Crystal chemistry of tetrahedrite

N. E. Johnson, J. R. Craig, J. D. Rimstidt

Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, U.S.A.

Abstract

The crystal chemistry of tetrahedrite can be rationalized by considering the structure, commonly written as $^{IV}M(1)_6{}^{III}M(2)_6[^{III}X^{IV}Y_3]_4{}^{VI}Z$ [where M(1) = Cu, Fe, Zn, Mn, Hg, Cd; M(2) = Cu, Ag; X = Sb, As, Bi, Te; Y and Z = S, Se], to be generally analogous to sodalite, i.e., a framework of corner-connected $M(1)Y_4$ tetrahedra forming a series of cavities that contain $ZM(2)_6$ octahedra rather than an interframework cation or anion as in sodalite. Adaptation of modeling techniques originally applied to sodalite-group minerals allows for the interpretation of the structural effects of composition on tetrahedrite that has been previously hindered by the lack of structural studies.

Framework rotation (ϕ) is caused by the rotation of the framework tetrahedra about their $\bar{4}$ axes and is increased by increases in the M(1)–Y and X–Y bond lengths, but decreased by increases in the spinner-blade length. Distortion of framework tetrahedra is negligibly affected by the M(1)–Y bond length and greatly affected by the X–Y bond length. Increases in the spinner-blade length cause the distortion to decrease, then increase, implying a state of no distortion to the framework polyhedra at particular values of the spinner-blade length and ϕ.

Because the structural effects of temperature, pressure, and composition are somewhat analogous in minerals, these results indicate that natural tetrahedrite composition may provide some indication of the thermal and baric conditions at the time of formation.

Introduction

Tetrahedrite, the most common representative of the sulfosalt group, is a frequent minor constituent in many types of ore deposits worldwide and often carries significant amounts of Ag. Because well-developed crystals are not uncommon, it was among the first minerals to be examined as the science of crystal-structure analysis developed.

Initial solution of the tetrahedrite structure was by Machatschki (1928a, 1928b) who noted a marked similarity of the tetrahedrite and sphalerite powder patterns. Following this, Pauling and Neumann (1934) solved the structure by using Laue and oscillation photographs and described a complicated relationship between the tetrahedrite and sphalerite structures. This interpretation led to the description of the tetrahedrite structure as a "complex defect derivative" of the sphalerite structure (Ross, 1957). Despite the results and discussions of Wuensch (Wuensch, 1964; Wuensch et al., 1966), which clearly indicate that this is at best misleading, the sphalerite derivative view is still prevalent in current mineralogical literature (Wuensch, 1974; Johnson, 1982; Pattrick and Hall, 1983).

Recent research into the theoretical geometries of crystal structures (Smith and Bennett, 1981, 1984; Hawthorne, 1983) have begun to make sense out of the enormous array of mineral and intermetallic structures. One such line of inquiry led to the realization that many structures previously considered complex, including tetrahedrite, could be related quite easily to the well-understood silicate-framework structure of sodalite (Hellner and Koch, 1981; Koch and Hellner, 1981; Nyman and Hyde, 1981). However, no studies have appeared extending this concept and adapting research on silicate-framework structures to nonsilicate frameworks. Tetrahedrite is uniquely suited for such an approach, because it accepts a large range of substitutions (Johnson et al., 1986) without seriously distorting the structure; thus it has been referred to as a "sulfide amphibole" (Sack and Loucks, 1985).

The concept of tetrahedrite as a framework analogous to sodalite is not altogether new. Belov and Pobedimskaya (1969) clearly referred to this but attributed the original insight to Pauling, following his solutions of the sodalite and tetrahedrite structures (Pauling, 1930; Pauling and Neumann, 1934). However, as noted by Nyman and Hyde (1981), no mention of this relationship can be found in either of the two studies by Pauling.

