Crystal structure refinement of an arsenic-bearing argentian tetrahedrite

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Abstract

The crystal structure of a synthetic tetrahedrite, composition $Cu_{8.44}Ag_{2.12}Fe_{1.44}$ $Sb_{2.70}As_{1.30}S_{13}$, has been refined using full-matrix least-squares methods to a weighted disagreement index of 4.6% for 169 independent observed diffractions. The effects of the substitutions of Ag for Cu and As for Sb on the distances and bond-angles in the tetrahedrite structure are separable, as has been noted previously for substitutional effects on the tetrahedrite lattice parameter. The presence of arsenic in natural tetrahedrite appears to restrict the amount of silver present. This restriction can be rationalized crystallographically.

Introduction

The tetrahedrite group of minerals consists of tetrahedrite, $(Cu,Fe)_{12}Sb_4S_{13}$; tennantite, $(Cu,Fe)_{12}As_4S_{13}$; freibergite, $(Ag,Cu,Fe)_{12}(Sb,As)_4S_{13}$; goldfieldite, $Cu_{12}(Sb, As)_4(Te,S)_{13}$; and hakite, $(Cu,Hg,Ag)_{12}Sb_4(Se,S)_{13}$ (Fleischer, 1980). These minerals have body-centered cubic structures, space group $I\bar{4}3m$. The currently-accepted structure for minerals in the tetrahedrite group was proposed by Pauling and Neuman (1934) in their examination of tennantite. More recent structural determinations have confirmed this general structure for a number of these minerals—tetrahedrite (Wuensch, 1964), mercurian tetrahedrite (Kalbskopf, 1971; Kaplunnik et al., 1980), argentian tetrahedrite (Kalbskopf, 1972), goldfieldite (Kalbskopf, 1974), and copper-rich and copper-poor synthetic tetrahedrites (Makovicky and Skinner, 1979). The structure of tennantite was reexamined by Wuensch et al. (1966).

Although the effects of single substitutions on the tetrahedrite structure have been reported (arsenic for antimony by Wuensch et al. (1966); silver for copper by Kalbskopf (1972)), there have been no previous crystallographic studies of multiply-substituted tetrahedrites. Charlat and Levy (1975) determined that the effects of substitutions on the unit-cell parameter of tetrahedrite are independent for Ag substitution for Cu, Cu^{2+} substitution for Fe, Hg substitution for Fe, and As substitution for Sb. However, the same authors have noted a negative correlation between silver and arsenic in natural tetrahedrites from world-wide occurrences (Charlat and Levy, 1974,

Fig. 6), which suggests possible interaction between Ag/Cu and As/Sb substitutions. More recent electron microprobe analyses (Fig. 1) confirm the trend seen by Charlat and Levy; however, many of the newer analyses are richer in silver for their antimony content than previously noted.

In order to determine whether a crystallographic control could account for the observed silver-arsenic antipathy, we determined the crystal structure of a (Ag, As)-bearing synthetic tetrahedrite.

Crystal structure refinement: experimental

Starting material

Tetrahedrite was synthesized using a flux technique modified from Boorman (1967). Starting material was a homogeneous glass made as described by Maske and Skinner (1971) from reagent Cu, S (Maske and Skinner, 1971), Ag (American Smelting and Refining Co., catalog #65844, Lot 1, 99.99+% pure), Fe sponge (United Mineral and Chemical Corporation, Lot 15890, 99.999% pure, reduced under hydrogen gas as described in Tatsuka and Morimoto (1977)), and 2:1 antimony-arsenic alloy (Laboratory of B. J. Skinner, Yale University, batch labeled "CTB 229 Sb/As 67/33"). The charge contained Ag, Fe, Cu, Sb, As, and S in the ratio 6.70:1.00:6.80:4.44:2.19:6.42 by weight.

