COMPOSITIONAL TRENDS IN TETRAHEDRITE

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ABSTRACT

Available compositional data for 1271 samples of natural tetrahedrite and 295 of synthetic tetrahedrite were examined. They show: compositional ranges of four to ten Cu, zero to six Ag, and a total of two (Fe, Zn, Hg) atoms, complete substitution (up to four atoms) among As, Sb and Te, and a total of 13 atoms of S per formula unit. Data on contents of Pb, Bi and Cd in natural samples are insufficient to define their compositional ranges, and virtually no data exist on other substitutions, involving Co, Ni, Mn and Au. A generalized formula $(Cu,Ag)_6Cu_4(Fe,Zn,Cu,Hg,Cd)_2(Sb,As,Bi,Te)_4(S,Se)_{13}$ is proposed on the basis of these compositions. The cell dimension is a linear function of chemical elements in the formula except in Ag-rich tetrahedrite, where it increases with Ag content, up to four Ag atoms per formula unit, and then decreases. Ag and As have a low tolerance for each other in the structure, and plots of Fe *versus* Ag, Zn *versus* Ag, and Hg *versus* Cu suggest that incorporation of Ag is controlled by several factors. For the purpose of explaining compositional variations in tetrahedrite, the simple Brillouin-zone model of bonding (Johnson & Jeanloz 1983) is superior to any ionic model.

Keywords: synthetic and natural tetrahedrite, Brillouin zone, Ag–Fe–Zn–Hg–Cd–As–Te–Bi substitution.

SOMMAIRE

On a examiné les données disponibles sur la composition de 1271 échantillons de tétraédrite naturelle et 295 spécimens de tétraédrite synthétique. Ces données indiquent: des domaines de composition pouvant aller de quatre à dix atomes de Cu et de zéro à six Ag, un total de deux atomes (Fe, Zn, Hg), substitution complète (jusqu'à quatre atomes) entre As, Sb, et Te, et 13 atomes de S du total par unité formulaire. Les données sur la teneur des échantillons naturels en Pb, Bi et Cd sont insuffisantes pour définir leurs domaines de composition; quant aux données sur les autres substitutions, impliquant Co, Ni, Mn et Au, elles sont pratiquement inexistantes. On propose ici la formule généralisée $(Cu,Ag)_6Cu_4(Fe,Zn,Cu,Hg,Cd)_2(Sb,As,Bi,Te)_4(S,Se)_{13}$ qui est fondée sur les données susmentionnées. La dimension de la maille est fonction linéaire des éléments chimiques qui entrent dans la formule, sauf pour échantillons riches en Ag, où elle augmente avec la teneur en Ag, de zéro à quatre Ag par unité formulaire, après quoi elle diminue. Dans la structure, Ag et As ont l'un pour l'autre peu de tolérance; les courbes de Fe, Zn et Hg, en fonction de Ag, Ag et Cu, respectivement, portent à penser que l'introduction d'Ag dépend de plusieurs facteurs. Pour expliquer les variations de composition dans la tétraédrite, le modèle simple de la liaison chimique par zone de Bril-
louin (Johnson & Jeanloz 1983) est préférable à tout modèle ionique.

(Traduit par la Rédaction)

Mots-clés: tétraédrite, synthétique et naturelle, zone de Brillouin, substitutions Ag–Fe–Zn–Hg–Cd–As–Te–Bi.

INTRODUCTION

In the most recent thorough studies of the chemical composition and physical properties of natural tetrahedrite, Charlat & Lévy (1974, 1975, 1976) proposed, on the basis of a suite of 54 samples from selected localities worldwide, the general formula $(CuAg)_{10}(Fe,Zn,Cu,Hg,Cd)_2(Sb,As)_4S_{13}$. Subsequent studies have confirmed that Se substitutes for S (Johan & Kvaček 1971, Brodin *et al.* 1979), and Bi + Te substitute for As + Sb (Oen & Kieft 1976, Mozgova *et al.* 1979). Other studies report the presence of Pb, Co, Ni, Au and Mn (Schroll & Azer Ibrahim 1958, Bishop *et al.* 1977, Pattrick 1978, Basu *et al.* 1981, 1984a).

The tetrahedrite structure, as described by Wuensch (1964), can be written as: $^{IV}M1_6{}^{III}M2_6$ $[^{III}X^{IV}Y_3]_4{}^{VI}Z$, where $M1$ represents Cu or Ag, $M2$ represents Cu, Fe, Zn, Hg or Cd, X stands for Sb, As, Bi or Te, and Y and Z could be either S or Se. Although the existence of the six-co-ordinated Z anion in the structure (the 13th S atom) has been generally accepted, there has been some resistance (Belov & Pobedimskaya 1969, Kaplunnik *et al.* 1980, Babushkin *et al.* 1984) to this in favor of a 12-S-atom model. Furthermore, the distribution of the two metal (M) sites in the crystal structure does not match that of metal atoms in the general chemical formula above. Several authors (Godonikov & Il'yasheva 1973, Johnson & Jeanloz 1983, Miller & Craig 1983, Pattrick & Hall 1983) have collected compositional data from published sources in order to review tetrahedrite chemistry or to illustrate a point germane to their research. Because the chemical composition of a mineral reflects the underlying crystal chemistry, a large base of analytical data may provide information on crystallochemical relationships. This report is a comprehensive compilation and analysis that clarifies some reported relationships, unearths other ones that exist in tetrahedrite-group minerals, and thereby serves as a guide for future research. To minimize confusion, the use of varietal names of
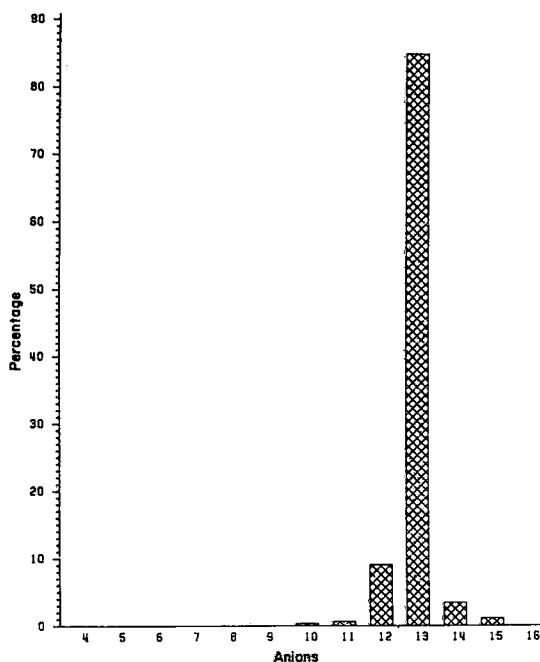
FIG. 1. Number of anions (S, Se) per formula unit.

