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Silver substitution into synthetic zinc, cadmium, and iron tetrahedrites

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ABSTRACT. The limits and effect on cell size of silver substitution into synthetic tetrahedrite, $Cu_{10}(Zn,Fe,Cd_2)Sb_4S_{13}$, are investigated for comparison with natural tetrahedrite. The limit of Ag substitution into natural zincian tetrahedrite is ~ 4 atoms per half unit cell and into iron tetrahedrite ~ 6.5 atoms (with rare exceptions). The cell size of natural tetrahedrite increases with increasing Ag content up to 4 atoms but decreases with further Ag substitution. The highest Ag substitution achieved in synthetic tetrahedrites was 4.7 atoms in Zn_2-tetrahedrite, 7.02 atoms in Cd_2-tetrahedrite and 6.80 atoms in Fe_2-tetrahedrite. The cell size of synthetic tetrahedrites shows a continuous increase with increasing Ag content, the largest cell size of a = 10.927 Å being in the Cd_2-tetrahedrite with 7.02 atoms Ag. The iron content of tetrahedrite systematically increased from 1.1 to 2.0 atoms per half unit cell tetrahedrite with increase from 0 to ~ 4 atoms Ag. The different limit of Ag substitution between Zn_2 and Cd_2 tetrahedrite can be explained by size constraints on the expanding structure. An explanation is given for a limit of 7 atoms Ag substitution in tetrahedrite using a combined electron band/molecular orbital approach.

THE limits of Ag substitution and the cell size changes observed in natural tetrahedrite–tennantites reveal unsolved problems as to the nature and controls of substitution. This study provides information on these points by the use of synthetic tetrahedrites where the chemistry of the mineral can be simplified and the availability of substituting elements controlled. The conditions of synthesis do not reproduce the processes involved in nature but the products of the runs can be more easily used to determine cell size variation with composition than chemically complex natural tetrahedrites.

The general formula representing the naturally occurring tetrahedrite–tennantite series is $(Cu,Ag)_{10}(Zn,Fe,Cd,Hg,Cu)_2(Sb,As,Bi)_4S_{13}$ (denoted $M^{+}_{10}M^{2+}_{2}M^{3+}_{4}S_{13}$). The mineral has a cubic structure based on that of sphalerite with a space group of $I\bar{4}3m$. Investigations of the mineral structure have been made by Pauling and Neuman (1934), Wuensch (1964), Wuensch *et al.* (1966), and Makovicky and Skinner (1979); fig. 1 depicts a half unit cell of tetrahedrite based on this work. Sulphur atoms in 6-fold coordination form 'corners' to the cell and are bonded to six Cu atoms in a triangular planar site in 3-fold coordination. The remaining S atoms are in tetrahedral sites bonded to one of the Cu atoms in 3-fold coordination, an Sb atom and two Cu atoms in 4-fold coordination (fig. 1). In a half unit cell of an end-member tetrahedrite, $Cu_{12}Sb_4S_{13}$, there are six Cu atoms in 3-fold coordination and six Cu atoms in 4-fold coordination. Four of the ^{IV}Cu atoms are presumably as Cu^+ and two as Cu^{2+}. However, in most natural tetrahedrites the two Cu^{2+} atoms are replaced by a divalent element such as Zn^{2+} which usually occupies a tetrahedral site in sulphides. Figs. 2 and 3 display possible electronic distributions and determined bond lengths for tetrahedrites.

In this paper all microprobe analyses have been recalculated to $M^{+} + M^{2+} = 12$ atoms in the ideal formula $M^{+}_{10}M^{2+}_{2}M^{3+}_{4}S_{13}$. Compositions are usually quoted as atoms per half unit cell, assuming stoichiometry of the unit cell = 2 $[(Cu,Ag)_{10}(Zn,Fe)_2Sb_4S_{13}]$. Non-stoichiometry has often been recorded in tetrahedrites, especially those without $2M^{2+}$ substituting for two Cu atoms; however this does not significantly affect the analyses quoted in this paper.

Work on the synthetic systems Cu–Sb–S and Cu–As–S (Cambi and Elli, 1965; Hall, 1972; Skinner *et al.*, 1972; Maske and Skinner, 1971; Tatsuka and Morimoto, 1973; 1977; Luce *et al.*, 1977; and Makovicky and Skinner, 1978) have revealed

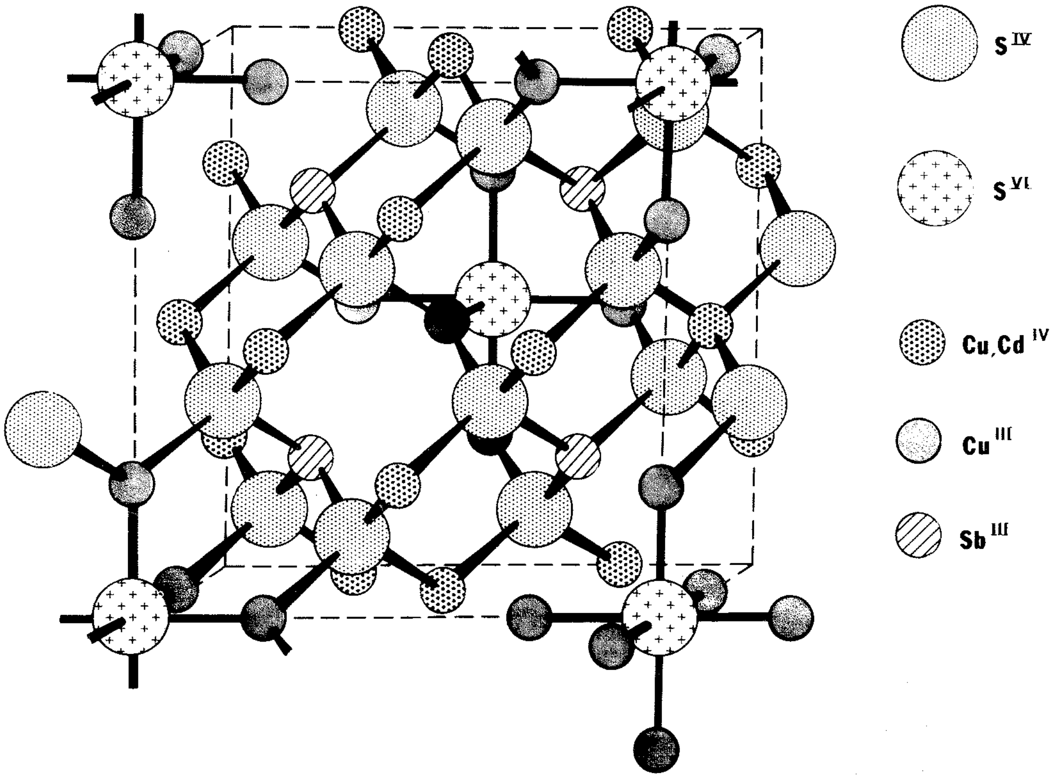


FIG. 1. A half unit cell of tetrahedrite redrawn from Hall (1971); after work by Pauling and Neuman (1934) and Wuensch (1964). The tetrahedral site may be occuppied by Zn and Fe as well as Cu and Cd as shown.