The glass was then ground under acetone and mixed with an approximately equal volume of eutectic KCl/LiCl flux at 110°C, baked in silica-glass capsules at 400°C for four periods of one week each, with transfer into new capsules at 110°C between successive bakings. The charge was quenched in cold water,
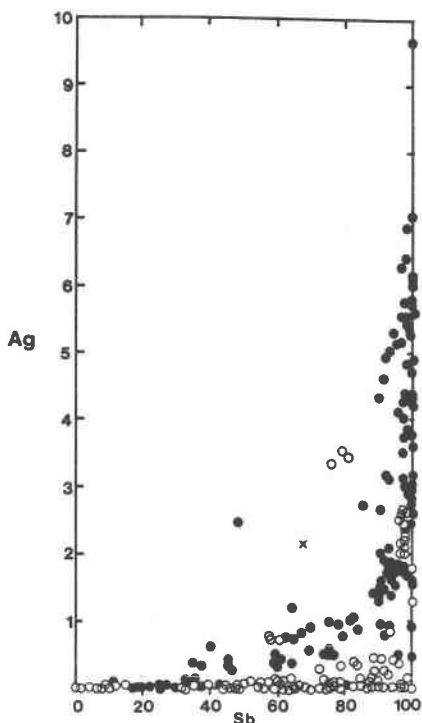
Fig. 1. Silver content (in number of atoms per 4 atoms Sb + As) versus percent Sb over (Sb + As), microprobe analyses of Bi-, Se-, and Te-free tetrahedrites. Open circles: analyses shown by Charlat and Levy (1974). Filled circles: additional analyses (Araya et al., 1977 (El Teniente, Chile)); Basu et al., 1981 (Rajpura-Dariba, India); Birch, 1981 (Mt. Wills, Australis); Bishop et al., 1977 (Sark, Channel Islands); Cech and Hak, 1979 (Jihlava, Czechoslovakia); Chen et al., 1980 (Timmins, Ontario); Johnson, 1982 (Orcopampa, Peru); Kvacek et al., 1975 (Kutna Hora, Czechoslovakia); Miller and Craig, 1983 (Coffer District, Virginia); Naik, 1975 (Espeland, Norway); Nash, 1975 (Park City, Utah); Novgorodova et al., 1978 (Uzbekistan); Pattrick, 1978 (Tyndrum, Scotland); Petruk et al., 1971 (Cobalt, Ontario); Riley, 1974 (Mt. Isa, Australia); Sakiya, 1982 (Chudan ore deposit, USSR); Sandecki and Amcoff, 1981 (Garpenberg Nora, Sweden); Shimada and Hirowatari, 1972 (Tsushima Island, Japan); Stanley and Vaughan, 1981 (Lake District, England); Sugaki et al., 1982 (Hokkaido, Japan); Tsepin et al., 1977 (Uzbekistan); Wu and Petersen, 1977 (Casapalca, Peru); Wuensch et al., 1966 (Lengenback, Switzerland); and Yui, 1971 (various, Japan)). X: refined composition, synthetic crystal used in this study.

opened, rinsed with water and acetone, and stored in an evacuated silica glass capsule until needed.

Tetrahedrite synthesized from the above starting composition was found to be intimately intergrown with quenched sulfide melt glass. Compositions of both phases were determined by electron microprobe (ARL microprobe with the KRISEL automation system, running at 15 kV and 25 nA, with synthetic tetrahedrite and proustite standards and the Ziebold–Ogilvie correction scheme (Ziebold and Ogilvie, 1964)). The average microprobe composition of tetrahedrite from this charge is given

in Table 1. The coexisting melt (microprobe composition $Cu_{1.21}Ag_{13.46}Fe_{.01}Sb_{3.46}As_{0.85}S_{13}$, mass absorption coefficient approximately that of tetrahedrite for $MoK\alpha$ and $CuK\alpha$ radiation) was indistinguishable from the tetrahedrite under binocular-microscope examination. The melt decreased the intensity of X-ray diffractions, sometimes erratically. To minimize this effect, a number of crystals were examined, and that crystal for which X-ray intensitites were maximized (least amount of melt) was chosen for further work. Data were collected from the octant of reciprocal space for which diffractions had the highest intensities.

