polyhedron	Number and type of contact	Sulfur-sulfur contact distance	
		Binnite, present work	Tetrahedrite, Wuensch (1964)
SbS_3 or AsS_3 pyramid	3 S(1)–S(1)	3.399 ± .013 Å	3.611 ± .009 Å
CuS_3 triangle	2 S(1)–S(2)	4.034 ± .008	4.114 ± .006
	1 S(1)–S(1)	3.489 ± .011	3.385 ± .007
CuS_4 tetrahedron	2 S(1)–S(1) (normal to $\bar{4}$)	3.851 ± .013	3.753 ± .009
	4 S(1)–S(1) (inclined to $\bar{4}$)	3.799 ± .011	3.859 ± .008
Van der Waals contact distance (Pauling, 1960)		3.70 Å	

Some insight into the nature of the distortions in the structure may be obtained from a consideration of the sulfur-sulfur contact distances in the metal-atom coordination polyhedra. The van der Waals contact distance for sulfur[5] given by Pauling (1960) is 3.70 Å. The sulfur-sulfur contact distances in binnite and tetrahedrite are given in Table 7.

The sulfur atoms which form the base of the SbS_3 tetrahedron in tetrahedrite are separated by a distance somewhat shorter than the van der Waals contact distance. The As—S bond length is 0.2 Å shorter than the Sb—S bond length. This must result in either a further departure from orthogonality in the S—As—S bond angle, or a further decrease in the sulfur-atom separation in the AsS_3 pyramid. The present results indicate a balance between the two effects: the sulfur-contact distance decreases by 0.21 Å, and the bond angle increases by an additional 3°14′. This drawing together of the S atoms increases the S(1)—Cu(2)—S(1) bond angle in the CuS_3 triangle from 96°18′ to 101°12′. This change is probably energetically favorable because this S(1)—S(1) separation in tetrahedrite is the closest sulfur-sulfur-contact distance found in the two structures.

Because of the changes in the geometry of the CuS_3 triangles, the dimensions of the spinner have changed. The length of the triangles,

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[5] Sulfur-sulfur contacts considerably smaller than this are commonly observed. Takéuchi and Nowacki (1964), for example, find sulfur-sulfur distances of 3.166 and 3.155 Å within the Mo octahedron in rhombohedral molybdenite, and 3.50 Å for the inter-layer separations.

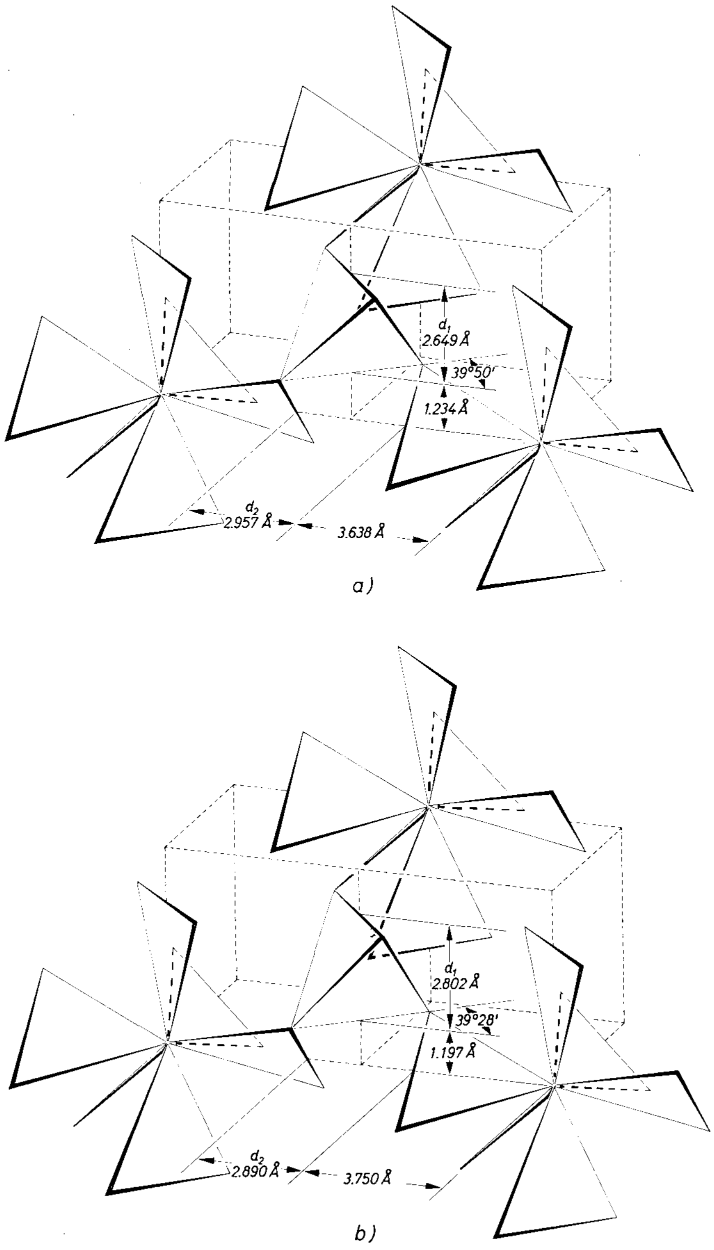

Fig. 4. The CuS_4-tetrahedron linkage between neighboring spinners. *a)* Binnite. *b)* Tetrahedrite