tetrahedrite-series members (tennantite, freibergite, schwatzite, *etc.*) has been avoided; such members are described as As-rich tetrahedrite, Ag-rich tetrahedrite, Hg-rich tetrahedrite, *etc.*

The data base for this paper consists of reported compositions of 1271 samples of natural tetrahedrite from various ore-deposits and 295 of synthetic tetrahedrite. The data were not critically evaluated except to remove clearly inaccurate analytical data (*e.g.*, totals equalling 93%, 30 weight % Fe). The following information is considered for each composition: Cu, Ag, Fe, Zn, Hg, Cd, As, Sb, Bi, S, Pb, Te, Mn and Se contents in weight %, and the length of the unit-cell edge *a* (in Å), where given. Data on other reported substitutions are sufficiently rare and their reported importance is sufficiently small that they can be ignored. The weight percentage was converted to number of atoms based on 29 atoms per formula unit. Two additional variables were considered during the processing: BZ, the number of valence electrons per unit cell, and CHR, the net ionic charge per formula unit (after Johnson & Jeanloz 1983). The results were then plotted as functions of each other or as functions of their frequency. A complete listing of all the data may be obtained from the authors, and will be included in the Ph.D. dissertation of the first author.
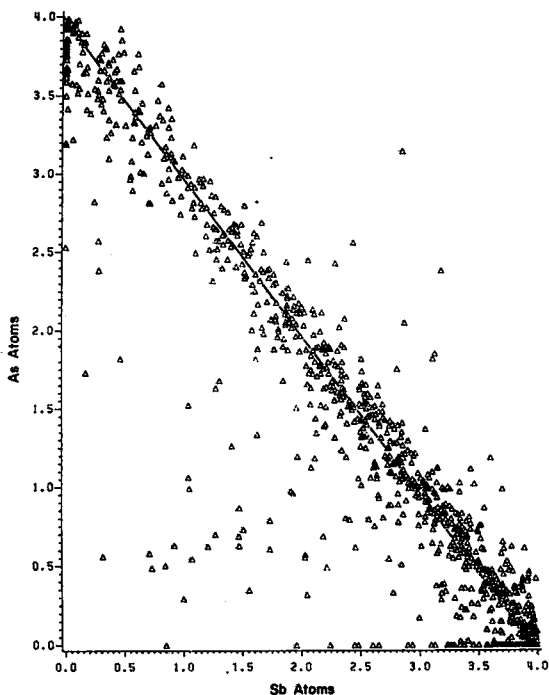

FIG. 2a. Number of As atoms *versus* number of Sb atoms for samples of natural tetrahedrite. Dashed line is ideal solid-solution.
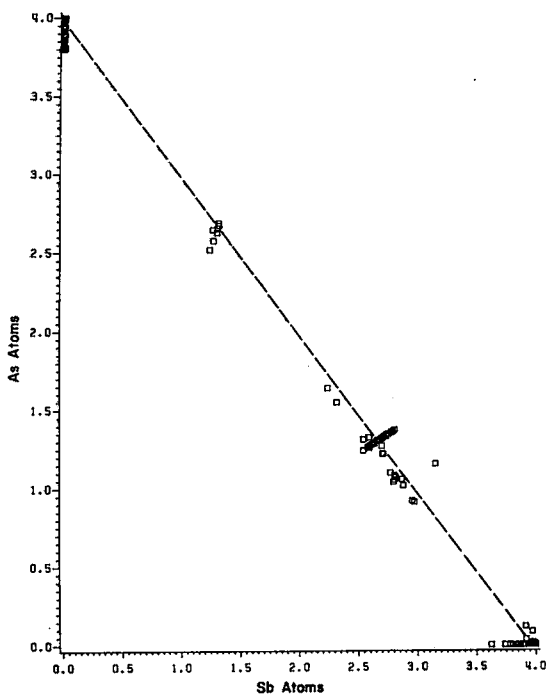

FIG. 2b. Number of As atoms *versus* number of Sb atoms for samples of synthetic tetrahedrite. Dashed line is as in Figure 2a.

RESULTS

S and Se contents

Recalculating weight % values to the mean atomic % S indicates that the hypothesis of 12 S atoms per formula unit can be rejected at the 99.9% confidence level. By far the largest number of reported tetrahedrite compositions (85%) have 13 S atoms per formula unit (Fig. 1), effectively ending the debate as to whether tetrahedrite contains 12 or 13 sulfur atoms. The S content does seem to decrease slightly as the Cu content decreases, but the maximum density in population occurs near 10 Cu and 13 S atoms. The paucity of data sets (6) with detectable Se does not permit any generalization regarding the mechanism of Se substitution.

Sb, As, Bi and Te contents

Analytical data for both natural and synthetic samples support the long-held premise of complete solid-solution between the Sb and As end-members (Figs. 2a,b). The relatively even distribution of compositions indicates that the geochemical conditions necessary for the formation of all members of the solid solution are widespread. Bi-rich tetrahedrite is relatively rare, and the limited data indicate no apparent correlation of Bi with Sb or As contents in spite of the suggestion of Bohmer (1964) that Bi substitutes for Sb but not for As. The maximum Bi content found in our data base is approximately two atoms per formula unit at a Cu content of approximately 10 atoms per formula unit. The relatively few data on Te suggest a maximum of 3 to 3.5 atoms substituting on a 1-to-1 basis for Sb (Fig. 2c); this observation is consistent with Kalbskopf's (1974) findings.

