

## A Brillouin-zone model for compositional variation in tetrahedrite

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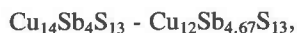
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### Abstract

A Brillouin-zone analysis based on a nearly-free electron model for tetrahedrite, an important copper antimony sulfide, successfully explains the observed compositional limits for synthetic and natural tetrahedrites. Tetrahedrite should occur with greater than 204 and up to 208 valence electrons per unit cell (filling the 52nd Brillouin zone); it should be most stable with 208 valence electrons. The classical formula  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  is not expected to occur. This model predicts that filling a zone (*e.g.*, by substituting Fe or Zn for Cu) should cause electrical resistivity to increase. This is confirmed by experimental results which show that a tetrahedrite with about 208 valence electrons per unit cell (approximate composition  $\text{Cu}_{10}(\text{Fe},\text{Zn})_2(\text{Sb},\text{As})_4\text{S}_{13}$ ) has a resistivity  $10^7$  times higher than that of a tetrahedrite with approximately 205 valence electrons (composition  $\text{Cu}_{12.12}\text{Sb}_{4.09}\text{S}_{13}$ ). The Brillouin-zone model also agrees with observed limits to tetrahedrite composition: natural tetrahedrite samples are stoichiometric with compositions restricted to two divalent cations per formula unit, while synthetic samples, which are not stoichiometric, have compositions bounded by the line



as expected.

### Introduction

Tetrahedrite is one of a family of common sulfosalt minerals, containing Cu, Sb, S, and sometimes As, Ag, Fe, Zn, Hg, Bi, Te, Cd, Pb, and Se. Its mineralogical significance derives, in part, from the fact that it is one of the silver-ore phases of greatest economic importance. Natural tetrahedrites are described approximately by the chemical formula  $\text{A}_{10}\text{B}_2\text{C}_4\text{D}_{13}$ , where A = Cu, Ag; B = Cu, Fe, Zn, Hg, Cd, Pb; C = Sb, As, Bi, Te; D = S, Se (Springer, 1969; Charlat and Levy, 1974; Cech and Hak, 1979; Patrick, 1978; Johan and Kvacek, 1971; Sandeck and Amcoff, 1981; Basu *et al.*, 1981). This formula, while complicated, is stoichiometric. By contrast, synthetic tetrahedrites in the Cu–Sb–S system show considerable variation in the number of atoms per formula unit (*i.e.*, the number of atoms per 13 sulfurs). All of the room temperature compo-

sitional data fit within the range  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ – $\text{Cu}_{14}\text{Sb}_4\text{S}_{13}$ – $\text{Cu}_{12}\text{Sb}_{4.67}\text{S}_{13}$ ; none of these endpoints is reached (Tatsuka and Morimoto, 1977; Mako-vicky and Skinner, 1978; see Fig. 1).

These variations can be accounted for by a simple, ionic (integer charge per atom) model, and such a model leads one to predict correctly some of the apparent limits on the compositional variation of natural and synthetic tetrahedrites. The fact that sulfides and sulfosalts are not ionic in character is well established, however. We are therefore motivated to consider an alternative, and physically more plausible approach, such as that of the Brillouin-zone model discussed by H. Jones (1975). Not only is this model, as applied in the present study, as easily used as the ionic model, but more significantly, the Brillouin-zone model is of substantially greater predictive value: (1) It successfully predicts

Table 1. Ionic charge and number of valence electrons per atom

Element	Ionic Charge per Atom	Number of Valence Electrons per Atom
Cu	+1, +2	1
Ag	+1	1
Fe	+2	2
Zn	+2	2
Hg	+2	2
Cd	+2	2
Pb	+2	2
Sb	+3	3
As	+3	3
Bi	+3	3
Te	+4	4
S	-2	6
Se	-2	6

the observed compositional limits which are in accord with the ionic model; (2) It gives additional compositional limits not predicted by the ionic model, including an accounting for the inaccessibility of the "classical" (Pauling and Neuman, 1934) tetrahedrite formula  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  ( $\text{A}_{10}\text{B}_2\text{C}_4\text{D}_{13}$ ,  $\text{A} = \text{B} = \text{Cu}$ ,  $\text{C} = \text{Sb}$ ,  $\text{D} = \text{S}$ ) in the pure Cu-Sb-S system; and (3) It predicts variations of physical properties, such as relative resistivities, for some tetrahedrites, which cannot be determined from the ionic model.