non-stoichiometry in end-member tetrahedrite-tennantites. These studies show there to be a compositional field extending towards the Cu-rich corner of the Cu-Sb-S and Cu-As-S phase diagrams. The Cu-poor end of this field does not, however, extend quite far enough to include the compositions $Cu_{12}Sb_4S_{13}$ and $Cu_{12}As_4S_{13}$ and Makovicky and Skinner (1978) suggest this is because the interatomic distances have reached their minimum. The composition restriction may also be influenced by the Cu^{2+}/Cu^{+} ratio in the valence band. Tatsuka and Morimoto (1973) and Makovicky and Skinner (1978) showed that some of the Cu incorporated in end-member tetrahedrites is interstitial and therefore highly mobile. Tatsuka and Morimoto (1977) studied the system Cu-Fe-Sb-S and found that on increasing the Fe content from 0 to 2 atoms per half unit cell the compositional field narrowed to a single point at a composition equivalent to the ideal formula $Cu_{10}Fe_2Sb_4S_{13}$. In nature, the end members, tetrahedrite ($Cu_{12}Sb_4S_{13}$) and tennantite ($Cu_{12}As_4S_{13}$), are rare and appear to occur replacing other phases (Springer, 1969; Karup-Møller, 1974); thus the presence of M^{2+} atoms appears to stabilize the tetrahedrite structure and compositions. Johnson and Jeanloz (1983) have recently explained compositional limits of tetrahedrites using a Brillouin-zone model.

Substitutions into tetrahedrite-tennantite

M^{3+}. The series is defined by the substitution of As (tennantite) for Sb (tetrahedrite) in the 'trivalent' site in the mineral forming a complete solid solution series. The substitution of Bi for As and Sb in tetrahedrite-tennantites is rare and is only recorded from mineralization with Bi-rich mineralogies (Boldyreva and Borodayev, 1973; Oen and Kiefe, 1976). The rarity can be in part explained by the comparative inability of Bi to form regular co-ordination polyhedra in sulphides and its preference for forming other sulphosalts rather than tetrahedrite. Tellurium-bearing tetrahedrites have also been reported (Springer, 1969; Novgorodova *et al.*, 1978).

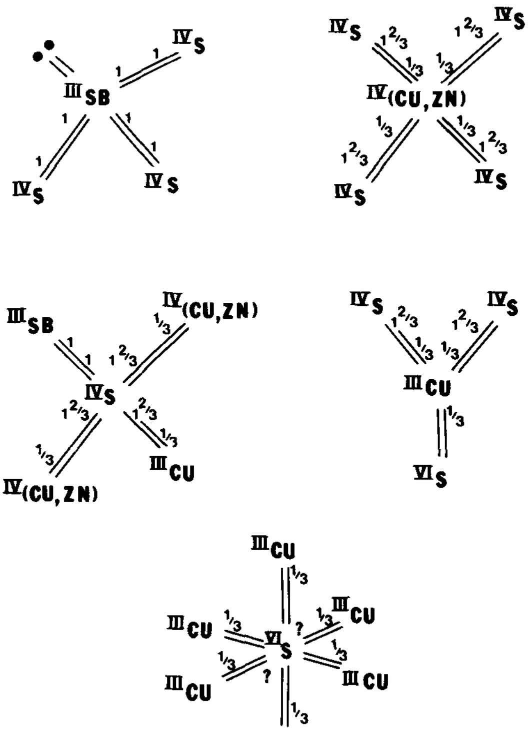


FIG. 2. Possible electron distribution in tetrahedrite (after Hall, 1971) (?uncertain distribution, see text).

M^{2+}. The commonest elements (M^{2+}) substituting for the two Cu^{2+} in end-member tetrahedrite–tennantites are Zn and Fe. Hall (1972) explained this substitution using the band model of semiconductors and demonstrated how Zn^{2+} and Fe^{2+} in tetrahedral coordination could occupy one-third of the tetrahedral sites contributing two electrons to the valence band and Cu^+ only one (fig. 2). Any further substitution of Cu^+ would cause instability of the structure due to an excess of electrons beyond the number required for a filled valence band. Examination of a large number of microprobe analyses of natural tetrahedrites by Charlat and Levy (1974) and Pattrick (1981) revealed that in Fe-rich varieties of the mineral some of the analyses showed more than 10 atoms of Cu (per half unit cell) to be present. Charlat and Levy (1974) suggested that up to 0.8 atoms Cu^{2+} could be included if the other 1.2 atoms of the M^{2+} are Fe. The evidence from microprobe analyses of natural Zn-rich varieties shows a strict adherence to two atoms of Zn in a half unit cell, although Hall (1972) synthesized a tetrahedrite of approximate composition $Cu_{11}Zn_1Sb_4S_{13}$. An explanation for this feature of natural tetrahedrites is given by Hall *et al.* (1974).