X-ray diffraction data collection and refinement

The crystal, a complex polyhedron 70 μm in size, was oriented by means of oscillation and precession photographs. No satellite or body-center-forbidden diffractions were seen in zero-, first-, and second-level precession photographs. A Picker FACS-1 automated four-circle diffractometer was used for data collection. Intensity measurements were made with θ–2θ scans, using Nb-filtered $MoK\alpha$ radiation. Almost 2800 diffractions in one octant of reciprocal space were collected; body-center-forbidden diffractions ($h + k + l$ odd) were not collected. Two standard diffractions were monitored every 2 hours; their intensities did not vary significantly. Preliminary least-squares refinement of the unit-cell edge yielded a unit cell parameter of 10.530(4)Å, refining on 12 diffractions with 2θ angles between 13.395° and 31.26°. Intensities were corrected for absorption and Lorentz polarization using the correction program OBSTF (Burnham 1966), and symmetry-averaged to produce 169 independent diffractions with intensities greater than 2.5σ. Refinement was carried out using the neutral atom scattering factors of Cromer and Mann (1968) and coefficients for anomalous scattering from the *International Table for X-Ray Crystallography, Volume IV* (1974); and using the full-matrix least-squares refinement program RFINE (Finger, 1969). Diffractions were weighted by the factor

$$w = \frac{1}{\sigma_F^2}$$

where σ_F is defined in Burnham et al. (1971).

The model structure was refined successively for scale factor, atomic positions, occupancies, isotropic temperature factors,

Table 1. Compositions of tetrahedrite-group minerals discussed in this paper

Code	Composition	Reference
TNAG2MLJ	$Cu_{8.44}Ag_{2.12}Fe_{1.44}Sb_{2.70}As_{1.30}S_{13}$	J1983
WTD	$Cu_{9.70}Ag_{.09}Zn_{1.77}Fe_{0.18}Sb_{3.92}S_{13}$	W1964
WTN	$Cu_{10}(Zn,Fe)_2Sb_{0.60}As_{3.40}S_{13}$	W1966
FRKALB	$Cu_{8.56}Ag_{1.44}(Zn,Cu)_2Sb_4S_{13}$	K1972

Notes to Table 1:

J1983: Johnson and Burnham, this work
W1964: Wuensch (1964); composition from Johnson (1982)
W1966: Wuensch et al. (1966)
K1972: Kalbskopf (1972)

and anisotropic temperature factors. Occupancies were fixed after refinement, as the scale factor was largely correlated with Cu(2) and Sb site occupancies; all other factors were varied in every cycle subsequent to their initial variation. Pattrick and Hall (1983) suggest that silver goes into the Cu(1) site rather than the Cu(2) site; we did not see this effect. In order to determine occupancies correctly we refined other model structures with different, fixed amounts of Ag in the Cu(2) site and As in the Sb site; these resulted in higher disagreement indices than the accepted model. A trial structure in which the Sb site was split into distinct Sb and As positions was also unsuccessful by this criterion. Observed and calculated structure factors for the final refinement, TNAG2MLJ, are given in Table 2.[1]

Positional parameters for TNAG2MLJ are shown in Table 3; first-nearest-neighbor bond distances and bond angles are given in Table 4. Notation for sites is taken from Wuensch et al. (1966) and Makovicky and Skinner (1979). The LP (lone pair) site, a concept taken from Moore (1981), is defined as sitting above the Sb site in the ⟨111⟩ directions, thereby making the Sb site tetrahedrally coordinated. This site is filled by two lone pair electrons from the atom in the Sb site.