### Ionic model

Balancing charges is easily performed for natural and synthetic tetrahedrite formulae. In particular, a formal charge is assigned to every element, as shown in Table 1, except that Cu may be either +1 or +2. The two choices for the charge on copper give one degree of freedom (or ambiguity) for this model, and lead to the compositional limits discussed below.

#### *Natural tetrahedrites: two divalent cations per formula unit*

In the tetrahedrite structure ( $\bar{I}43m$ ,  $Z = 2$ ), there are two metal equipoints (12d and 12e, each with six-fold multiplicity per formula unit, with tetrahedral and trigonal planar coordination, respectively), one semimetal equipoint (8c, with fourfold multiplicity, with triangular pyramidal coordination), thirteen sulfur sites (equipoints 24g and 2a, with tetrahedral and octahedral coordination, respectively) (Weunsch, 1964), and twelve "mobile ion" loci (equipoint 24g, roughly three-coordinated) (Makovicky and Skinner, 1979). Nowhere is there a metal equipoint with multiplicity of two or less, and divalent cations seem to congregate in the 12d

equipoint (Makovicky and Skinner, 1979; Kalbskopf, 1971). Yet there is an apparent limit of two, not six, divalent cations per formula unit (Charlat and Levy, 1974), which satisfies the ionic formula  $\text{A}_{10}\text{B}_2^2+\text{C}_4^3+\text{D}_{13}^{2-}$ . As copper may be +1 or +2, the "classical" formula  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  ( $= \text{Cu}_{10}^+\text{Cu}_2^+\text{Sb}_4^3+\text{S}_{13}^{2-}$ ) is permitted.

#### *Synthetic Cu-Sb-S tetrahedrites*

The overstrict interpretation "two divalent cations per formula unit" is not applicable for synthetic tetrahedrites, as the occurrence of mobile ions (Makovicky and Skinner, 1979) permits the total number of atoms per formula unit (per 13 sulfurs) to be variable. There still must be 26 positive charges per formula unit. This gives an upper limit to the number of atoms in synthetic tetrahedrite along the composition line  $\text{Cu}_{14}\text{Sb}_4\text{S}_{13}$ - $\text{Cu}_{12}\text{Sb}_{4.67}\text{S}_{13}$ , which is confirmed by experimental observations (Fig. 1).

#### *Compositional lower limits on numbers of atoms*

There is nothing in the ionic model which restricts the number of (nonsemimetal) cations to 12 or more per formula unit. Kalbskopf (1974) has reported copper vacancies in synthetic tellurium end-member tetrahedrite,  $\text{Cu}_{10}\text{Te}_4\text{S}_{13}$ , and Makovicky and Skinner (1979) report partial vacancy of the 12d equipoint in a synthetic tetrahedrite with composition near  $\text{Cu}_{12.3}\text{Sb}_4\text{S}_{13}$ . One might therefore expect a hypothetical  $\text{Cu}^{2+}$  end-member tetrahedrite,  $\text{Cu}_7^+\text{Sb}_4\text{S}_{13}$ , which has not been seen; in fact, even the "classical" tetrahedrite composition  $\text{Cu}_{10}^+\text{Cu}_2^+\text{Sb}_4\text{S}_{13}$  is not found in synthesis experiments (Fig. 1). The simple ionic model offers no insight here.