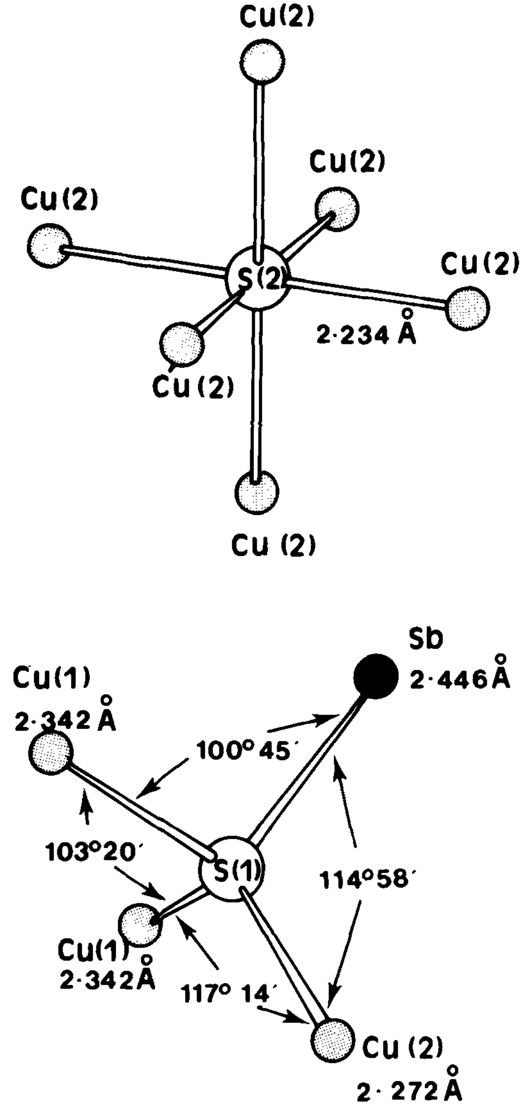


FIG. 3. Distribution of metal atoms round sulphur and M-S bond lengths in tetrahedrites (after Wuensch, 1964): Cu(1) = tetrahedral coordination; Cu(2) = triangular coordination; S(1) = tetrahedral coordination; S(2) = octahedral coordination.

They point out that Fe^{3+} with an unpaired configuration of electrons is stabilized in tetrahedral sites whereas divalent Fe with a d^6 configuration is not. If Fe^{3+} is bonded into tetrahedrites the charge balance can be maintained by replacing some of the Fe by Cu^+ such that $Cu^+ + Fe^{3+} \rightleftharpoons 2Fe^{2+}$. Hall *et al.* (1974) also demonstrate that the only tetrahedrite with a stable 'simple' d^{10} closed shell configuration would be one with a formula of $Cu_{10}Zn_2Sb_4S_{13}$ and the second most stable would be a tetrahedrite of formula $Cu_{11}Fe_1Sb_4S_{13}$ with iron as Fe^{3+}.

Though rarer than Fe- and Zn-rich tetrahedrites, Hg-rich varieties have been recorded from many localities (Bernhard, 1957; Steed, 1975; Mozgova *et al.*, 1979). Kalbskopf (1971) shows that Hg^{2+} substitutes for the Cu^{2+} atoms in 4-fold coordination and Mozgova *et al.* (1979) record both end member tetrahedrites and tennantites with $2Hg^{2+}$. An occurrence of Cd-rich tetrahedrite close to Cd_2 in composition has been recorded (Pattrick, 1978) as has a tennantite containing 4.6 wt. % Pb (~ 0.4 atoms) (Bishop *et al.*, 1977). The stability of Zn and Cd in 4-fold coordination explains their substitution into tetrahedrite-tennantites. The lack of more occurrences of Cd-rich tetrahedrites is probably due to the preferential substitution of Cd into coexisting sphalerite (Pattrick, 1981). Fe and Hg are less commonly found in 4-fold coordination though ^{IV}Fe occurs in chalcopyrite ($CuFeS_2$) and stannite (Cu_2FeSnS_4) and ^{IV}Hg in metacinnabar (^{IV}Hg ^{IV}S). This incorporation of Pb^{2+} into tetrahedrite-tennantites is not easily explained because it exists in other sulphosalts in poorly defined sites of large coordination number and variable bond length.

M^+. The substitution of Ag for Cu in tetrahedrites (but not tennantites) is common. There is no valence restriction on the Ag substitution and a composition of $Ag_{10}(Zn,Fe)_2Sb_4S_{13}$ is a theoretical possibility (Hall, 1972). Analyses of natural tetrahedrites with more than 6.5 atoms Ag are rare and may be inaccurate. For instance Kvacek *et al.* (1975) record a tetrahedrite of composition $Cu_{2.8}Ag_{7.8}Zn_{0.2}Fe_{1.4}Sb_{3.1}S_{9.5}$ and Riley (1974) found tetrahedrites at Mt. Isa, Queensland with up to 46 wt. % Ag (~ Ag_9) though the analyses were incomplete. One exception to this is the microprobe analysis of a tetrahedrite from Janggun mine, Korea, with a composition of $(Cu_{0.77}Ag_{9.14})(Fe_{1.91}Zn_{0.24})Sb_4S_{12.88}$, close to the theoretical end-member tetrahedrite $Ag_{10}Fe_2Sb_4S_{13}$ (Imai and Lee, 1980). Most analyses of tetrahedrites from this mine have Ag < 5 atoms per half unit cell.

Kalbskopf (1972) suggested that initially Ag substitutes for the six Cu atoms in triangular planar sites (fig. 1) and only if these are 'full' will the Ag displace the four Cu atoms in tetrahedral coordination. This might explain the paucity of argentian tetrahedrites with Ag > 6 atoms per half unit cell. However, examination of over 300 microprobe analyses of argentian tetrahedrites containing Fe and Zn as the divalent elements revealed that the most Ag-rich tetrahedrites were also Fe-rich (fig. 4). The inference from fig. 4 is that the normal limit of Ag substitution in Zn_2 tetrahedrites is ~ 4 atoms Ag per unit cell but for Fe-rich tetrahedrites the limit is higher, ~ 6.5 atoms.

Sugaki *et al.* (1975) examined experimentally the solubility of Ag in Fe-rich tetrahedrite. They found that in tetrahedrites containing 2 wt. % iron the maximum Ag content was 8.3 wt. %. However, if the Fe content was raised to 7.3 wt. % (~ 2.0 atoms per half unit cell) the maximum Ag concentration rose to more than 24.5 wt. % (~ 4.0 atoms). These data show that Ag substitution is controlled by Fe substitution, though the maximum solubilities achieved are less than that revealed by natural tetrahedrite.

Cell size variations in tetrahedrite-tennantites

Variations of cell size in tetrahedrite-tennantite are largely dependent on the covalent radii of the substituting elements. Table I gives the covalent radii and bond lengths of elements found in tetrahedrite-tennantites, although in some cases, the M-S bond lengths given do not have 'direct' application to the sites they occupy in tetrahedrite-tennantite.