Cu content

The ideal tetrahedrite and tennantite compositions are usually given as $Cu_{12}Sb_4S_{13}$ and $Cu_{12}As_4S_{13}$, respectively. However, the majority of compositions examined in this study contain 10 atoms of Cu per formula unit (Fig. 3a). A significant percentage have fewer than 10, down to a minimum of 4, but fewer than 12% contain more than 10. This is consistent with the experimental findings of Tatsuka & Morimoto (1977), who found that synthetic tetrahedrite with less than 0.5 atoms of Fe per formula unit breaks down, after annealing, to a mixture of famatinite, digenite and chalcocite. This also agrees with the generalized formula proposed by Charlat & Lévy (1974), which indicates that Cu beyond 10 atoms per formula unit substitutes for the two Fe or Zn atoms normally present.

In contrast, most synthetic compositions of tetra-

TABLE 1. PUBLISHED SOURCES OF DATA USED IN THIS PAPER, INCLUDING NUMBER OF SAMPLES AND THEIR ORIGIN (NATURAL OR SYNTHETIC)

| Reference	Analyses	Reference	Analyses
Abulgazina et al. (1975)	1 N	Luce et al. (1977)	35 S
Arana (1977)	1 N	Maske & Skinner (1971)	14 S
Araya et al. (1977)	17 N	McQueen (1984)	4 N
Atanasov (1975)	3 N	Miller & Craig (1983)	32 N
Azer Ibrahim (1958)	7 N	Morowic & Kubica (1972)	14 N
Basu et al. (1981)	5 N	Mozgova et al. (1979)	184 N
Basu et al. (1984a)	6 N	Mozgova et al. (1980)	28 N
Basu et al. (1984b)	12 N	Mposkos (1983)	1 N
Birch (1981)	1 N	Naik (1975)	4 N
Bishop et al. (1977)	1 N	Nash (1975)	8 N
Boldyreva & Borodayev (1974)	2 N	Nikitin (1929)	25 N
Brodin et al. (1979)	3 N	Nishiwaki et al. (1971)	5 N
Burkhart-Baumann (1984)	6 N	Novgorodova et al. (1978)	41 N
Čech & Hak (1979)	6 N	Oen et al. (1973)	1 N
Černý & Harris (1978)	4 N	Oen & Kieft (1976)	5 N
Charlat & Lévy (1974)	161 N	Pattrick (1978)	16 N
Chen & Petruk (1980)	14 N	Pattrick (1984)	21 N
Chen et al. (1980)	4 N	Pattrick & Hall (1984)	25 S
Cortelezzi & Baran (1973)	1 N	Petruk et al. (1971)	9 N
Cox (1977)	9 N	Raabe & Sack (1984)	25 N
Czamanske & Hall (1975)	1 N	Ransome (1909)	1 N
Doelter (1926)	138 N	Riley (1974)	24 N
Dunin-Barkovskiy et al. (1970)	3 N	Sandecki & Amcoff (1981)	21 N
Eidsmo et al. (1984)	73 N	Shimada & Hirowatari (1972)	14 N
Godovnikov & Il'yasheva (1973)	88 N	Shimazaki (1974)	12 N
Hak & Tupper (1979)	12 N	Springer (1969)	29 N
Hall (1972)	10 S	Stanley & Ixer (1982)	4 N
Hall & Czamanske (1972)	3 N	Sugaki et al. (1975)	38 S
Hintze (1904)	26 N	Sugaki et al. (1984)	3 N
Hwang & Meyer (1982)	8 N	Tatsuka & Morimoto (1973)	16 S
Imai & Lee (1980)	10 N	Tatsuka & Morimoto (1977)	15 S
Indolev et al. (1971)	9 N	Thorpe et al. (1976)	2 N
Ixer & Stanley (1980)	6 N	Thum (1982)	8 N
Ixer & Stanley (1983)	27 N	Timofeyevskiy (1967)	7 N
Jasinski (1983)	2 N	Tsepin et al. (1977)	3 N
Johan & Kvacek (1971)	1 N	Tsepin et al. (1979)	2 N
Johnson (1982)	137 S	Vasil'yev & Lavrent'yev (1973)	2 N
Karup-Møller (1974)	6 N	Vaughan & Ixer (1980)	1 N
Kovalenker et al. (1981)	2 N	Wu & Petersen (1977)	7 N
Kvaček (1977)	1 N	Yui (1971)	11 N
Kvaček et al. (1975)	2 N	Yushkin (1978)	3 N
Lind & Makovicky (1982)	5 S	Zakrzewski & Nugteren (1984)	14 N
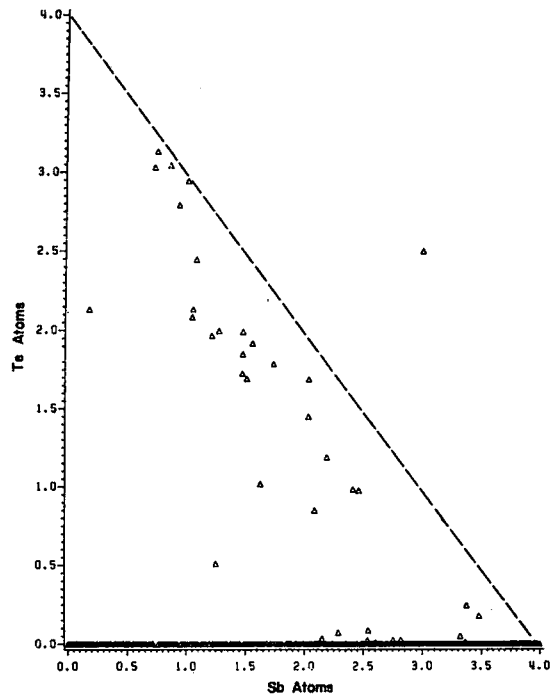
FIG. 2c. Number of Te atoms *versus* number of Sb atoms for samples of natural tetrahedrite. Dashed line is as in Figure 2a.
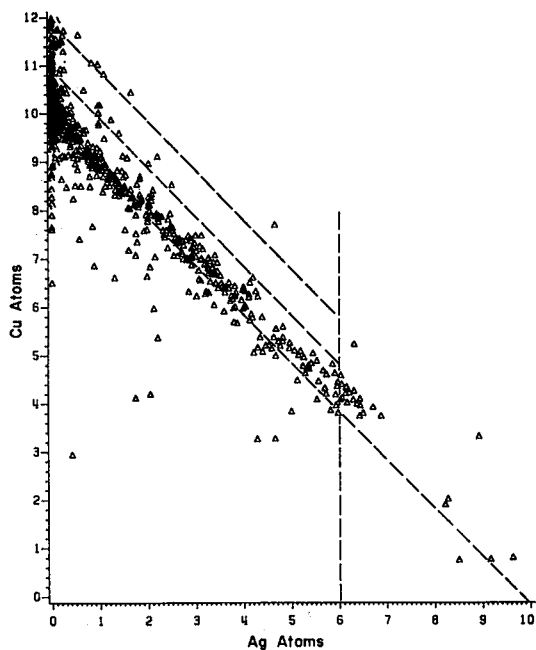
FIG. 3a. Number of Cu atoms *versus* number of Ag atoms for samples of natural tetrahedrite. Uppermost dashed line is for six Cu atoms in $M1$ site, middle line is for five Cu atoms in $M1$ site, and lowermost line is for four Cu atoms in $M1$ site.
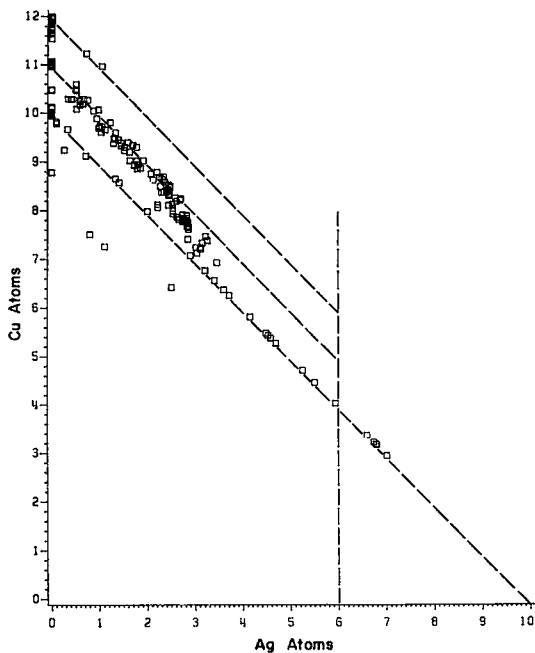