### Zone model

#### *History*

The Brillouin zone concept was developed by H. Jones from the discovery by Hume-Rothery (1948) that the ratio of valence electrons to atoms was constant for many alloy phases with the same structures (see review of Jones, 1975). However, Hume-Rothery has pointed out that "the number of (valence) electrons per unit cell is more fundamental than the number per atom" (Hume-Rothery, 1963, p. 330), because it is the properties of the fundamental repeat unit of the crystal (the Brillouin zone in reciprocal space) that determines the bonding states. Furthermore, as the number of atoms per

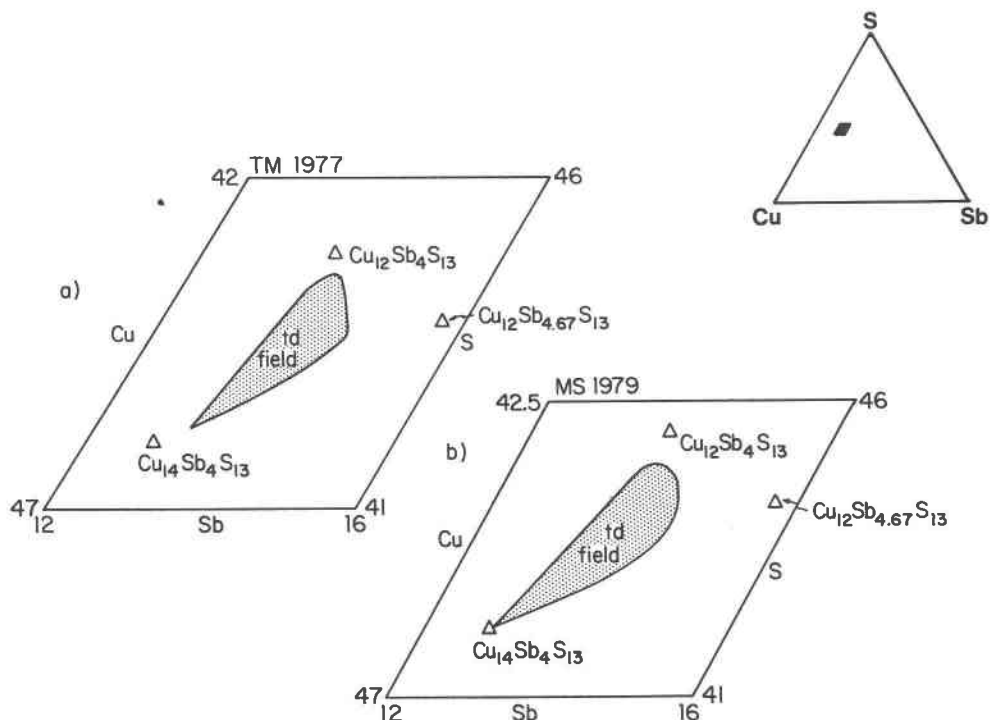


Fig. 1. Tetrahedrite stability field at room temperature, data from synthesis experiments. Portion of the Cu-Sb-S triangle (see insert): Cu at lower left, Sb at lower right, S at top. Tie lines to other phases not shown. (a) Data of Tatsuka and Morimoto (1977); (b) Data of Makovicky and Skinner (1978).

formula unit is variable for tetrahedrite, we shall follow his suggestion here.

Subsequently, A. J. Frueh reported Brillouin-zone calculations for chalcopyrite, bornite, digenite, chalcocite, covellite (1954), stromeyerite (1955), and argentite (1961). Also, Hall (1972) contended that a zone model could explain the limits of iron and zinc substitution into tetrahedrite, but provided no details.

#### Calculation for tetrahedrite

The first Brillouin zone for a compound consists of the volume closer to the origin than to any other point of the compound's reciprocal lattice. Since tetrahedrite has space group  $I43m$ , its lattice is body-centered, and the (non-primitive) first Brillouin zone is bounded by the dodecahedron  $\langle 110 \rangle$  (see Jones, 1975, p. 55-59). This volume is filled by 4 electrons, counting spin multiplicity.

The numbers of valence electrons per atom for the elements in tetrahedrite corresponds in most cases to the formal charges of the ionic model (see Table 1); the differences are that sulfur, with a charge of  $-2$ , has 6 valence electrons, and that

there is only one value for the number of valence electrons for copper, as we assume that the filled copper 3d shell contributes no electrons. (We have thus stripped away the single degree of freedom that the ionic model contained; we will replace it with a more restricted variation, that of the total number of valence electrons per unit cell.) The number of valence electrons per unit cell for some synthetic and hypothetical tetrahedrite formulae are shown in Table 2, with the number of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  atoms per formula unit for the ionic model listed for comparison. All of these formulae are allowed by the ionic model.