Ellipsoids of vibration for each of the atom positions are given in Table 5[1], and the structure is shown in Figure 2. Thermal motion for Cu(2) is strongly anisotropic, with the largest amplitude perpendicular to the Cu(2)–S(1)–S(2) plane, and the smallest amplitude parallel to the S(1)–S(1) edge of the Cu(2)S$_3$ triangle. Such behavior has been noted for the Cu(2) site in silver-bearing tetrahedrite by Kalbskopf; it is best explained as thermal motion, rather than as splitting of the Cu(2) site into two sites out of the plane of the Cu(2)S$_3$ triangle.

The Sb atom vibrates with the least amplitude in the direction of the lone pair (⟨111⟩), which would be the likely direction of (As, Sb) positional disordering. Although (Ag,Cu) disordering causes an increase in thermal motion for Cu(2), As and Sb fill an average Sb site without changing its thermal motion.

Discussion

We compare refinement TNAG2MLJ with the following earlier refinements: natural tetrahedrite (Wuensch, 1964; labeled "WTD"), natural tennantite (Wuensch et al., 1966; labeled "WTN"), and natural argentian tetrahedrite (Kalbskopf, 1972; labeled "FRKALB"). Approximate compositions for the crystals used for these refinements are given in Table 1. We redetermined the composition of WTD by electron microprobe analysis of a companion crystal from the same locality, Harvard specimen #82561. Positional parameters for all refinements are given in Table 3, and bond distances and angles in Table 4. Table 6 contains polyhedral sizes and distortion parameters for all refinements.

Although the natural tetrahedrites studied by Wuensch (1964), Wuensch et al. (1966), and Kalbskopf (1972) contain zinc and synthetic tetrahedrite TNAG2MLJ does not, as the substitution of iron for zinc does not affect the unit cell edge (Charlat and Levy 1975), and as tetrahedral-

[1] To obtain a copy of Tables 2 and 5, order Document AM-85-260 from the Mineralogical Society of America, Business Office, 2000 Florida Avenue, NW, Washington, D. C. 20009. Please remit $5.00 in advance for the microfiche.

Table 3. Refined parameters with errors, TNAG2MLJ; parameters for WTD, WTN, and FRKALB

Site	Parameter	TNAG2MLJ	WTD	WTN	FRKALB
	Scale	0.2044(10)	–	–	–
Cu(1) 12d ¼½0	Occupancy Cu	0.633(12)	1.0	1.0	1.0
	Occupancy Fe	0.24(*)			
	β_{11}	0.0049(7)	.0028	.0031	.0043
	β_{22}	0.0016(3)	.0027	.0017	.0029
	B$_{equiv}$	1.20(20)	1.19	0.91	1.49
Cu(2) 12e x00	Occupancy Cu	0.6467(*)	1.0	1.0	.76
	Occupancy Ag	0.3533(*)	–	–	.24
	x	0.2160(6)	.2150	.2154	.2170
	β_{11}	0.0101(7)	.0032	.0014	.0052
	β_{22}	0.0122(4)	.0130	.0153	.0120
	β_{23}	−0.0068(6)	.0094	−.0142	−.0079
	B$_{equiv}$	5.11(80)	4.19	4.46	4.28
Sb 8c xxx	Occupancy Sb	0.675(*)	1.00	0.15	1.00
	Occupancy As	0.325(*)	–	0.85	–
	x	0.2683(2)	.2682	.2605	.2683
	β_{11}	0.0023(1)	.0026	.0023	.00274
	β_{12}	−0.0004(1)	−.0003	.0004	−.00026
	B$_{equiv}$	1.00(16)	1.11	0.96	1.21
S(1) 24g xxz	Occupancy S	1.0(*)	1.0	1.0	1.0
	x	0.1238(6)	.1152	.1206	.1194
	z	0.3661(7)	.3609	.3555	.3652
	β_{11}	0.0066(4)	.0045	.0035	.0024
	β_{33}	0.0039(7)	.0026	.0012	.0026
	β_{12}	0.0030(7)	−.0008	−.0016	.0002
	β_{23}	−0.0011(5)	−.0001	−.0006	.0005
	B$_{equiv}$	2.52	1.23	1.14	1.10
S(2) 2a 000	Occupancy S	1.0(*)	1.0	1.0	1.0
	B	5.20(40)	1.14	1.52	6.84
	R	11.8	3.9	8.3	3.5
	R$_w$	4.6	4.7	–	4.8