FIG. 3b. Number of Cu atoms *versus* number of Ag atoms for samples of synthetic tetrahedrite. Dashed lines are as in Figure 3a.

hedrite fall into three groups with 4, 5 or 6 Cu atoms per $M1$ site (Fig. 3b), corresponding to a total Cu content of 10, 11 or 12 atoms. This results from the many syntheses of tetrahedrite compositions in the range of 10 to 12 atoms per formula unit. In contrast, tetrahedrite with as few as three total Cu atoms was synthesized by Pattrick & Hall (1983).

Ag content

The work of Wuensch (1964), which showed that there are six three-co-ordinated sites in the structure, and that of Kalbskopf (1972), suggest a maximum of six Ag atoms per formula unit. Charlat & Lévy (1974), however, proposed a maximum of 10 Ag atoms per formula unit. The data gathered in this study (Fig. 4a) indicate that although there are rare compositions that approach 10 atoms, the vast majority indeed have fewer than six Ag atoms.

Several authors (Charlat & Lévy 1974, Wu & Petersen 1977, Miller & Craig 1983) have noted that there is a distinct correlation between the Sb and Ag contents. Figure 4a, a plot of As *versus* Ag contents, shows that, in fact, Ag and As have little tolerance for each other in the tetrahedrite structure; the presence of only one atom of As decreases (neglecting scatter) the maximum number of Ag atoms contained from six to one.

In a study of Ag-rich tetrahedrite from the Mt. Isa deposit, Riley (1974) noted that the cell expands with increasing Ag content, up to a maximum of four Ag atoms per formula unit; samples with progressively higher Ag contents show a decreasing length of the cell edge. Figure 4b shows that this is a general trend for all Ag-bearing tetrahedrite, but this decrease contrasts with the relatively linear cell-dimension variations resulting from other compositional substitutions.

The plot of the unit-cell dimension of compositions of synthetic tetrahedrite (Fig. 4c) is basically linear up to seven atoms of Ag, and does not display the break at four Ag atoms nor the subsequent decrease from four to six atoms that samples of natural tetrahedrite show.