On inspection, it is evident that formulae for which tetrahedrites are found correspond to over 204 and up to 208 valence electrons per unit cell. 204 valence electrons completely fill the 51st Brillouin zone (51 times the volume of the first Brillouin zone), and 208 valence electrons completely fill the 52nd Brillouin zone.

We recall that in order for a substance to be an insulator or semiconductor, its number of electrons per unit cell must completely fill an integral number of multiples of the first Brillouin zone. Otherwise,

Table 2. Composition and existence of synthetic tetrahedrites

Composition	Zone Model: Valence Electrons per Unit Cell	Ionic Model: Atoms per Formula Unit (Cu,Ag) <sup>+1</sup> Cu <sup>+2</sup>	Found?	Notes
A <sub>10</sub> <sup>+1</sup> B <sub>2</sub> <sup>+2</sup> C <sub>4</sub> <sup>+3</sup> D <sub>13</sub> <sup>-2</sup>	204-208	10	0-2	a
Cu <sub>10</sub> Fe <sub>2</sub> Sb <sub>4</sub> S <sub>13</sub>	208	10	0	yes b
Cu <sub>12.23</sub> Sb <sub>4.08</sub> S <sub>13</sub>	204.9	10.70	1.53	yes c
Cu <sub>12.43</sub> Sb <sub>4.34</sub> S <sub>13</sub>	206.9	11.88	0.55	yes d
Cu <sub>13.77</sub> Sb <sub>4.08</sub> S <sub>13</sub>	208.0	13.77	0.0	yes e
Cu <sub>12</sub> Sb <sub>4</sub> S <sub>13</sub>	204	10	2	no f
Cu <sub>7</sub> Sb <sub>4</sub> S <sub>13</sub>	194	0	7	no g
Cu <sub>10</sub> Te <sub>4</sub> S <sub>13</sub>	208	10	0	yes h

Notes to Table 2:

- a General "ionic" formula for natural tetrahedrites  
 b Hypothetical endmember, Pauling and Neuman (1934)  
 c Cu-poor tetrahedrite, Tatsuka and Morimoto (1977)  
 d Sb-rich tetrahedrite, *ibid.*  
 e Cu-rich tetrahedrite, *ibid.*  
 f Suggested tetrahedrite formula, Pauling and Neuman (1934)  
 g Hypothetical Cu<sup>+2</sup> tetrahedrite, this paper  
 h Synthetic tellurian tetrahedrite, Kalbskopf (1974)

there are accessible (conduction) states into which electrons may be excited by the addition of small increments of energy, and the compound is metallic.

### Large zone polyhedron

While it has been common practice to determine the shape of the polyhedron in reciprocal space filled by the valence electrons of a compound (*e.g.*, Frueh, 1954, 1955, 1961; Jones, 1975), such a determination is based on the assumption that electrons and X-rays are Bragg-scattered equivalently. This assumption has been shown to be incorrect for diamond structure compounds, for which more exact calculations have been carried out (see Harrison, 1979, p. 446-447). Hence the determination of a polyhedron is no longer widely employed (*e.g.*, gamma brass structure, Pearson *et al.*, 1976) and will not be described here.

### Discussion: predictions and comparisons

#### Comparison with the ionic model

The ionic model predicts a two-divalent-cation-per-formula-unit limit for the compositions of natural tetrahedrites; this limit corresponds to 208 va-

lence electrons per unit cell (see Table 2), and is thus a compositional limit for the Brillouin-zone model as well. (In a semiconductor, electron states are roughly continuous in energy up to the band gap, where there is a Brillouin-zone boundary. We assume a nearly-free electron model, which is to say that a zone fills completely until its boundary is reached, and there is an energy barrier for tetrahedrite at the 52nd Brillouin zone boundary—208 valence electrons per unit cell.) Similarly, the line Cu<sub>14</sub>Sb<sub>4</sub>S<sub>13</sub>—Cu<sub>12</sub>Sb<sub>4.67</sub>S<sub>13</sub> limiting the composition of synthetic tetrahedrites is the 208 valence electron contour (Fig. 2); so that both models agree on this (observed) limit as well.