Notes to Table 3:

(*) indicates value was fixed, not refined

Cu(1): $\beta_{33} = \beta_{22}$, $\beta_{12} = \beta_{13} = \beta_{23} = 0$.

Cu(2): $\beta_{33} = \beta_{22}$, $\beta_{12} = \beta_{13} = 0$.

Sb: $\beta_{22} = \beta_{33} = \beta_{11}$, $\beta_{13} = \beta_{23} = \beta_{12}$.

S(1): $\beta_{22} = \beta_{11}$, $\beta_{23} = \beta_{13}$.

S(2): Position isotropic.

$B_{equiv} = \frac{4}{3} \sum_i \sum_j \beta_{ij}(\vec{a}_i \cdot \vec{a}_j)$ is the eqivalent isotropic temperature factor (Hamilton, 1959).

ly coordinated iron and zinc are similar in size (Pattrick and Hall 1983), this substitution will not be discussed below.

The effect of Ag substitution for Cu

All bond distances, except the Sb–S(1) distance, are affected by silver substitution for copper in Cu(2) (Table 4). The Sb-LP (lone pair) distance, which is not shown, is fixed at 0.50Å for all models; the Cu(2)-LP distance measures the Cu(2)–Sb second-nearest-neighbor distance. The presence of silver increases the Cu(2)–S(1)

Table 4. Bond distances: WTD, WTN, FRKALB, TNAG2MLJ, and TNAG2MLJ–calculated.

Parameter	WTD	WTN	FRKALB	TNAG2MLJ	TNAG2MLJ calculated
Distances(Å):					
Cu(1)-S(1)	2.342	2.337	2.338	2.34(4)	2.334
Cu(2)-S(1)	2.272	2.258	2.354	2.43(4)	2.387
Cu(2)-S(2)	2.234	2.204	2.279	2.27(2)	2.289
Sb-S(1)	2.446	2.246	2.436	2.39(4)	2.355
Sb-LP	.50	.50	.50	.50	.50
Cu(2)-LP	3.000	3.059	3.047	3.04(5)	3.069
S(1)-S(1) base	3.386	3.490	3.547	3.61(5)	3.663
Cu(2)-Cu(2)	3.159	3.117	3.223	3.22(5)	3.237
Bond Angles:					
S(1)-Cu(1)-S(1)	106.53°	110.98°	107.90°	111(2)°	110.25°
S(1)-Cu(1)-S(1)	110.96°	108.72°	110.27°	109(2)°	109.09°
S(1)-Cu(2)-S(1)	96.31°	101.20°	97.34°	99(2)°	99.70°
S(1)-Cu(2)-S(2)	131.85°	129.40°	131.33°	131(1)°	130.15°
S(1)-Sb-S(1)	95.13°	98.37°	97.16°	98(2)°	99.36°
Sb-LP-Cu(2)	142.55°	143.95°	142.37°	142(2)°	142.82°
Cu(2)-LP-Cu(2)	63.55°	61.28°	63.85°	64(2)°	63.12°
Sb-S(1)-Cu(2)	114.96°	114.95°	113.95°	114(2)°	113.47°
Cu(2)-S(1)-Cu(1)	117.23°	115.00°	115.41°	113(2)°	113.70°
Sb-S(1)-Cu(1)	100.75°	104.44°	102.65°	105(2)°	104.96°
Cu(1)-S(1)-Cu(1)	103.33°	101.42°	105.16°	106(2)°	105.29°
Cu(2)-S(2)-Cu(2)	90.00°	90.00°	90.00°	90.00°	90.00°