The purpose of this paper is to clearly define how tetrahedrite is based on a framework of corner-connected tetrahedra and to apply the crystallochemical techniques developed for sodalite to model the structural effects of the observed compositional variations. For consistency with previous work on the subject (Johnson et al., 1986, 1987), the following structural formula will be used: $^{IV}M(1)_6{}^{III}M(2)_6[^{III}X^{IV}Y_3]_4{}^{VI}Z$, where M(1) = Cu, Fe, Zn, Mn, Hg, and Cd, M(2) = Cu and Ag, X = Sb, As, Bi, and Te, and Y and Z = S and Se.
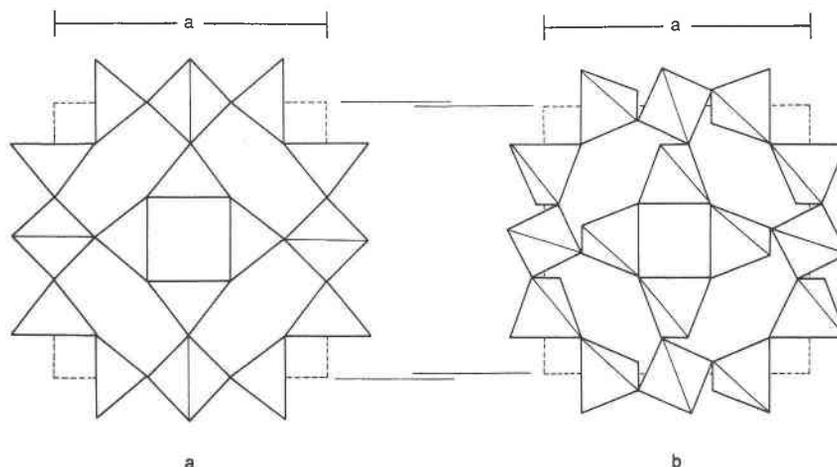
Fig. 1. Interpretation of rotation of corner-connected tetrahedral framework: (a) Idealized fully expanded framework. (b) Idealized partially collapsed framework.

THE STRUCTURE OF TETRAHEDRITE

Framework of M(1)Y₄ tetrahedra

Figure 1, modified from Taylor (1972), displays the relationship between two types of corner-connected tetrahedral frameworks. In Figure 1a, the framework tetrahedra are all oriented so that the tetrahedral edges normal to the $\bar{4}$ axes are at right angles relative to one another and to the unit-cell dimensions. In this orientation, the cavity created by the framework has the maximum volume possible, and the framework is referred to as fully expanded. Figure 1b shows the same framework, but with the tetrahedra rotated away from the ideal positions. The net result of this rotation is to decrease the unit-cell size and shrink the framework cavity; this orientation is referred to as a collapsed framework. The symmetry of the ideal expanded framework is $Im3m$, but as the tetrahedra

Fig. 2. Schematic drawing showing how the framework rotation angle ϕ is related to the translation of the tetrahedral corner (Y) anions.

rotate, the symmetry decreases to $I\bar{4}3m$. Figure 2 demonstrates how the degree of rotation can be quantified, as the angle ϕ is calculated directly from the fractional coordinates of the tetrahedral corners. This approach follows that of Nyrman and Hyde (1981), who tabulated rotations for several compounds, including tetrahedrite. They found that intermetallic compounds tend toward small rotations ($<15°$), silicate minerals toward moderate rotations ($10–30°$), and sulfides toward large rotations ($>45°$).

Figure 3 consists of two views of a fully expanded framework, and two views of a framework rotated 50°, which is approximately the amount of rotation for tetrahedrite and other minerals of the tetrahedrite series. The most obvious difference between the two can be found in the linked six-membered rings of the framework. In the ideal case, these rings are hexagonal, but for tetrahedrite, the hexagon has collapsed to a triangular shape.

Cavity polyhedron

The geometry as well as the size of the cavity formed by the framework changes with the angle of rotation. Connecting the framework Y atoms inside the cavity produces an imaginary Archimedian semiregular polyhedron; for the expanded framework, this polyhedron takes the shape of a truncated octahedron (Fig. 4a), whereas for a framework rotated 45°, the polyhedron is a truncated tetrahedron (Fig. 4b) (Nyman and Hyde, 1981). The truncated tetrahedron is also referred to as a Laves polyhedron (Belov and Pobedimskaya, 1969).