As another example, synthetic tellurium end-member tetrahedrite Cu<sub>10</sub>Te<sub>4</sub>S<sub>13</sub> may be explained as Cu<sub>10</sub>Te<sub>4</sub><sup>4+</sup>S<sub>13</sub><sup>2-</sup>, or again as having 208 valence electrons per unit cell (Te contributes 4 valence electrons due to the stabilization of the 5s shell, analogous to Sb).

#### Resistivity measurements

While resistivity measurements are not directly convertible to band gap values, it is possible to predict relative resistivities of samples for which the 52nd Brillouin zone is unfilled (metallic behavior) and filled (semiconductor behavior). Samples with less than 208 valence electrons should have lower electrical resistivities than samples in which the zone is filled, since electrons must cross the band-gap energy barrier (a statistically unlikely event at room temperature) in order to contribute to conduction in the latter solid. The electrical resistivities of a synthetic tetrahedrite (grown according to Tatsuka and Morimoto, 1973) with composition Cu<sub>12.12</sub>Sb<sub>4.09</sub>S<sub>13</sub>, and a natural tetrahedrite from Horhausen, Germany (Harvard specimen #82561, microprobe composition Cu<sub>9.94</sub>Ag<sub>0.01</sub>Fe<sub>0.18</sub>Zn<sub>1.77</sub>Sb<sub>3.97</sub>As<sub>0.11</sub>S<sub>13.0</sub>), were measured by using a two-point probe. For both samples, resistance was measured with a laboratory-built Cross-Correlator (described Stratton *et al.*, 1981), employing platinum-grid contacts attached with silver-epoxy paint to freshly scraped surfaces on the sample. Sample surface areas and lengths were measured visually at 70× using a binocular microscope with a calibrated eyepiece. The first sample, with 204.8±0.1 valence electrons per unit cell, has a resistivity less than 3 × 10<sup>-5</sup> ohm-meters (indistinguishable from a short circuit on the Cross-Correlator) compared with a resistivity of 375 ohm-meters (*i.e.*, at least 10<sup>7</sup> higher) for the second sample, which has 207.8±0.3

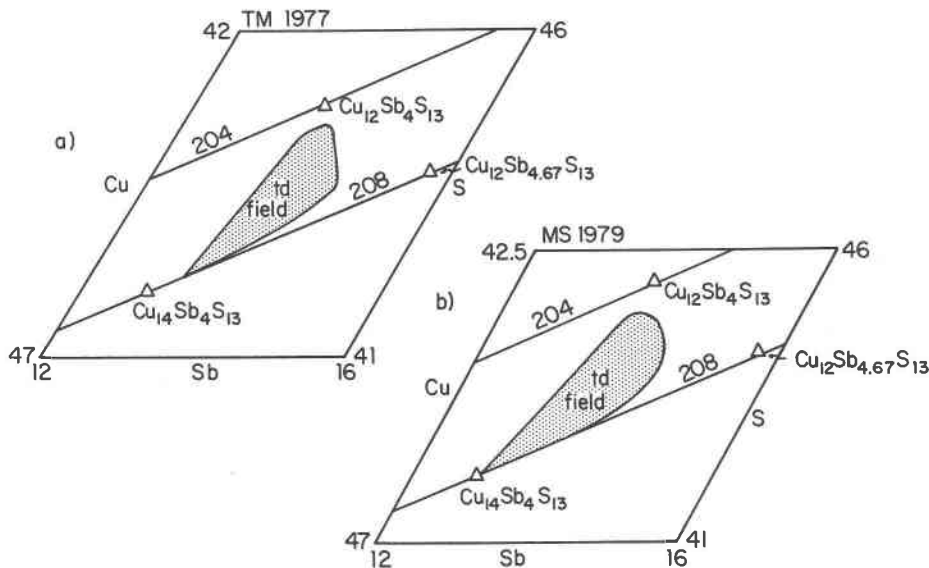


Fig. 2. Figure 1 contoured for number of valence electrons per unit cell, tetrahedrite structure. The number of electrons increases toward the lower right corner. (a) and (b) as in Figure 1.

valence electrons per unit cell. This result confirms the behavior predicted by the zone model.