Fe, Zn, Hg, Cd and Mn contents

Figures 5a, 5b and 5c are plots of Fe, Zn and Hg concentration as a function of Sb. The only apparent relationship is that of higher Hg content with higher Sb content, which may be an artifact of the limited number of data on Hg-tetrahedrite. There does appear to be a fairly well-defined limit of two atoms per formula unit for each element. This is consistent with the limits proposed by Charlat & Lévy (1974). The Cd data that do exist are insufficient to make the same observation definitive, but those data that are available, and the chemical similarity of Cd
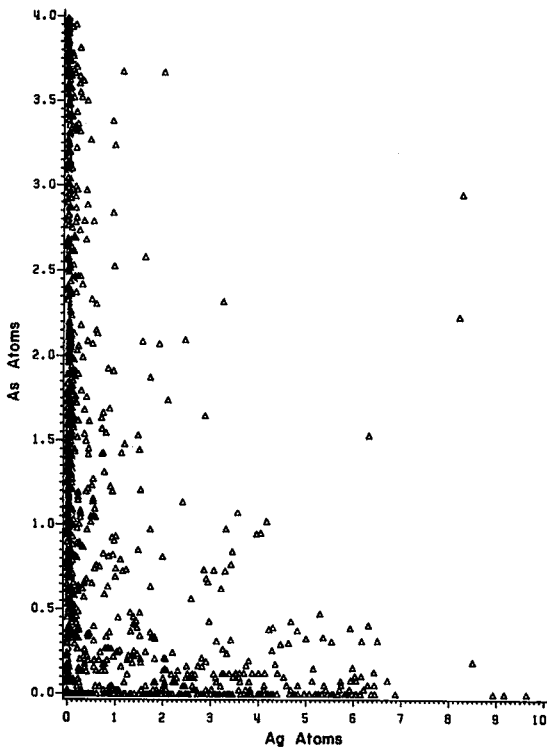
FIG. 4a. Number of As atoms *versus* number of Ag atoms for samples of natural tetrahedrite.
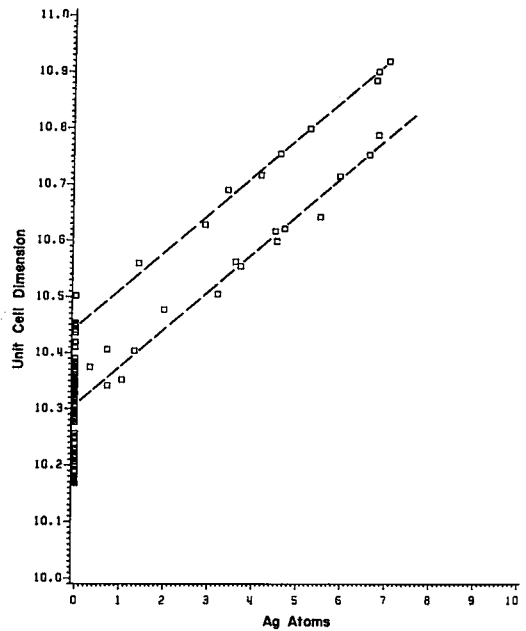

FIG. 4c. Plot of cell dimension (in Å) *versus* number of Ag atoms for synthetic tetrahedrite; the lower line is for Fe- and Zn-bearing tetrahedrite, the upper line is for Cd-bearing tetrahedrite.
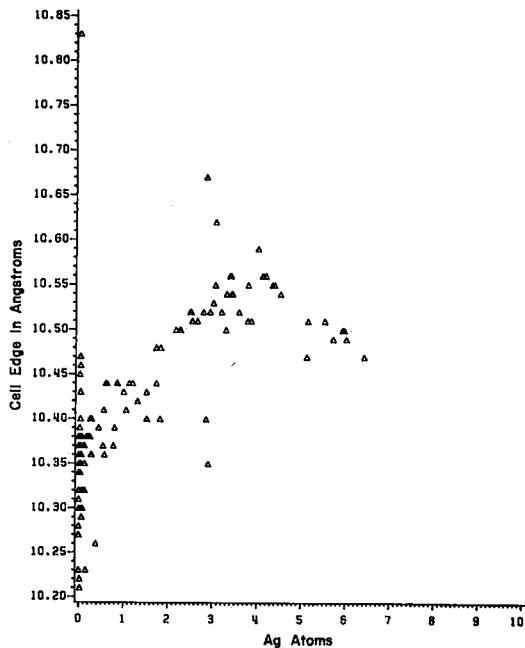

FIG. 4b. Plot of cell dimension (in Å) *versus* number of Ag atoms for samples of natural tetrahedrite.

to Zn and Hg, suggest an analogous situation. As shown in Figure 5d, Hg content is greatest when the Cu content is 10 atoms, and decreases sharply if Cu is higher or lower. The decrease on the low-Cu side appears to indicate an antipathetic relation between Hg and Ag.

Figures 5e and 5f display relationships between Fe and Ag, and between Zn and Ag, respectively. Both Fe and Zn display complete (up to two atoms) substitution where there are fewer than two atoms of Ag; if Ag increases beyond this value (to a maximum of six), Zn decreases, whereas Fe remains between one and one-half and two atoms. This effect has been noted by Pattrick & Hall (1983) for selected natural samples. This positive correlation of Fe with Ag may lead to a secondary positive correlation of Fe with Sb, consistent with that found by Raabe & Sack (1984) for natural samples.