Unlike sodalite or galkhaite, the tetrahedrite cavity does not contain a single large anion, but instead hosts a $ZM(2)_6$ octahedron. The M(2) cations are also bonded to two of the framework Y anions, forming a triangular "spinner blade" as described by Wuensch (1964). Y anions at the adjacent corners of these blades describe the truncated corners of the Laves polyhedron (Fig. 5).
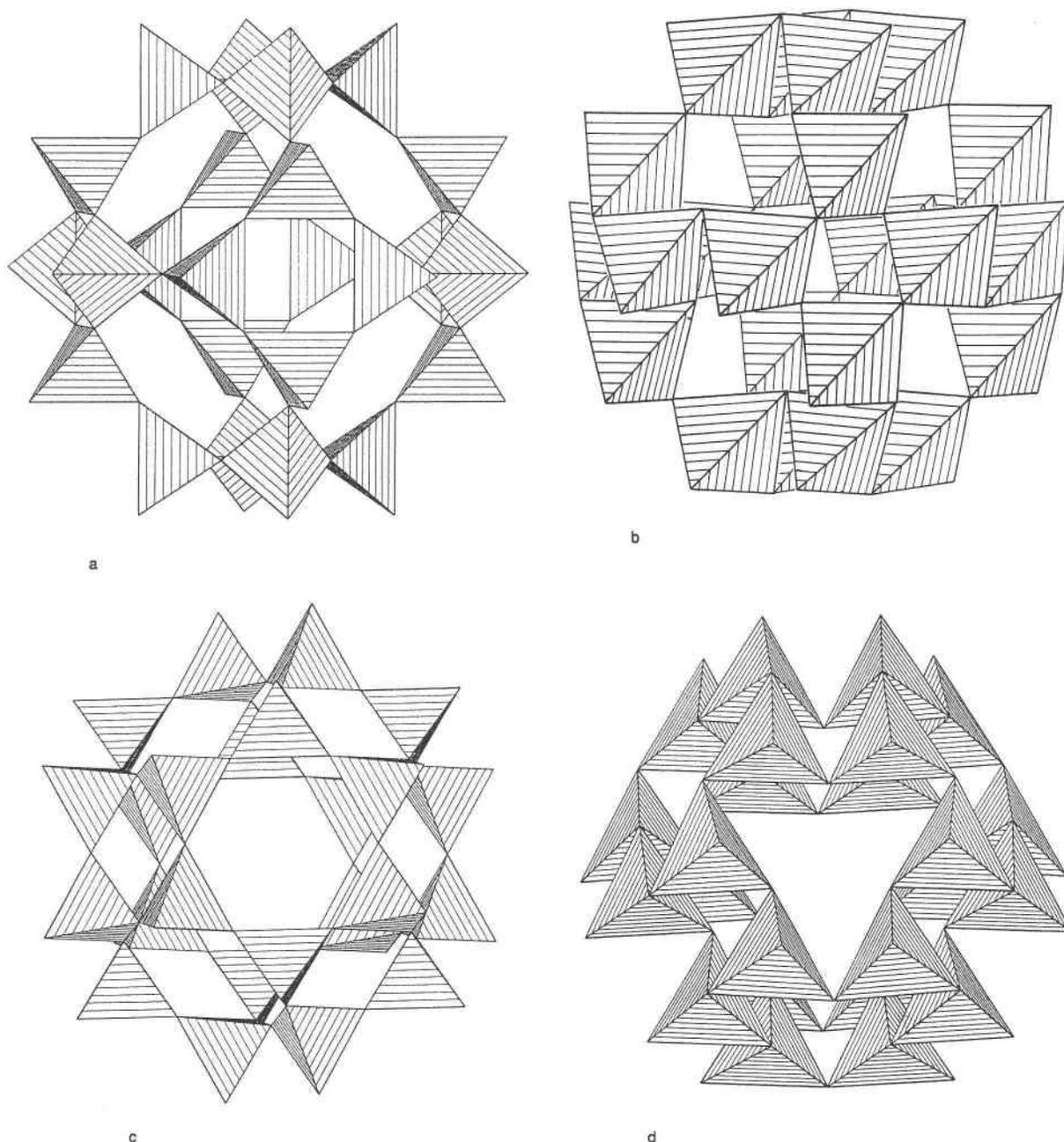
Fig. 3. Crystal-structure drawings of corner-connected tetrahedral frameworks: (a) Ideal expanded, viewing direction slightly off (100). (b) Tetrahedrite, slightly off (100). (c) Ideal expanded, slightly off (111). (d) Tetrahedrite, slightly off (111).