### Stability

It takes little energy to add electrons to tetrahedrite up to the 208 valence electron limit, where there should be the greatest number of states per unit energy (see Mott and Jones, 1958, p. 171). The effect of this increase in the number of states as the band edge is approached is to minimize the average energy increment per valence electron added. This is seen in Figure 3, where the average energy it takes to add an electron to the 52nd Brillouin zone of tetrahedrite is plotted as a function of the total number of electrons. Since it takes less energy to add an electron close to the band edge, it becomes energetically favorable for synthetic tetrahedrites to exsolve into high-electron (208 valence electrons) and residual (nearly 204 valence electrons) tetrahedrite phases, consistent with the results of Tatsuka and Morimoto (1977) and Makovicky and Skinner (1978).

Similarly, we would expect natural tetrahedrite compositions to cluster around the 208 valence electron value. This appears to be the case. For Table 3, we have calculated the number of valence electrons per unit cell from 121 microprobe analyses of natural tetrahedrites reported in the literature (Springer, 1969; Charlat and Levy, 1974; Cech and Hak, 1979, Patrick, 1978), normalized to 4 semi-

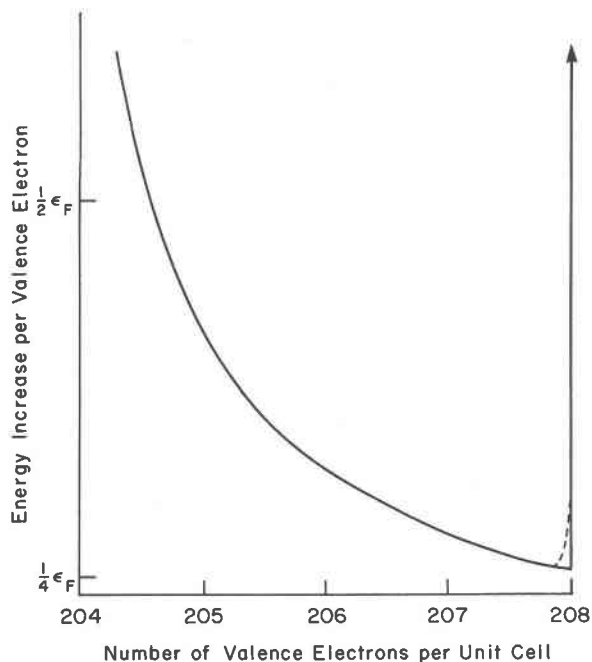


Fig. 3. Increase in the electronic contribution to the total energy per valence electron (in units of the Fermi Energy,  $E_F$ ) plotted against the number of valence electrons per unit cell for the 52nd Brillouin zone. The solid curve is valid at 0 K (static lattice) for an idealized parabolic distribution of valence electron states as a function of energy, given a single-valued cutoff energy  $E_F$  (free-electron model). The dashed curve (where different) is calculated for  $kT = 0.1 E_F$ , or a temperature of 472°C (near the melting temperature of tetrahedrite) for a 1.0 eV band gap. The minimum energy for this curve occurs at slightly more than 207.78 valence electrons per unit cell.

Table 3. Natural tetrahedrites: number of valence electrons per unit cell

Number of Valence Electrons per Unit Cell	Number of Analyses						Total
	Springer (1969)	Charlat & Levy (1974)	Cech & Hak (1979)	Patrick (1978)	Sandecki & Amcoff (1981)	Basu et al. (1981)	
< 204.0	1	0	0	0	0	0	1
204.0-204.5	2	0	0	1	1	0	4
204.5-205.0	0	0	0	0	0	0	0
205.0-205.5	1	0	0	1	0	1	3
205.5-206.0	0	1	1	2	0	1	5
206.0-206.5	0	5	0	5	3	2	15
206.5-207.0	1	5	0	4	6	2	18
207.0-207.5	4	12	0	1	7	1	25
207.5-208.0	9	23	0	1	4	0	37
208.0-208.5*	2	6	0	0	0	0	8
> 208.5*	1	1	0	1	0	2	5
Total	21	53	1	16	21	9	121

\*These compositions also violate ionic model constraints.

metals per formula unit (13 sulfurs per formula unit assumed). Considering the variety of sources, the clustering of tetrahedrite compositions about 208 valence electrons per unit cell is quite pronounced. Again, this is in agreement with the Brillouin zone model, but is unexpected according to the ionic model.