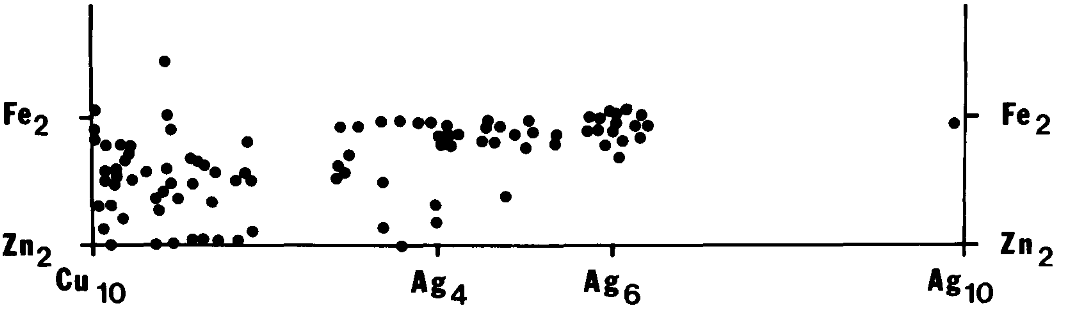


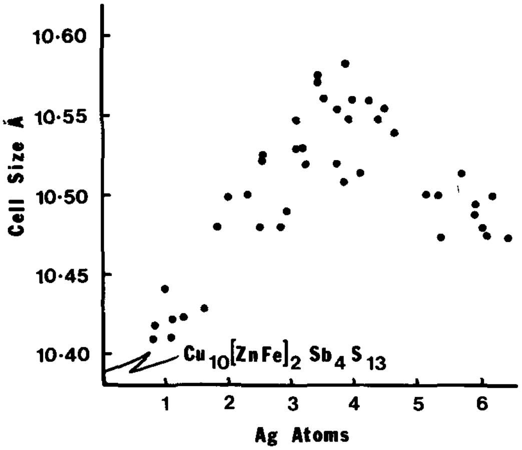
FIG. 4. Variation of Cu-Ag content of argentian tetrahedrites, with Fe-Zn content. (Numerical values are atoms per half unit cell represented by the general formula $(Cu,Ag)_{10}(Zn,Fe)_2Sb_4S_{13}$).

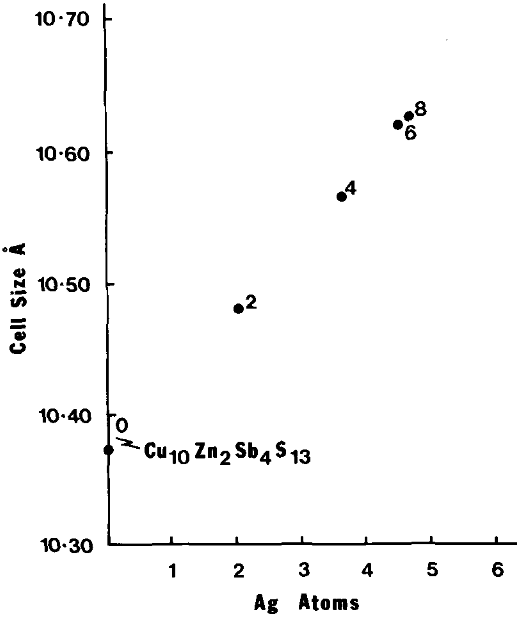
The cell parameter *a* of tetrahedrite–tennantites varies with composition. Machatschki (1928) determined a cell size of $a = 10.189$ Å for a tennantite and $a = 10.55$ Å for a tetrahedrite. Pauling and Neuman (1934), in their determination of the structure of the mineral, calculated the *M*–S bond lengths in 'binnite' $(Cu,Fe)_{12}As_4S_{13}$ and also determined the cell size as $a = 19.19$ Å. Wuensch (1964), and Wuensch *et al.* (1966) went further and compared the bond lengths in $Cu_{10}(Zn,Fe)_2As_4S_{13}$ with those in tetrahedrite $Cu_{10}(Zn,Fe_2)Sb_4S_{13}$; they found bond lengths of 2.246 Å for As–S and 2.446 Å for Sb–S thus explaining the larger cell size in tetrahedrite. Charlat and Levy (1975) studied the cell size variation of natural tetrahedrite–tennantites with composition. They calculated the cell size of a tetrahedrite of composition $Cu_{10}(Zn,Fe)_2Sb_4S_{13}$ to be $a = 10.386$ Å, which is in good agreement with the $a = 10.383$ Å found for synthetic $Cu_{10}Zn_2Sb_4S_{13}$ (Hall, 1972) and $a = 10.384$ Å for synthetic $Cu_{10}Fe_2Sb_4S_{13}$ (Tatsuka and Morimoto, 1977). They then produced the formula of the cell size changes for substitutions into this tetrahedrite as a (Å) $= 10.386 + 0.056$ (per atom Ag) $+ 0.058$ (Hg) $- 0.031$ (Cu) $- 0.039$ (As). These changes in cell size are largely similar to those that could be predicted from Table I. Charlat and Levy (1975) noted in natural tetrahedrites that Fe substitution for Zn caused no cell size change. The effect of the substitution of Bi into $Cu_{12}Sb_4S_{13}$ determined by Mozgova *et al.* (1979) is $+0.093$ Å per atom.

The substitution of Ag for Cu would expected to increase the cell size of tetrahedrites because of the larger size of the Ag atom. Riley (1974), in the study on argentian tetrahedrite from Mt. Isa, Queensland, found that the cell size of tetrahedrites increased with increasing Ag content up to Cu_6Ag_4, but with further Ag substitution began to decrease. This trend accords with other published cell size data (fig. 5), Riley (1974) suggests that this phenomenon is caused by the substitution of the Cu occupying two different sites and may be related to the difference in ionic character of Ag–S and Cu–S bonds and to differences in packing. Riley (1974) called the argentian tetrahedrites with > 4 atoms Ag per half unit cell freibergites. The reflectance data of Imai and Lee (1980) appear to confirm this structural change in argentian tetrahedrites from the Janggun Mine although Indolev *et al.* (1971) record a cell size decrease in tetrahedrites over the range 2.2 to 3.9 atoms Ag. The decrease of the cell size with > 4 atoms Ag could be evidence for a change of Ag substitution from the four tetrahedrally coordinated Cu atoms to Ag substitution of the Cu atoms in 3-fold coordination, but it also could be a feature unique to Fe-rich tetrahedrites. It is possible that whatever causes the cell size to decrease with > 4 Ag atoms could occur with < 4 atoms Ag in some tetrahedrites thus decreasing the

Table I. Covalent radii and M–S bond lengths of elements substituting in tetrahedrite–tennantites. (Data from: Pauling, 1960; Wuensch, 1964, 1966; Pauling and Huggins, 1934; Wedepohl, 1969; Hall, 1971). (* not actually in tetrahedral co-ordination in tetrahedrite–tennantites but in a similar site, see Figs. 1 and 3).