XY₃ pyramid

A Group VA metal pyramid is one of the characteristic structural attributes of sulfosalt minerals (Nowacki, 1969). In tetrahedrite, the semimetal is bonded to the three adjacent Y anions of the Laves polyhedron, forming a pyramidal cap that sits upon the truncated corner (Fig. 5). All four of these corners are so occupied, and the pyramids extend out of the six-membered rings of the framework (Fig. 6). Lone pairs of the semimetal atoms then extend away from the framework toward the hexagonal faces of Laves polyhedra contained within adjacent cavities.

THE TETRAHEDRITE MODEL

Several studies have modeled the sodalite structure in order to interpret the effects of thermal expansion and compositional variation on the framework of silicate and aluminate tetrahedra. Taylor and Henderson (1978),
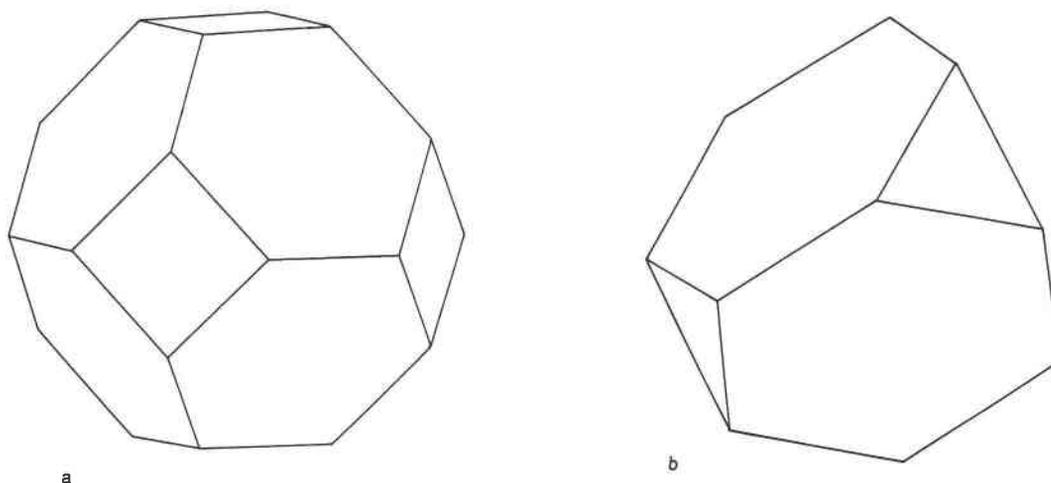
Fig. 4. Internal Archimedian semiregular polyhedra formed by the cavities of frameworks: (a) Truncated octahedron in frameworks rotated less than 45°. (b) Truncated tetrahedron, also referred to as a Laves polyhedron, in frameworks rotated more than 45°.

Dempsey and Taylor (1980), and Beagley et al. (1982) have all used iterative computer procedures to model the framework, whereas Hassan and Grundy (1984) chose a simple geometric model. As noted by the latter authors, the two approaches are essentially equivalent in their results.

The few data available for tetrahedrite make interpretation of the structural effects of composition difficult. Hence at present, modeling offers the only means of determining the effects of composition in tetrahedrite. Therefore, it was decided to follow the approach of Hassan and Grundy (1984) and to derive a geometric model for tetrahedrite.

For the sodalite model, two pieces of information are required: the T–O distance for the framework tetrahedra and either the unit-cell dimension or the O–O distance for the framework tetrahedra. In silicate and aluminosilicate frameworks, both the T–O and the O–O distances are reasonably constant for a given composition and can be predicted from the Shannon and Prewitt (1969) crystal radii. In the frameworks of tetrahedrite and the tetrahedrite-series minerals, however, although the M–Y distance can be considered constant, the Y–Y distance cannot. Therefore, for a tetrahedrite model, the unit-cell dimension is required; for most compositions, this value can be predicted accurately (Johnson et al., 1987), and for other compositions, a cell edge can be reasonably closely interpolated from existing data. Furthermore, the model is sufficiently insensitive to cell-edge variations so that errors in a predicted cell dimension as large as 0.05 Å do not adversely affect the results.