The classical (Pauling and Neuman, 1934) tetrahedrite composition is not reached in the synthetic Cu-Sb-S system, and the simple ionic model used here fails to explain this. In the Brillouin zone model, the energy increment per valence electron increases as we decrease the number of valence electrons below 208 per unit cell (Fig. 3). Also, Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>, with 204 valence electrons which fill the 51st Brillouin zone, corresponds to the first discontinuity in energy per valence electron that is reached by decreasing the number of electrons. We therefore expect that any change in the relative stabilities of structures for the tetrahedrite composition is likeliest to occur at 204 valence electrons per unit cell, rather than at any marginally higher (or lower) number of valence electrons. On this basis, as multiphase assemblages are stable for tetrahedrite compositions with less than 204 valence electrons per unit cell (see Tatsuka and Morimoto, 1977, and Makovicky and Skinner, 1978), tetrahedrite with the "classical" composition should not occur, as is indeed observed.

### Conclusions

The simple Brillouin zone model presented here leads to the same compositional limits for tetrahedrite as the ionic model, and further predicts the avoidance of the composition Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>, which

has been noted (Makovicky and Skinner, 1978), but not explained previously. In addition, the Brillouin-zone model explains the clustering of natural tetrahedrite compositions at the limiting value of 208 valence electrons per unit cell, which is also seen. However, the model's most obvious success lies in the prediction of the relative resistivities of 52nd-Brillouin-zone-filled and -unfilled tetrahedrites: a prediction subsequently confirmed, and completely foreign to ionic models. Because the bonding in sulfides and sulfosalts is far from being ionic, any model invoking a balancing of formal ionic charges is physically suspect. We demonstrate that an alternative model which may be more realistic for such minerals, that based on the number of valence states in the Brillouin zone, is indeed considerably more successful in predicting the chemical and physical properties of the tetrahedrite group of minerals.

### Acknowledgments

The authors would like to thank the following individuals for their advice and help: Prof. H. Tuller, Dr. A. McHale, H. Fujimoto (Department of Materials Science, M.I.T.); Prof. D. Turnbull, and Dr. C. Lobb (Division of Applied Sciences, Harvard); M. Parisi (Intermetrics, Inc.); Prof. G. R. Rossman and A. Hoffmeister (Department of Geological and Planetary Sciences, C.I.T.); Prof. B. J. Wuensch (Department of Materials Science, M.I.T.); and Prof. C. W. Burnham (Department of Geological Sciences, Harvard). Helpful comments were provided by M. S. T. Bukowinski, T. J. Shankland, and the reviewers. This work was supported by NSF grant EAR 81-08592, the Harvard Materials Research Laboratory, and the A.P. Sloan Foundation. M.L.J. was also supported on NSF grant EAR 79-20095.

### References

- Basu, K., Bortnykov, N., Mookherjee, A., Mozgova, N., and Tsepin, A. I. (1981) Rare minerals from Rajpura-Dariba, Rajasthan, India III: Plumbian tetrahedrite. *Neues Jahrbuch für Mineralogie Abhandlungen*, 141, 280-289.
- Cvech, F., and Hak, J. (1979) Tetrahedrite high in silver, zinc, and cadmium from Jihlava, Czechoslovakia. *Casopis pro mineralogii a geologii*, 24, 83-87.
- Charlat, M., and Levy, C. (1974) Substitutions multiples dans la série tennantite-tétraédrite. *Bulletin de la Société française de Minéralogie et de Cristallographie*, 97, 241-250.
- Frueh, A. J., Jr. (1954) The use of zone theory in problems of sulphide mineralogy. *Geochimica et Cosmochimica Acta*, 6, 79-89.
- Frueh, A. J., Jr. (1955) The crystal structure of stromeyerite, AgCuS: a possible defect structure. *Zeitschrift für Kristallographie*, 106, 299-307.
- Frueh, A. J., Jr. (1961) The use of zone theory in problems of sulfide mineralogy. Part III: polymorphism of Ag<sub>2</sub>Te and Ag<sub>2</sub>S. *American Mineralogist*, 46, 654-660.
- Hall, A. J. (1972) Substitution of Cu by Zn, Fe, and Ag in