Element	Valence	Covalent r.	Co-ord.	M–S (Å)	
Cu	1	1.35	4	2.31(1), 2.337(2), 2.342(3)	((1)Covellite, (2)tennantite, (3)tetrahedrite)
Cu	1	-	3	2.25, 2.204(4), 2.234(5)	((4)tennantite, (5)tetrahedrite
Cu	2	-	4	2.19	(Covellite)
Ag	1	1.53	4	2.64	(Ag_2S, average)
Zn	2	1.31	4	2.35	(ZnS)
Fe	2	-	4	2.36(7), 2.23(8)	((7)Stannite, (8)FeS)
Cd	2	1.48	4	2.52	(CdS)
Hg	2	1.48	4	2.53	(Cubic HgS)
Sb	3	1.36	4*	2.45	(Tetrahedrite)
As	3	1.18	4 *	2.246	(Tennantite)
Bi	3	1.40	variable	2.54 - 3.07	(Irregular co-ord. in Bi_2S_3)
S	2	1.04	4	(Σcov. r.)	





FIGS. 5 and 6. FIG. 5 (*left*). Cell size determinations on natural argentian tetrahedrites from published data compared to the cell size increase calculated by Charlat and Levy (1975). Data from: Riley, 1974; Charlat and Levy, 1975; Petruk, 1971; Indolev *et al.*, 1971; Atanasov, 1975; Timofeyevskiy, 1967 and Patterson, 1970) (data recalculated to compensate for substitution of As, Hg, and Cu^{2+}). FIG. 6 (*right*). Cell size variation with Ag content of synthetic Zn-rich tetrahedrite (errors less than filled circles—numbers by filled circles denote number of Ag atoms in starting composition).

cell size of the tetrahedrite below the maximum. Some of the variation of cell size for the same Ag content in fig. 5 may be accounted for by this mechanism, as well as by analytical errors.

In their experimental work, Sugaki *et al.* (1975) found a linear increase in cell size with Ag substitution into iron tetrahedrite. However, their maximum cell size of 10.612 ± 0.002 Å represents a tetrahedrite of Ag content of ~ 4.0 atoms, so the cell size decrease observed by Riley (1974) might not be revealed in their runs.

The behaviour of Ag-rich tetrahedrites is discussed further below.

Experimental methods and results

The syntheses were carried out in tube furnaces in pure silica glass tubing sealed under vacuum. High purity elements (99.998 %) were used. The charges were made up to starting compositions equivalent to the intended tetrahedrite compositions and weighed exactly 1 g. Runs were made at various temperatures but it was found that at 400 °C a good yield was obtained in a reasonable time. The runs lasted for 7 days after which charges were quenched, ground up and returned to the furnace for a further 7 days. Three series were run to evaluate the effect of Ag substitution into Zn_2, Fe_2, and Cd_2 tetrahedrites. An end-member starting composition was run viz: $Cu_{10}Zn_2Sb_4S_{13}$, and starting compositions equivalent to the substitution of one atom of Cu by Ag for each Ag atom up to the theoretical end-member $Ag_{10}Zn_2Sb_4S_{13}$.

The cell size of the tetrahedrites produced was determined using X-ray diffraction analysis from the observed strong reflections in the 2θ range 20–60°. Cu-K_α radiation was used and the internal standards were silica and α-alumina. The estimated errors are $< \pm 0.002$ Å. Microprobe analyses were performed on Microscan 5 and Cameca Cambebax microprobes using wavelength spectrometry. Standards used were metallic Cu, Ag, Zn and Cd, FeS_2, GaSb, ZnS (pure synthetic), and CdS. The use of metals was not ideal and improved analyses were obtained using $CuFeS_2$, and synthetic $CuSbS_2$ and $AgBiS_2$. Analyses of tetrahedrite from individual charges proved to be very consistent; only in charges containing argentian zincian-tetrahedrite was there any evidence of inhomogeneity.

Argentian zincian tetrahedrites. A series of starting compositions from $Cu_{10}Zn_2Sb_4S_{13}$ to $Ag_{10}Zn_2$ Sb_4S_{13} were run at 400 °C and all results are summarized in Table II. All charges, except the Ag_{10} sample, produced tetrahedrite. The low cell-

Table II. Summary of the synthetic argentian zincian tetrahedrites produced.

Starting Composition	% Tetrahedrite	Ag Content (atoms)	Cell size (Å)
$Cu_{10}Zn_2Sb_4S_{13}$	95	-	10.370
$Cu_8Ag_2Zn_2Sb_4S_{13}$	95	2.00	10.478
$Cu_6Ag_4Zn_2Sb_4S_{13}$	80	3.60	10.565
$Cu_4Ag_6Zn_2Sb_4S_{13}$	40	4.49	10.620
$Cu_2Ag_8Zn_2Sb_4S_{13}$	20	4.70	10.625

size for the end-member $Cu_{10}Zn_2Sb_4S_{13}$ may be accounted for by a slight deficiency of Zn in the tetrahedrite produced. This deficiency is probably due to a lack of equilibrium resulting from the preservation of relic refractory ZnS grains. An increase in grain size through the sequence is explained by the lowering of reaction and melting temperatures with increase in silver content. As might be expected, argentiferous phases, pyrargyrite and miargyrite tend to be interstitial to tetrahedrite. This tendency towards segregation of the charge is a problem and means that the microprobe analysis of synthetic zincian-tetrahedrites might not exactly reflect the average composition of the tetrahedrite in the charge. Slight inaccuracies in the cell size-composition plot may be explained this way. The cell size of 10.370 Å for pure Zn_2 tetrahedrite appears anomalously low compared to published data.

The limit of substitution of silver in zincian-tetrahedrite is determined to be 4.7 atoms corresponding to a cell-size of 10.625 Å (Table II).

Argentian cadmium-tetrahedrite. A series of starting compositions from $Cu_{10}Cd_2Sb_4S_{13}$ to $Ag_{10}Cd_2Sb_4S_{13}$ were run at 400 °C and the results are summarized in Table III. The charge with a starting composition of $Cu_{10}Cd_2Sb_4S_{13}$ produced tetrahedrite very close to that composition. The ease with which cadmium tetrahedrite is formed suggests that its rarity in nature is probably a function of the availability of Cd. X-ray diffraction data for the cadmium tetrahedrite produced gave the cell size of $Cu_{10}Cd_2Sb_4S_{13}$ as a = 10.505 Å. This represents an increase of 0.06 Å per atom Cd substituting for Zn and Fe (assuming that for $Cu_{10}(Zn,Fe)_2Sb_4S_{13}$ a = 10.386 Å).