Tetrahedrite has one more atom in the asymmetric unit than does sodalite; hence it is necessary to predict four bond lengths: the metal–Y anion distance in the framework tetrahedra [M(1)–Y]; the metal–Z anion distance in the Laves polyhedron [M(2)–Z]; the metal–Y anion distance connecting the Laves polyhedron and the framework [M(2)–Y]; and the semimetal–Y anion distance (X–Y). Shannon (1981) provides sulfide crystal radii for some of these, but not for a semimetal in a trigonal pyramidal coordination or for metals in planar threefold coordination. Radii for these atoms were obtained by selecting data from Edenharter (1976) that fit the above coordination restraints. The radii used in the modeling are listed in Table 1.

One of the assumptions made in using crystal radii in this manner is that the atoms act as spheres. However, Figure 7a shows that the lengths of the M(2)–Z and the M(2)–Y bonds in tetrahedrite diverge as the Ag content increases, indicating that threefold Ag is distinctly aspherical relative to threefold Cu. To improve the accuracy of the model, it was decided to use two radii for Ag. Because of this, neither the M(2)–Z or the M(2)–Y bond lengths alone are adequate for gaging the expansion or contraction of the structure. As shown in Figure 7b, the length of the spinner blade, measured from the Z anion through the M(2) cation to a point midway between the two Y anions, increases linearly as a function of Ag content and combines both the M(2)–Z and the M(2)–Y bonds. The calculated spinner-blade length is therefore used in place of either the M(2)–Z or the M(2)–Y bond lengths.

The high symmetry of tetrahedrite and the small number of atoms in the asymmetric unit produce the result that all the atoms lie on special positions in the structure. Of 15 fractional coordinates for all the atoms in the asymmetric unit, there are only four independent variables, which results in a system of four equations (one for each of the bond lengths listed above) and four unknowns. Therefore, a model structure can be calculated given the unit-cell dimension and four predicted bond lengths. Once the fractional coordinates have been determined, the ro-
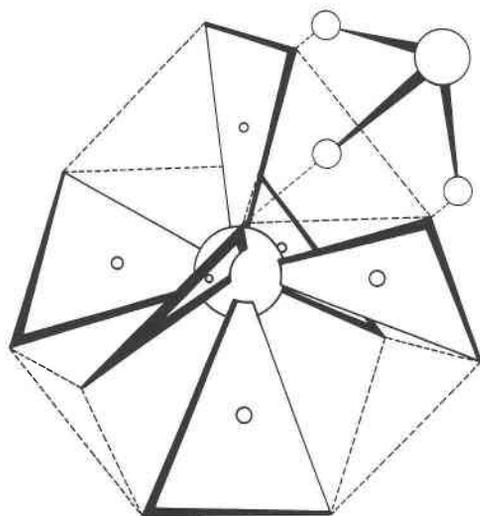
Fig. 5. Internal structure of tetrahedrite framework cavity. The central Z anion is bonded to six M(2) cations, which are then bonded to the framework Y anions. XY_3 pyramids sit upon the truncated corners (after Wuensch, 1964).
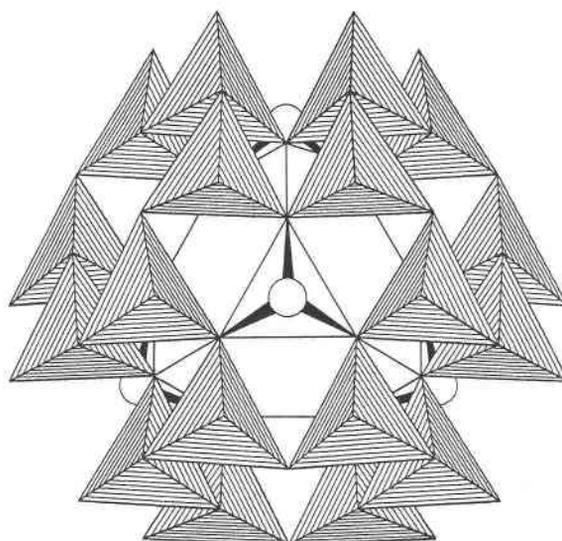
Fig. 6. One complete framework unit of the tetrahedrite structure.

tation angle ϕ can be calculated, along with the amount of tetragonal distortion of the framework tetrahedra relative to ideal tetrahedra (Depmeier, 1984).