- synthetic tetrahedrite,  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ . Bulletin de la Société française de Minéralogie et de Cristallographie, 95, 583–594.
- Harrison, W. A. (1979) Solid State Theory. Dover, New York.
- Hume-Rothery, W. (1948) Atomic Theory for Students of Metallurgy. Institute of Metals, London.
- Hume-Rothery, W. (1963) Electrons, Atoms, Metals and Alloys. Dover, New York.
- Johan, Z., and Kvacek, M. (1971) La Hakite, un nouveau minéral du groupe de la tétraédrite. Bulletin de la Société française de Minéralogie et de Cristallographie, 94, 45–48.
- Jones, H. (1975) The Theory of Brillouin Zones and Electronic States in Crystals. North-Holland, London.
- Kalbskopf, R. (1971) Die Koordination des Quecksilbers im Schwazit. Tschermaks Mineralogische und Petrographische Mitteilungen, 16, 173–175.
- Kalbskopf, R. (1974) Synthese und Kristallstruktur von  $\text{Cu}_{12-x}\text{Te}_x\text{S}_{13}$ , dem Tellur-Endglied der Fahlerze. Tschermaks Mineralogische und Petrographische Mitteilungen, 21, 1–10.
- Makovicky, E., and Skinner, B. J. (1978) Studies of the sulfosalts of copper. VI. Low-temperature exsolution in synthetic tetrahedrite solid solution,  $\text{Cu}_{12+x}\text{Sb}_{4+y}\text{S}_{13}$ . Canadian Mineralogist, 16, 611–623.
- Makovicky, E., and Skinner, B. J. (1979) Studies of the sulfosalts of copper. VII. Crystal structures of the exsolution products  $\text{Cu}_{12.3}\text{Sb}_4\text{S}_{13}$  and  $\text{Cu}_{13.8}\text{Sb}_4\text{S}_{13}$  of unsubstituted synthetic tetrahedrite. Canadian Mineralogist, 17, 619–634.
- Mott, N. F., and Jones, H. (1958) The Theory of the Properties of Metals and Alloys. Dover, New York.
- Patrick, R. A. D. (1978) Microprobe analyses of cadmium-rich tetrahedrites from Tyndrum, Perthshire, Scotland. Mineralogical Magazine, 42, 286–288.
- Pauling, L., and Neuman, E. W. (1934) The crystal structure of binnite,  $(\text{Cu,Fe})_{12}\text{As}_4\text{S}_{13}$ , and the chemical composition and structure of minerals in the tetrahedrite group. Zeitschrift für Kristallographie, 88, 54–62.
- Pearson, W. B., Brandon, J. K., and Brizard, R. Y. (1976) The gamma brasses. Zeitschrift für Kristallographie, 143, 387–416.
- Sandecki, J., and Amcoff, O. (1981) On the occurrence of silver-rich tetrahedrite at Garpenberg Nora, Central Sweden. Neues Jahrbuch für Mineralogie Abhandlungen, 141, 324–340.
- Springer, G. (1969) Electronprobe analyses of tetrahedrite. Neues Jahrbuch für Mineralogie Monatshefte, 24–32.
- Stratton, T. G., Reed, D., and Tuller, H. L. (1981) Study of boundary effects in stabilized zirconia electrolytes. Advances in Ceramics, 1, 114–123.
- Tatsuka, K., and Morimoto, N. (1973) Compositional variation and polymorphism of tetrahedrite in the Cu–Sb–S system below 400°C. American Mineralogist, 58, 425–434.
- Tatsuka, K., and Morimoto, N. (1977) Tetrahedrite stability relations in the Cu–Sb–S system. Economic Geology, 72, 258–270.
- Wuensch, B. J. (1964) The crystal structure of tetrahedrite,  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ . Zeitschrift für Kristallographie, 119, 437–453.

*Manuscript received, March 5, 1982;  
accepted for publication, October 11, 1982.*