The Ag content of tetrahedrites produced increased with the Ag content of the starting compositions (Table III). In runs up to starting composition Ag_4 the tetrahedrite was slightly higher in Ag than the intended composition. At starting compositions higher than Ag_4, the percentage of tetrahedrite produced decreased and its Ag content was lower than intended (Table III). The highest Ag content produced was 7.02 atoms; the theoretical end-member $Ag_{10}Cd_2Sb_4S_{13}$ was not produced.

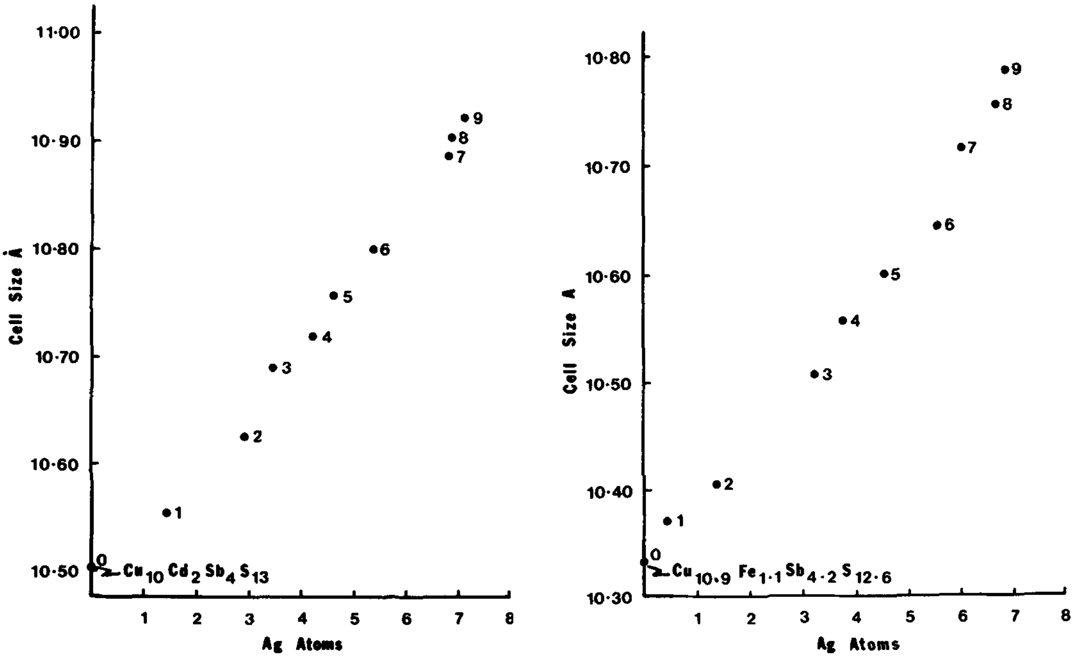
Table III. Summary of the synthetic argentian cadmium tetrahedrites produced.

Starting Composition	% Tetrahedrite	Ag Content (atoms)	Cell size (Å)
$Cu_{10}Cd_2Sb_4S_{13}$	98	-	10.502
$Cu_9Ag_1Cd_2Sb_4S_{13}$	95	1.41	10.561
$Cu_8Ag_2Cd_2Sb_4S_{13}$	95	2.90	10.631
$Cu_7Ag_3Cd_2Sb_4S_{13}$	93	3.41	10.693
$Cu_6Ag_4Cd_2Sb_4S_{13}$	95	4.16	10.720
$Cu_5Ag_5Cd_2Sb_4S_{13}$	90	4.59	10.759
$Cu_4Ag_6Cd_2Sb_4S_{13}$	80	5.26	10.804
$Cu_3Ag_7Cd_2Sb_4S_{13}$	98	6.74	10.892
$Cu_2Ag_8Cd_2Sb_4S_{13}$	92	6.78	10.908
$Cu_1Ag_9Cd_2Sb_4S_{13}$	90	7.02	10.927
$Ag_{10}Cd_2Sb_4S_{13}$	0	-	-

The cell size of the tetrahedrite shows a near-linear increase with Ag content (Table III, fig. 7), largest cell size of 10.927 Å representing tetrahedrite containing 7.02 atoms Ag.

The same starting compositions were also run at 340 °C and 500 °C. At 340 °C the charges did not reach equilibrium although the tetrahedrite produced had similar Ag contents to the corresponding charges run at 400 °C. At 500 °C the starting compositions up to Ag_3 produced more than 95% tetrahedrite with Ag contents greater than intended. The Ag_4 charge produced 80% tetrahedrite containing $Ag_{3.7}$ and the Ag_7 charge 50% tetrahedrite containing $Ag_{4.8}$. In the Ag_8 charge the contents (except CdS) were liquid at 500 °C and a small amount (15%) of 'star-shaped' tetrahedrite containing $Ag_{5.3}$ formed on quenching. There was much evidence of liquid being present in the charges with starting compositions $> Ag_4$ at 500 °C due to the run temperature being above the stability limits of Ag_3SbS_3 and $AgSbS_2$.

Other phases forming the charges were CdS, Ag_3SbS_3 and $AgSbS_2$. In the charges with starting compositions of Ag_9 and Ag_{10} a previously unrecorded Ag-Cd-Sb-S phase '*cm*' was produced. The phase has a composition close to $Ag_3CdSb_3S_7$. A charge was run at 500 °C with an equivalent starting composition and 98% of phase *cm* produced. X-ray diffraction analysis reveals it to have an identical structure to the quenchable high temperature (> 380 °C) cubic form of miargyrite, β-$AgSbS_2$ (Keighin and Honea, 1969). *Cm* may represent a member of a solid-solution series involving Cd substitution according to $2Cd^+ \rightleftharpoons Ag^+ + Sb^{3+}$ into miargyrite, $AgSbS_2$. Evidence from the 340 °C runs suggest there can also be Cd substitution into monoclinic miargyrite and that other members of the series include $Ag_6CdSb_6S_{13}$ and $Ag_2CdSb_2S_5$.



FIGS. 7 and 8. FIG. 7 (*left*). Cell size variation with Ag content of Cd-rich tetrahedrite. FIG. 8 (*right*). Cell size variation with Ag content of synthetic Fe-rich tetrahedrite (errors less than filled circles—numbers by filled circles denote number of Ag atoms in starting composition).

Table IV Summary of the synthetic argentian iron tetrahedrites produced.