The accuracy of this approach was tested by calculating the fractional coordinates, ϕ, and tetragonal distortion for those tetrahedrite-series minerals whose structures have been previously determined (Wuensch, 1964; Wuensch et al., 1966; Kalbskopf, 1972, 1974; Makovicky and Skinner, 1979; Kaplunnik et al., 1980; Johnson and Burnham, 1985; Peterson and Miller, 1986). With the exception of those structures containing significant vacancies (Kalbskopf, 1974; Makovicky and Skinner, 1979), differences between predicted and actual values were less than 4%.

RESULTS

The results of the modeling for varying compositions of tetrahedrite are found in Figures 8 and 9, which are plots of bond length versus framework rotation or percent distortion from ideality. Each point represents a specific composition, following the general formula for tetrahedrite (Johnson et al., 1986). As seen in Figure 8a, the effect on the framework of increasing the M(1)–Y and the X–Y bond lengths is an increase in the rotation. The increase appears to be a linear function of both the semimetal radii and the metal radii. These increases in ϕ can be rationalized by considering that the framework increases in size as the M(1)–Y and the X–Y bond lengths increase, but the Laves polyhedron does not. A framework so increased must therefore rotate through a greater angle ϕ in order to maintain contact with the unexpanded Laves polyhedron.

The opposite effect is displayed in Figure 8b; as the spinner-blade length increases, the Laves polyhedron ex-

pands, thereby decreasing the amount of rotation by expanding the framework from inside. This expansion is much more pronounced than the contraction discussed above, and these two effects may be used to explain some natural compositional variations. In As-rich tetrahedrite, the framework is small and therefore expanded, so that a large increase in the spinner-blade length that would be needed to accommodate Ag substitution would expand the framework beyond its range of stability. Hence, As and Ag substitutions should generally be mutually exclusive, which is in fact observed in natural minerals (Johnson et al., 1986).

There are two corollaries to this idea: (1) according to the modeled results, the effects of Ag and Bi substitution on the tetrahedrite framework are similar in magnitude and direction and could possibly tend to offset each other and allow for greater mutual substitution than otherwise possible and (2) there should be a critical angle for a framework of a given size, beyond which a framework structure is no longer the most stable configuration. Both of these points are discussed further below.

TABLE 1. Crystal radii used in modeling equations

Atom	Radius (Å)	Atom	Radius (Å)
IVFe	0.66	IIICu	0.55
IVCu	0.635	IIIAg*	0.83
IVZn	0.64	IIIAg**	0.62
IVCd	0.84	IIIAs	0.56
IVHg	0.84	IIISb	0.76
IVMn	0.725	IIIBi	0.89
S	1.70	IIITe	0.71
Se	1.84		

* Used for M(2)–Y bond.
** Used for M(2)–Z bond.

a)

a)

b)