Reports of Mn-rich tetrahedrite have recently been published (Basu *et al.* 1984a, Burkhart-Baumann 1984), but the available data are too meager to do more than suggest that Mn substitution is analogous to that of Fe, Zn, Hg and Cd. Experimental data on Fe, Zn, Hg, Cd and Mn content are scarce and appear consistent with the data on natural material.
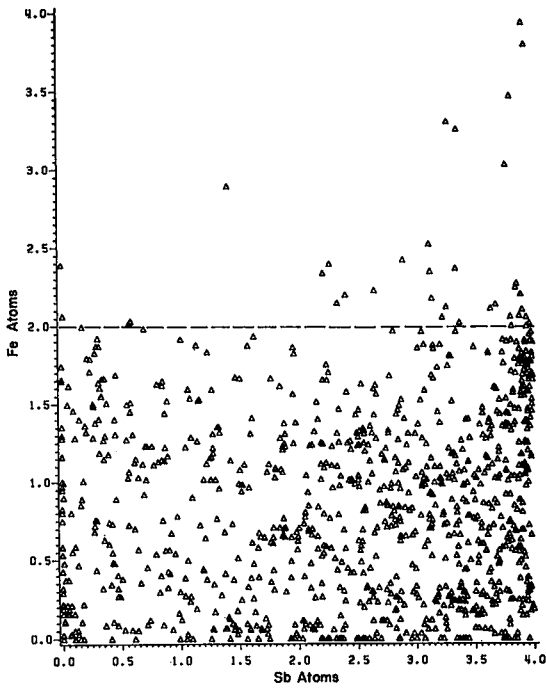
FIG. 5a. Number of Fe atoms *versus* number of Sb atoms for samples of natural tetrahedrite.
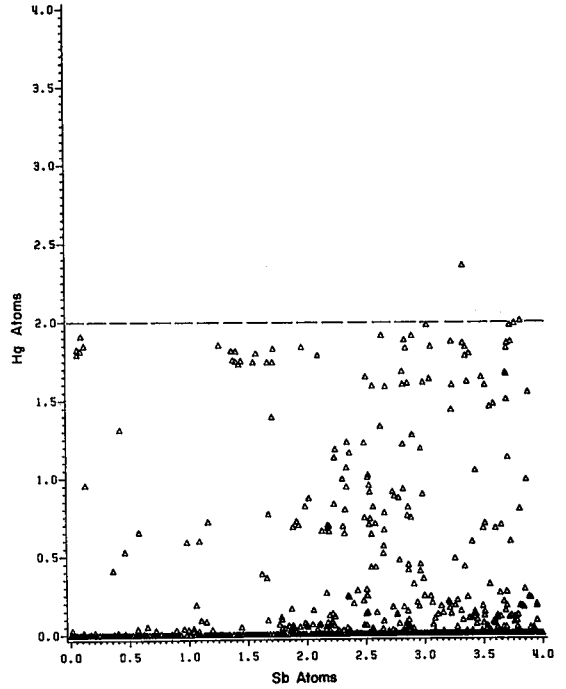
FIG. 5c. Number of Hg atoms *versus* number of Sb atoms for samples of natural tetrahedrite.
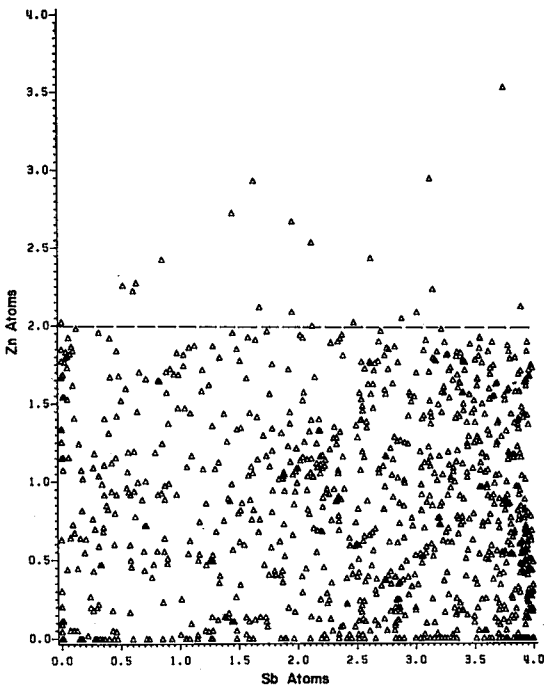
FIG. 5b. Number of Zn atoms *versus* number of Sb atoms for samples of natural tetrahedrite.
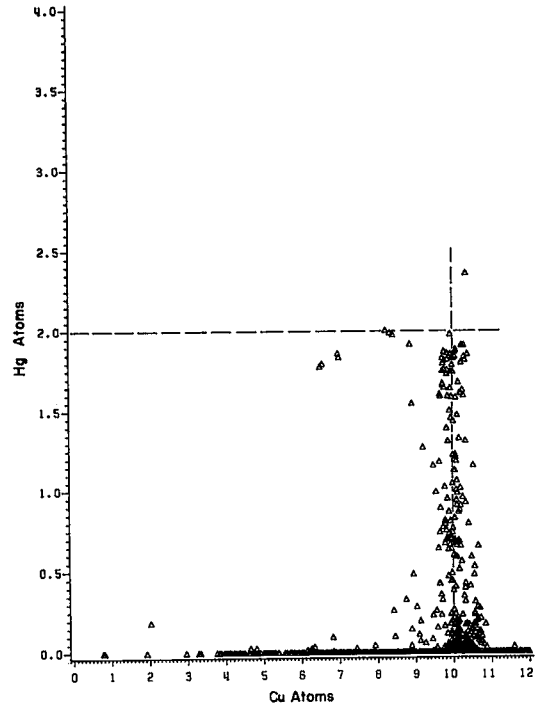
FIG. 5d. Number of Hg atoms *versus* number of Cu atoms for samples of natural tetrahedrite.

Pb content

Reports of Pb in tetrahedrite are exceedingly rare, a somewhat surprising fact, given the common occurrence of tetrahedrite with and within galena, and the apparent solid-solution between the two minerals, as evidenced by the submicroscopic exsolution-related inclusions of tetrahedrite in galena (Gasparrini & Lowell 1983, 1985). The only discernible trend in the Pb-bearing compositions reported is a slight tendency for them to be associated with Sb-rich compositions.

Brillouin zone (BZ) and ionic-charge (CHG) models

Johnson & Jeanloz (1983) proposed the use of a simple Brillouin-zone (BZ) model to account for the compositional variations in tetrahedrite. In this model, each atom contributes one or more valence electrons to a conduction band, and these electrons are summed over a unit cell. That paper, and a subsequent one (Jeanloz & Johnson 1984), use this model to account for several observations: 1) Compositional variations correspond to a range of between 204 and 208 valence electrons per unit cell.

2) The largest proportion of compositions is found at the upper limit of 208 valence electrons per unit cell. 3) The electrical resistivity increases as compositions approach the upper limit of 208 electrons per unit cell. 4) The optical absorption decreases as compositions approach the upper limit of 208 electrons per unit cell.