Starting Composition	% Tetrahedrite	Ag content (atoms)	Cell size (Å)	Average Composition of Tetrahedrite Cu	Ag	Fe	Sb	S
$Cu_{10}Fe_2Sb_4S_{13}$	75	-	10.329	10.88	0.00	1.12	4.27	12.57
$Cu_9Ag_1Fe_2Sb_4S_{13}$	85	0.33	10.375	10.59	0.33	1.08	4.14	12.48
$Cu_8Ag_2Fe_2Sb_4S_{13}$	70	1.33	10.405	9.47	1.33	1.20	4.33	12.71
$Cu_7Ag_3Fe_2Sb_4S_{13}$	85	3.21	10.507	7.26	3.21	1.55	4.22	12.64
$Cu_6Ag_4Fe_2Sb_4S_{13}$	60	3.72	10.557	6.40	3.72	1.88	4.20	12.55
$Cu_5Ag_5Fe_2Sb_4S_{13}$	90	4.53	10.602	5.54	4.53	1.93	4.19	12.46
$Cu_4Ag_6Fe_2Sb_4S_{13}$	60	5.51	10.647	4.55	5.51	1.92	4.22	12.50
$Cu_3Ag_7Fe_2Sb_4S_{13}$	80	5.94	10.720	4.10	5.94	1.96	4.22	12.72
$Cu_2Ag_8Fe_2Sb_4S_{13}$	70	6.60	10.759	3.42	6.60	1.98	4.28	12.78
$Cu_1Ag_9Fe_2Sb_4S_{13}$	30	6.80	10.794	3.22	6.80	1.98	4.33	12.80
$Ag_{10}Fe_2Sb_4S_{13}$			-					

Argentian iron tetrahedrites. Starting compositions from $Cu_{10}Fe_2Sb_4S_{13}$ to $Ag_{10}Fe_2Sb_4S_{13}$ were run at 400 °C and the results are summarized in Table IV. The Ag contents of the tetrahedrite produced are slightly below those of the starting composition (except for Ag_3) and more markedly so in higher Ag charges. The highest Ag content obtained was 6.80 atoms per half unit cell. The cell size showed a near linear increase with Ag content (fig. 8) with the most Ag-rich tetrahedrite having a cell size of $a = 10.794$ Å.

The Fe content of the tetrahedrites also shows a systematic increase (Table IV). In the charge with a starting composition of $Cu_{10}Fe_2Ag_0$ the tetrahedrite produced was $Cu_{10.88}Fe_{1.12}Ag_0$. As the Ag content of the charges increased, the Fe increased at the expense of Cu, reaching an upper limit close to Fe_2 in tetrahedrite containing $Ag_{4.5}$ (fig. 9). The cell size of $a = 10.329$ Å for the tetrahedrite of composition $Cu_{10.88}Fe_{1.12}$ reflects the low Fe content; Charlat and Levy (1975) suggested a drop in cell size of 0.031 Å per atom Cu substitution for Fe in natural $Cu_{10}Fe_2Sb_4S_{13}$. Thus a small part of the observed increase in the cell size from Ag_0 to ~ $Ag_{4.5}$ (fig. 8) can be attributed to increase in Fe content.

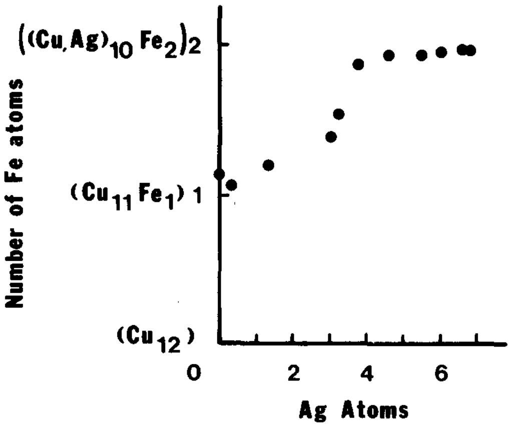


FIG. 9. Variation of the number of Fe atoms per half unit cell with increasing Ag content of synthetic tetrahedrite.

Other phases produced in the charges were FeS_2, $CuSbS_2$, Cu_3SbS_3, $AgSbS_2$, and $CuFeS_2$.

Discussion

In each of the series investigated the cell size increased with Ag content. There is evidence, however, that this increase is not quite constant (figs. 6, 7, and 8) being lowest in the low Ag tetrahedrites and increasing at a faster rate per atom Ag up to 4 atoms Ag when the increase appears to become more linear. The approximate cell size increases for Zn, Fe, and Cd tetrahedrites for 0 to 2 atoms Ag and more than 4 atoms Ag are given in Table V though more extensive investigation is required to confirm these observed variations. The average cell size increase suggested by Charlat and Levy (1975) was 0.056 Å per atom Ag.

Table V. Cell size increase with Ag substitution into tetrahedrites (data taken from figures 6, 7 and 8), per atom Ag substituted.

	0–2 atoms Ag	> 4 atoms
Zn	~ 0.055	0.058
Fe	~ 0.056	0.082
Cd	~ 0.046	0.069

In the runs involving Cd tetrahedrite at 400 °C with starting compositions < Ag_4 the tetrahedrite produced contained more than the intended Ag content. Further Ag substitution required 'excess' Ag in the charge (Table III). This was even more noticeable in the Cd tetrahedrite runs at 500 °C. This provides some evidence that the four ^{IV}Cu atoms (fig. 1) are replaced first with further substitution of the ^{III}Cu being more 'difficult'; in agreement with Riley's (1974) observation that at 4 atoms Ag there is a significant structural change in tetrahedrites. However in the synthetic Fe tetrahedrites there is no such pattern and this may represent random distribution of Ag between ^{III}Cu and ^{IV}Cu sites. Kalbskopf (1972) found a preference for Ag substitution of ^{III}Cu in natural tetrahedrite. This difference between natural and synthetic tetrahedrites may be in part explained by the substitution in synthetics being more disordered and therefore the Ag more randomly placed.

The limit of Ag substitution in Zn_2 tetrahedrites is ~ 4.7 atoms, similar to that in natural tetrahedrite (fig. 4), but the maximum in Cd_2 tetrahedrites is 7.02 atoms. Since both Zn and Cd would be similarly situated in a tetrahedral site (fig. 1), contributing $2e^-$ to the valence band, the increase in the substitution of Ag in Cd-rich tetrahedrites cannot be due to a difference in bonding. The difference in covalent radii may be the explanation with Cd having a significantly larger radius allowing increased substitution of the larger Ag for Cu; substitution of more than 4.7 atoms Ag into Zn-tetrahedrite must lead to too much strain on the structure. However, the same argument cannot be used to explain the higher substitution of Ag into synthetic and natural Fe tetrahedrite compared to

Zn tetrahedrite. This indicates different bonding characteristics for Fe and Zn in tetrahedrite. The limit of 6.80 atoms Ag in synthetic Fe tetrahedrite is similar to the usual limit in natural Fe tetrahedrite and close to the value of 7.02 atoms in synthetic Cd tetrahedrite. Bearing in mind the difference in covalent radii and bonding characteristics of Cd and Fe in tetrahedrites these similar limits of Ag substitution present a problem. Assuming this similarity is not coincidental it could either represent a compressional limit or a bonding constraint on Ag substitution. An alternative explanation to compressional limits on substitutions is provided by examination of the bonding in tetrahedrites using the combined electron band/molecular orbital approach and is described below.