b)
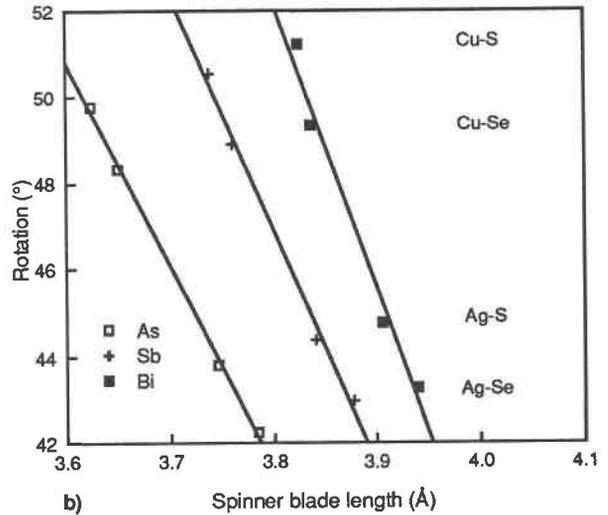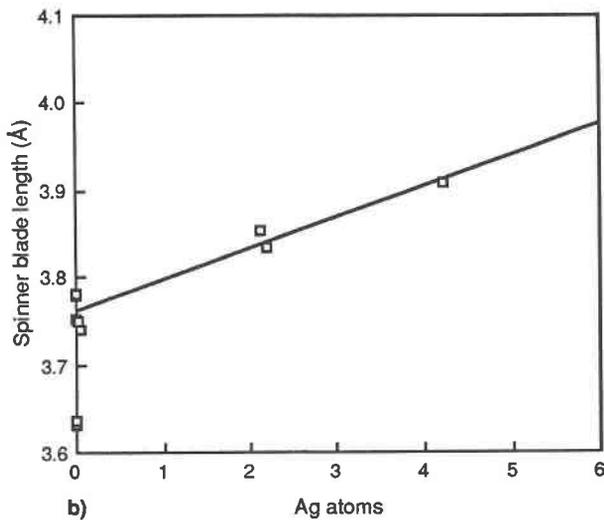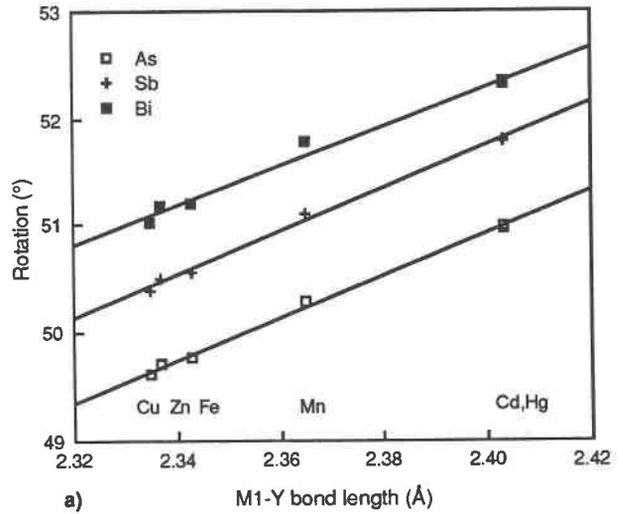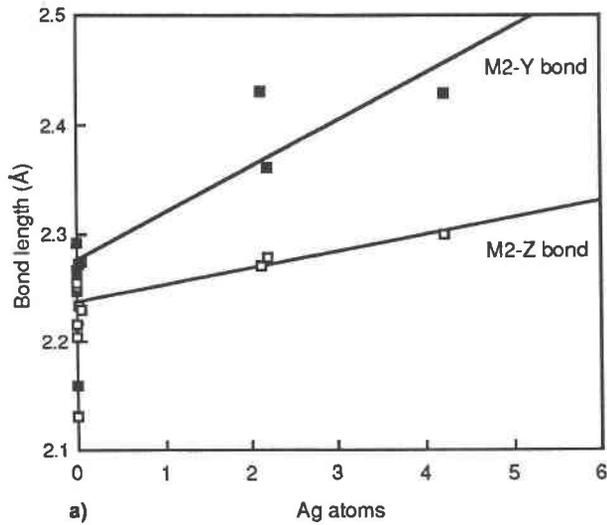
Fig. 7. (a) Plot of M(2)–Z and M(2)–Y bond lengths vs. number of Ag atoms in the M(2) site. (b) Plot of spinner-blade length (equals M(2)–Z plus [M(2)–Y]cos{∠[Y–M(2)–Y]/2}) vs. number of Ag atoms in the M(2) site.

Fig. 8. Plots of framework rotation angle ϕ vs. bond length: (a) M(1)–Y bond length. (b) M(2)–Z bond length.

Figure 9a displays the distortional effects on the framework tetrahedra of increasing the M(1)–Y and X–Y bond lengths. The most distinct feature is that the polyhedral distortion is negligibly affected by changes in the M(1)–Y bond length compared to the effect of changes in the length of the X–Y bond. This appears to be reasonable, because the position of the Y anion relative to the M(1) cation, which is the measure of distortion used here, is more influenced by the X–Y bond than the M(1)–Y bond.

It should also be noted that whereas the curves for Sb and As end members are approximately symmetric with

respect to ideality, the Bi end-member curve displays an absolute amount of distortion that is approximately twice that of the Sb and As curves. This may indicate that a pure Bi end-member tetrahedrite is not stable, a point consistent with the absence of reported natural Bi end-member tetrahedrite (Johnson et al., 1986) and absence of a synthetic Bi end member (N. E. Johnson, unpub. data). If such a Bi-rich tetrahedrite does occur, it may be due to a stabilizing effect created by the presence of Ag as discussed above.