Fig. 4, has decreased from 3.750 Å in tetrahedrite to 3.638 Å in binnite. Correspondingly, the elevation of the vertices of the triangles has increased from 1.197 Å to 1.234 Å. The packing of the spinners and associated AsS_3 or SbS_3 groups, and therefore the lattice constant, is determined by the geometry of the CuS_4-tetrahedron linkage. There are two dimensions of the tetrahedron which are critical in this respect. The distance d_1, Fig. 4, is the height of the tetrahedron along $\bar{4}$. This dimension determines the component of the separation, along a, of a spinner and its body-centered equivalent. The distance d_2 determines the separation along a of the edges of opposing triangles in translation-equivalent spinners. The distance d_1 can be changed only through distortion of the tetrahedron; d_2 may be modified through either distortion or rotation of the tetrahedron.

The greater length of the CuS_3 triangle in tetrahedrite causes d_2 to be the critical separation. The CuS_4 tetrahedron therefore distorts to minimize the two edges normal to $\bar{4}$. The corresponding sulfur-atom separation is 3.753 Å, which is close to PAULING's ideal van der Waals separation. As noted above, this distortion corresponds to a dilation of a regular tetrahedron along $\bar{4}$. The further collapse of the structure which could be attained by additional rotation of the tetrahedron is prevented by the van der Waals contact between Sb and S.

In binnite the decreased length of the CuS_3 triangles causes d_1 to be the critical separation. The tetrahedron therefore distorts to minimize this dimension, and the sulfur-atom separations which are inclined to $\bar{4}$ approach to a van der Waals separation of 3.799 Å. The distortion corresponds to a compression of a regular tetrahedron along $\bar{4}$. This distortion increases those sulfur-atom separations which are normal to $\bar{4}$, and no additional rotation of the tetrahedron is required in order to allow it to adjust to the separation d_2. Although the As atom is not in contact with its second-nearest sulfur neighbors, further collapse of the structure is limited by the extent to which the tetrahedron may be compressed. While the amount of rotation of the tetrahedron is the same in both binnite and tetrahedrite, it may be noted in Fig. 4 that these tetrahedra are rotated approximately 5° from the 45° orientation in an idealized sphalerite type of arrangement.

The packing of the sulfur atoms comprising the spinners is thus slightly different in binnite and tetrahedrite. In binnite the sulfur atoms at the outer edges of the spinners are in van der Waals contact with those of a spinner in the body-centered position. In tetrahedrite, in addition to the van der Waals contact of the Sb and sulfur atoms, the van der Waals contact between neighboring spinners occurs along [100] between opposing edges of triangles in translation-equivalent spinners.

Comparison of the results of refinement of photographic data and counter data

It is generally acknowledged that the data obtained for structure determinations by routine photographic techniques are to be expected to be less accurate than those obtained by counter methods. Little information is available, however, as to how great an influence this difference in accuracy actually has on the results of the refinement. The structures of binnite and tetrahedrite are essentially the same. It is therefore of interest to compare the results of these studies in this regard.

Certain differences in the two refinements have already been discussed. The absolute configuration of the structure could be readily established with the counter data which were obtained for tetrahedrite, while this could not be accomplished with the photographic data. As has been noted, however, this is at least partially due to the fact that the difference in computed structure factors is much less marked for the two configurations of binnite. As has also been noted above, the introduction of separate scale factors for the individual levels of photographic data may lead to serious interactions with certain anisotropic temperature-factor coefficients. One can therefore be less certain of the validity of such results when photographic data are employed. This problem may be resolved by the correlation of intensities on different levels by means of data obtained by rotation about an additional axis. The necessity of doing this, however, is incovenient. Unless it can be accurately done, it may still be necessary to introduce individual scale factors in the final stages of refinement.

Additional features of the two studies are compared in Table 8. As may be noted, a greater fraction of the available reflections is accessible with the photographic technique. This advantage is offset, however, by the fact that over four times as many reflections are undetectable. The introduction of individual scale factors results in a further lowering of the number of observed reflections per parameter. The disagreement index for the counter data is approximately half that obtained for the photographic data despite the greater number of reflections per parameter. Table 8 further shows that the average standard deviations of the parameters of the structure, and also of

Table 8. *Comparison of least-squares refinements employing photographic and counter techniques*

	Photographic technique (binnite, present study)	Counter technique (tetrahedrite, WUENSCH, 1964)
Total independent reflections in Cu$K\alpha$ sphere	150	153
Percent of reflections accessable	96.0%	88.9%
Percent of reflections undetectable	6.2%	1.5%
Number of observable reflections per paramerer	5.9	7.9
Overall precision of set of structure factors	—	± 3.0%
R for observable reflections	7.2%	3.9%
Average standard deviation in positional parameters	± .00059	± .00036
Average standard deviation in anisotropic temperature-factor coefficients	± .00063	± .00045
Average standard deviation in bond lengths	± .0071 Å	± .0046 Å
Average standard deviation in bond angles	±19′	±13′

the bond lengths and angles, are approximately 50% greater for the results obtained from the film data. It is reassuring to note, however, that the results of the two studies are still quite comparable.

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