The data base collected here is ideal for testing the first two premises; hence, the quantities BZ, the number of valence electrons per unit cell, and CHR, the net ionic charge per formula unit, were calculated for each composition. The number of electrons and the formal charges used for each atom were taken directly from Johnson & Jeanloz (1983). Figure 6a shows that the largest number of natural compositions do in fact occur at 208 valence electrons per unit cell, and 72% of all the compositions fall within the limits (204–208 valence electrons) predicted. The analogous calculations of net ionic charge (Fig. 6b) have the largest number of compositions (35%) at 0, which represents a balance of charge, but the remainder of the compositions have a net electric charge, which violates the premises of a purely ionic model. The calculations for compositions of synthetic tetrahedrite show the same tendencies (Figs.
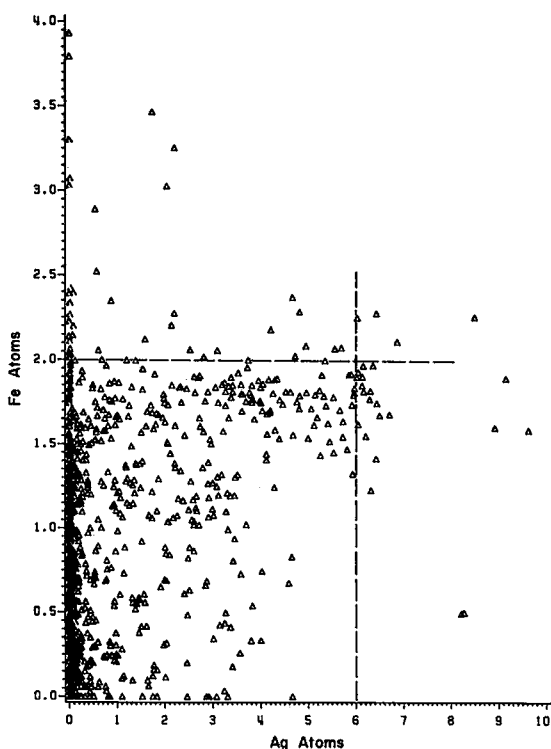

FIG. 5e. Number of Fe atoms *versus* number of Ag atoms for samples of natural tetrahedrite.
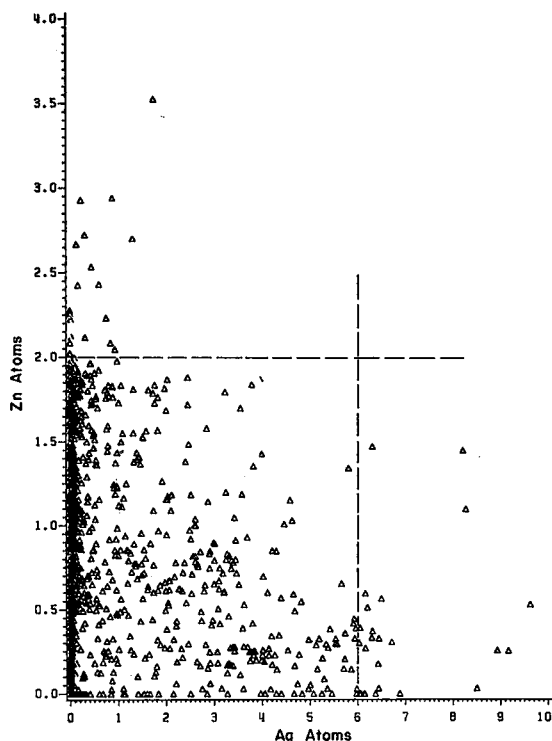
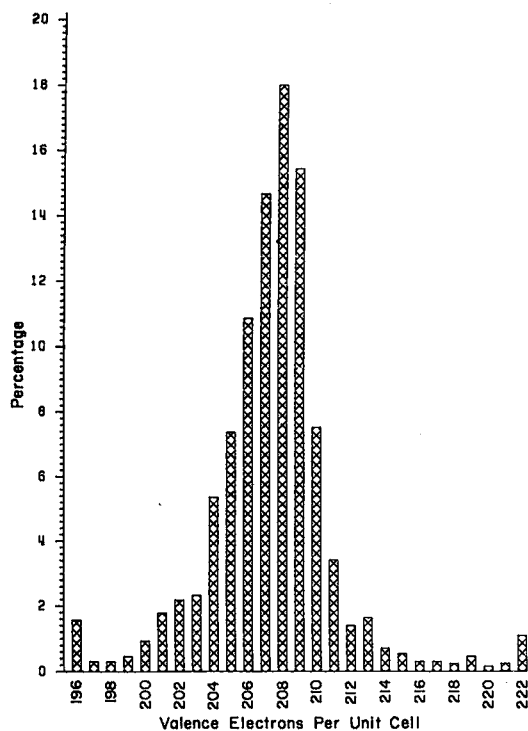FIG. 5f. Number of Zn atoms *versus* number of Ag atoms for samples of natural tetrahedrite.

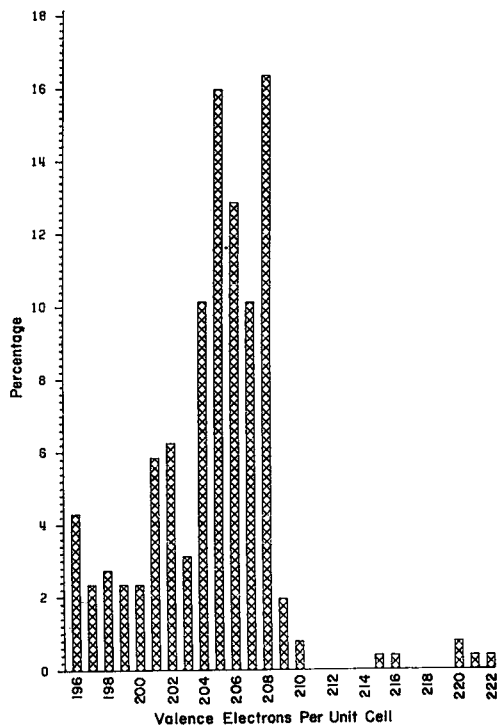FIG. 6a. Number of valence electrons per formula unit for samples of natural tetrahedrite.