The properties of semiconducting sulphides may be understood by accepting that they have a filled valence band separated from the conduction band by a small energy gap. The directional nature of the bonding in sulphides is controlled by the symmetry of atomic orbitals or combined atomic orbitals used in bonding and filled valence band results from the total valence electron contribution (VEC) equalling the total number of orbitals involved in bonding (Hall, 1971). This concept explains complex sulphide structures better than the similar but simpler concept of electron pair covalent bonds.

Tetrahedrite appears to be one of the few semiconducting sulphides that disobey the above rule. There are insufficient electrons to fill the valence band when the following structural/bonding formula of tetrahedrite is considered:

	$^{III}Cu_6^{1+}$	$^{IV}Cu_4^{1+}$	$^{IV}Zn_2^{2+}$	$^{III}Sb_4^{3+}$	$^{IV}S_{12}^{2-}$	$^{VI}S^{2-}$
hybrid orbitals	sp^2	sp^3	sp^3	$sp^{2(+1)}$	sp^3	p^3
VEC/atom	1	1	2	3(+2)	6	4

The hybrid atomic orbitals suggested above are chosen because their symmetry corresponds to the coordination site of the element. The $^{III}Cu^{1+}$ atoms are in threefold trigonal planar coordination, the $^{III}Sb^{3+}$ atoms are in threefold trigonal pyramidal coordination with a 'lone pair' in the 'unused' tetrahedral direction, the $^{VI}S^{2-}$ atom is in sixfold octahedral coordination with six ^{III}Cu atoms and all the other atoms are in tetrahedral coordination. The total VEC is 102 but the total number of orbitals involved in bonding is 105. A possible solution to this anomaly is that three Cu atoms contribute one *d*-electron each to the valence band and effectively become $Cu^{2+}(d^9)$. The formal charge on the ^{VI}S atom would then have to be 5^-. The limit of two divalent (Zn) atoms in the formula suggests that $Cu^{2+}(d^9)$ results from the trigonal planar coordination of the group of six Cu atoms around octahedral sulphur rather than from the electron deficiency in the structure. A peculiarity of the octahedral sulphur is that because of the orientation of the ^{III}Cu-3S triangles, each of the ^{III}Cu atoms sit in the centre of the edges of a tetrahedron around the ^{VI}S; each edge is one orthogonal axis of a Cu atom's atomic orbitals. There is therefore extensive overlap of Cu *p* and *d* orbitals oriented along these axes and delocalized electron bands representing Cu-Cu bonding may result. If the four $^{IV}Cu^+$ atoms are preferentially replaced by Ag further substitution might be limited to the three $^{III}Cu^+$ atoms and not the $^{III}Cu^{2+}$ atoms, thus putting a limit of 7 atoms Ag in tetrahedrite. This is based on the fact that Ag is less likely to form M^{2+} than Cu. The theory might be confirmed by detailed studies of bond-lengths in Ag-tetrahedrites with variable Ag concentrations.

The cell size decrease observed in natural Fe tetrahedrites with $> Ag_4$ was not found in either the synthetic Cd or Fe tetrahedrites. Riley (1974) suggested the cell size decrease was due to the change of Ag substitution from $^{IV}Cu^+$ to $^{III}Cu^+$ but these synthetic sulphides do not support this. In natural Fe tetrahedrites there must be a structural or bonding change, perhaps because of the preference of $Fe^{3+}(d^5)$ over $Fe^{2+}(d^6)$ in tetrahedral coordination, and perhaps resulting in non-stoichiometry towards a hypothetical tetrahedrite-like compound, $^{IV}Ag_8{}^{IV}Fe_2^{3+}{}^{III}Sb_4{}^{IV}S_{13}$ rather than the $Ag_{10}Zn_2Sb_4S_{13}$ end-member. Vaughan and Burns (1972) using Mössbauer analysis identified both Fe^{2+} and Fe^{3+} in natural tennantite. However in the synthetic charges the iron may all be present as Fe^{2+} and thus the synthesized Fe-series would behave like the Zn^{2+} and Cd^{2+} series.

In the iron tetrahedrites with Ag_0 and $Ag_{0.3}$ the Fe content is close to $Fe_{1.1}$ (Table IV suggests this composition is more stable than Fe_2). The charge balance could be achieved either by the extra Cu in the tetrahedral site being divalent or most of the Fe being trivalent (see above). In both cases rather than being either $^{IV}Fe^{3+}$ and $^{IV}Fe^{2+}$ or $^{IV}Cu^{2+}$ and $^{IV}Cu^+$ the atom concerned would form an intermediate valence type of cation. As silver substitution of the ^{IV}Cu atoms takes place the available sites for positioning of the $^{IV}(Cu^+/Cu^{2+})$ would be removed and thus the composition would move towards Fe_2 with increasing Ag content as seen in the synthetic tetrahedrite (fig. 9). In other words the Ag substitution would tend to 'stabilize' iron-rich tetrahedrites.

Sugaki *et al.* (1975) demonstrated the increased solubility of silver in tetrahedrites with increased substitution of Fe for Cu. The data presented here reveal a more complex inter-relationship.

The information provided by this synthetic study illustrates the complexities of substitutions into the tetrahedrite–tennantite series and firm conclusions are difficult to draw. The difference in variation of cell size between natural and synthetic Fe tetrahedrite is established. There is some evidence to support Ag substitution of the four ^{IV}Cu atoms before ^{III}Cu atoms in Cd tetrahedrite and that the limit of substitution of silver into a stable tetrahedrite is ~ 7 atoms. Further detailed studies of the site of substitution of Ag into a range of tetrahedrite is required and is being undertaken. A major problem concerns the bonding of Fe in tetrahedites and the role of Fe^{2+} and Fe^{3+}. Mössbauer work is being carried out on the synthetic tetrahedrites and argentian natural tetrahedrites which will provide a better understanding. A further problem that requires investigation is the bonding of the octahedral sulphur atom, and this may be the key to understanding much about the structure of tetrahedrite.

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