Table 6. Volumes and Distortions for site polyhedra, models WTD, WTN, FRKALB, TNAG2MLJ, and TNAG2MLJ–calculated

Parameter	WTD	WTN	FRKALB	TNAG2MLJ	TNAG2MLJ calculated
Cu(1):					
Volume	6.577	6.547	6.554	6.536	6.532
Q. E.	1.001	1.000	1.000	1.000	
A. V.	5.462	1.575	1.725	1.062	
Cu(2):					
Area	2.211	2.172	2.347	2.441	2.396
A. D.	35.538	28.203	33.987	31.783	30.452
Sb:					
Volume	2.408	1.820	2.349	2.182	2.096
Base Area	5.645	5.003	5.781	5.634	5.600
S(1):					
Volume	6.524	6.115	6.707	6.779	6.637
Q. E.	1.014	1.010	1.009	1.007	
A. V.	67.875	41.275	40.433	22.250	
S(2):					
Volume	14.866	14.275	15.785	15.686	15.993
LP:					
Volume	4.152	4.168	4.356	4.350	4.458
Q. E.	1.690	1.751	1.689	1.638	
A. V.	1915.563	2099.813	1891.663	1898.462	

Notes to Table 6:

Volumes in cubic angstroms, areas in square angstroms

Q. E. = Quadratic Elongation, defined in Robinson et al., 1971.

A. V. = Angle Variance, also defined in Robinson et al., 1971.

A. D. = Angle Difference, defined as the difference between the values of the paired and unpaired angles of an isosceles triangle.

S(1) volume is determined for the pyramid (without the LP).

Base Area is the area of the S(1)-S(1)-S(1) face of the Sb pyramid.

"TNAG2MLJ calculated" values calculated using an analogous expression to those given in the text.

distance slightly, increases the Cu(2)–S(2) and Cu(2)-LP distances considerably, and shrinks the Cu(1)–S(1) distance slightly.

The Cu(2)S$_3$ triangle and the S(1)–S(1)–S(1) triangle forming the base of the Sb pyramid (Sb polyhedron without considering the lone pair) increase in area with the addition of silver (Table 6); the S(1), S(2), and lone pair polyhedra increase in volume; and the Cu(1) tetrahedron and the Sb pyramid decrease in volume. All polyhedra become less distorted with the addition of silver.
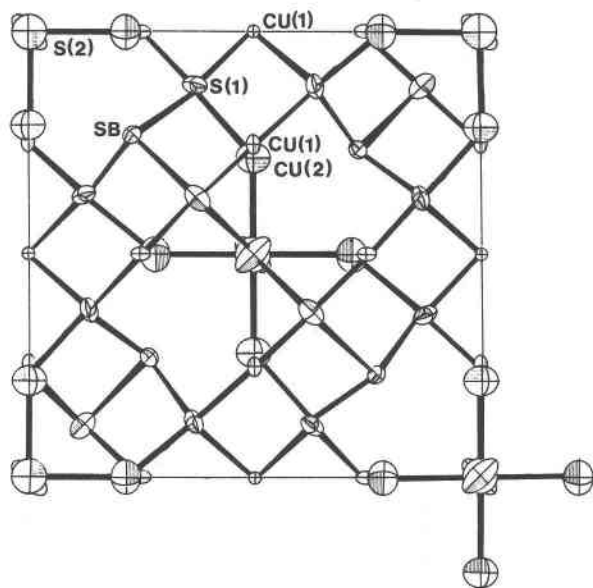

Fig. 2. Structure of one-half unit cell for TNAG2MLJ projected onto (001), origin at center of projection.

The effect of As substitution for Sb

The effects of substituting arsenic for antimony is discussed by Wuensch et al. (1966), with the exception of those involving the lone pair. The lone pair tetrahedron increases in volume, as the Cu(2) site is further away from the Sb site for tennantite than for tetrahedrite. With the exception of this polyhedron, all polyhedra become less distorted on replacement of antimony by arsenic.