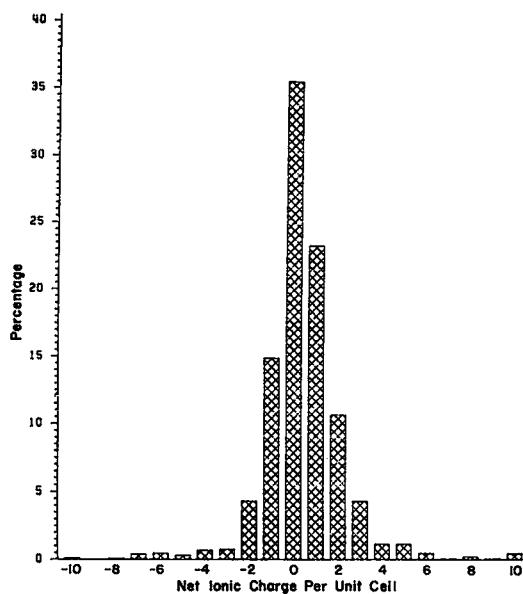FIG. 6c. Number of valence electrons per formula unit for samples of synthetic tetrahedrite.

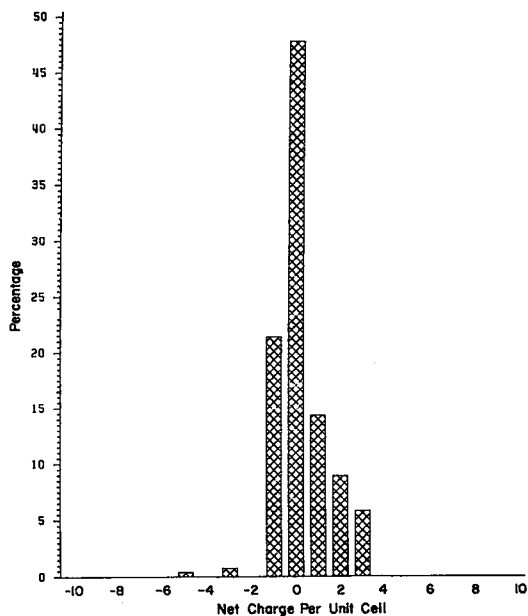FIG. 6b. Net ionic charge per formula unit for samples of natural tetrahedrite.

FIG. 6d. Net ionic charge per formula unit for samples of synthetic tetrahedrite.

6c, 6d). It is clear that these data substantiate the premise that the concept of a Brillouin zone is considerably more effective than a simple ionic model in explaining the nature of tetrahedrite.

Regression analysis of cell dimensions

Charlat & Lévy (1975) gathered cell-parameter data to complement the compositional data from their previous work (Charlat & Lévy 1974) and fit a linear equation to the results. Their equation relates the changes that Ag, Hg, Cu^{2+} and As contribute to a "standard" tetrahedrite of composition $Cu_{10}(Fe,Zn)_2Sb_4S_{13}$ and cell dimension of 10.386 Å. Their result is useful under their stated constraint of less than 20 weight % Ag and only for those substitutions available to them for examination. The much larger data-base in this study allows us to further generalize their results and to provide quantitative statistical information concerning the fit of the model to the data.

Techniques of multiple linear and nonlinear regression were used to analyze the relationship between cell dimensions and composition for this data set. Preliminary results for natural tetrahedrite indicate that an equation of the form:

$$a = \beta_0 + \beta_1 Ag + \beta_2 Fe + \beta_3 Zn + \beta_4 Hg + \beta_5 Sb + \beta_6 Ag^2$$

provides the best fit. The regressor variables are atoms/formula unit divided by the number of sites available (six for Ag, two for Fe, Zn and Hg, four for Sb), β_0 is the intercept, and β_{1-6} are the weights for the regressors. The resultant overall R^2 is 0.961833; the values for β_{0-6} and their associated partial F-tests are listed in Table 2. Predicted values of a have been found to be within 0.08 Å of their actual values. Further research on refining these relationships is underway and will be reported at a later date.

CONCLUSIONS

The body of tetrahedrite data indicates that there are a great many interrelated effects on tetrahedrite compositions, some of which are easily explained, whereas others are not yet understood. A generalized compositional formula of the form: $(Cu,Ag)_6$ $Cu_4(Fe,Zn,Cu,Hg,Cd)_2(Sb,As,Bi,Te)_4(S,Se)_{13}$ seems to best account for the range of composition of naturally occurring tetrahedrite. This suggests that there are three distinct metal sites in the structure, instead of the previously determined two. The data on synthetic tetrahedrite agree in general with those for natural tetrahedrite, but there are some marked discrepancies, especially concerning Ag-bearing tetrahedrite. More research is needed using the approach

TABLE 2. VALUES FOR REGRESSOR WEIGHTS, β_{0-6}, AND THEIR CORRESPONDING F_{obs} TESTS

Parameter	Estimate	F_{obs}
β_0 (intercept)	10.211	-
β_1 (Ag)	0.459	577.29
β_2 (Fe)	0.021	3.10
β_3 (Zn)	0.017	2.76
β_4 (Hg)	0.142	160.81
β_5 (Sb)	0.147	680.09
β_6 (Ag^2)	-0.346	276.09

of Tatsuka & Morimoto (1977), who studied the stability of synthetic tetrahedrite, particularly if we are to understand the graphic intergrowths of tetrahedrite, arsenopyrite and gudmundite that apparently result from tetrahedrite breakdown, as reported by Juve (1974), Sandecki & Amcoff (1981), Shadlun (1982), Miller & Craig (1983) and Basu et al. (1984b). Further research on less common and coupled schemes of substitution is also desirable.

ACKNOWLEDGEMENTS

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