Silver-arsenic interaction

Silver and arsenic do not directly compete for sites—the former going into Cu(2) and the latter into the Sb site. Moreover, these sites are not nearest neighbors, having either S(1) atoms or LP sites between them. Nevertheless, the amount of arsenic in tetrahedrite appears to dictate the upper limit of silver substitution (Fig. 1). This may happen in two ways: arsenic in the Sb site may decrease the area available for Ag in the Cu(2)S$_3$ plane, by moving closer to the S(2) site; or it may decrease the space available for anisotropic thermal motion of the Cu(2) atom (which will be proportional to the Cu(2)–Cu(2) distance) by decreasing the distance between adjacent S(1) sites at the base of the SbS(1)$_3$ pyramid. A third possibility, that As could interfere with the Cu(2) sites in

the lone pair $\langle 111 \rangle$ direction, is not indicated, as the Cu(2)-LP distance is greater for tennantite (WTN) than tetrahedrite (WTD).

The area of the Cu(2)S$_3$ triangle is shrunk by 2% with the replacement of Sb by As in the Sb site (Table 6). The S(1)–S(1) (base) and Cu(2)–Cu(2) second-nearest-neighbor distances are given in Table 4. Although the distance between basal sulfurs increases, their closer proximity to the origin causes the Cu(2)–Cu(2) distance to decrease by 1.5% with the total replacement of Sb by As. There is less room for the Cu(2) atom in tennantite compared to tetrahedrite, in both the in-plane and out-of-plane directions.

Extra room is necessary for silver compared to copper, as silver has the larger ionic radius (Shannon, 1981). As a result of this, both the Cu(2)S$_3$ area and the Cu(2)–Cu(2) distance increase in tetrahedrite with the replacement of Cu by Ag. If the effects of As and Ag substitition are independent, we would expect to see less silver substituted into tetrahedrite with increasing As content, regardless of arsenic-silver interaction.

If the effects of As and Ag substitutions are independent, then the value of any property (bond distance, angle, etc.) should be expressible as a linear combination of the values of that property for endmembers WTD, WTN, and FRKALB, weighted by the relative amounts of As and Ag for the sample under discussion. For TNAG2MLJ, this may be expressed as:

$$X{-}M_{TNAG2MLJ(CALC)} = X{-}M_{WTD}$$

$$+ \frac{32.5}{85} (X{-}M_{WTN} - X{-}M_{WTD})$$

$$+ \frac{2.12}{1.44} (X{-}M_{FRKALB} - X{-}M_{WTD})$$

for the bond distance between arbitrary atoms X and M, and similarly for bond angles, polyhedral volumes and angle differences (but not distortion parameters of Robinson et al. (1971)). The deviations of actual properties from their calculated values are in all cases less than the errors in the refinement; hence there is no reason to assume interdependence.

Conclusions

The crystal structure has been determined for synthetic tetrahedrite with 24.3 wt.% Ag and 7.9 wt.% As. Based on this and previous structure refinements (Wuensch, 1964; Wuensch et al. 1966; Kalbskopf, 1972), we have demonstrated that the substitution of Ag for Cu and As for Sb affect the tetrahedrite structure independently for the most part. The substitutions tend to distort the structure in opposite directions, but both substitutions make the Cu(1) tetrahedron smaller and more regular, and

make the Sb pyramid smaller. The presence of arsenic in the Sb site decreases the space available in the Cu(2) site, both in the in-plane (Cu(2)S$_3$ triangle) and in the out-of-plane directions. This explains the lack of silver in arsenic-rich tetrahedrite samples.

The effect of substitutions on the unit-cell parameter of tetrahedrites was explored by Charlat and Levy (1975), but this is the first report of the effect of multiple substitutions on the tetrahedrite structure.

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