The curves in Figure 9b, rather than trending parallel to the ideal line, intersect it, resulting in compositions for which the framework tetrahedra show no distortion. This

a)

b)

Fig. 9. Plots of framework rotation angle ϕ vs. percent distortion of framework tetrahedra: (a) M(1)1–Y bond length. (b) M(2)–Z bond length.

DISCUSSION

The results of the modeling appear to be qualitatively correct for all compositions of tetrahedrite attempted, and at least semiquantitatively correct for many as well. The exceptions to this are the magnitudes of rotation and distortion predicted for Ag-rich tetrahedrites. It seems unlikely that ranges of framework rotations greater than 10° and polyhedral distortions of nearly 30% (corresponding to a change in physical dimension of a framework tetrahedron of 1 Å) are reasonable. Possibilities for these discrepancies include too large crystal radii being used for Ag or that not all six of the M(2) sites are occupied by Ag.

The estimates of the Ag radii appear to be reasonable, based on available data (Edenharter, 1976), but as Shannon (1981) noted, sulfosalts, with their irregular coordination polyhedra, complicate efforts to obtain characteristic metal-sulfur radii. More accurate modeling may simply require more accurate radii.

It has recently been suggested that Fe and Zn may preferentially substitute into the M(2) site in Ag-rich tetrahedrite (Peterson and Miller, 1986) or that Ag may substitute into the M(1) site (Pattrick and Hall, 1983; O'Leary and Sack, 1987). Attempts to test the first assertion were unsuccessful as little data exist for the crystal radii of metals in planar threefold coordination, and the uncertainty in extrapolating threefold radii from tetrahedral radii masked any differences in modeled structures. All structure refinements of Ag-bearing tetrahedrite published to date have found that Ag preferentially substitutes into the M(2) site. None of these studies, however, have examined tetrahedrites with greater that approximately four atoms of Ag per formula unit, the point at which it is suggested that tetrahedral Ag becomes important (O'Leary and Sack, 1987). Ag is less common in tetrahedral than threefold coordination in sulfosalts, and the tetrahedra are usually highly distorted (Edenharter, 1976). Models utilizing tetrahedral Ag were found to show less framework rotation but considerably greater distortion than those models with only threefold Ag.

Taylor (1972) described a mechanism to explain the thermal expansion behavior of certain members of the sodalite group. He proposed that the initial effect of increased temperature on the framework would be to expand the framework by decreasing the amount of rotation. Once an ideal fully expanded state was achieved, further thermal expansion would occur by lengthening of the bonds in the structure. A curve of thermal expansion versus temperature would therefore contain a discontinuity, T_d, the point at which the framework first reached the fully expanded state. Subsequent work (Taylor and Henderson, 1978; Henderson and Taylor, 1978) found such a discontinuity in some sodalite minerals but not in others. This led to an interpretation that the frameworks were further constrained by nonframework cations and could expand by rotation to a certain point and no further, which is another approach to the concept that each framework had a critical value for the angle ϕ.

is consistent with the above-mentioned concept of a critical angle; if a framework is not stable beyond a certain angle of rotation, then there must be an angle where the framework has the highest stability, i.e., where the strain on structural elements is minimized. The intersections of the distortion curves with the zero-distortion line differ depending on the Group VA metal occupying the X site: For As, the "ideal" spinner-blade length and ϕ are 3.59 Å and 51.1°; for Sb and Bi, the values are 3.76 Å and 49.3° and 3.86 Å and 48.0°, respectively. This "ideal" framework angle should fall approximately halfway between a critical angle of expansion and a critical angle of collapse.

Hazen (1977) noted that in silicate minerals, the structural effects of changing pressure, temperature, and composition were often analogous. There have been no investigations of the structure of tetrahedrite at pressures or temperatures above ambient conditions, and only a preliminary attempt was made at low temperatures (Johnson, 1982). However, it seems reasonable that such studies could be successfully interpreted by application and extension of the principles outlined here. If the composition of a tetrahedrite sample represents the most stable structural state at the temperature and pressure of formation, and if re-equilibration after changes in temperature and pressure is sluggish, then the possibility exists for the development of a geothermometer or a geobarometer.

The one existing low-temperature structure refinement (Johnson, 1982) indicates that rotation of the framework is indeed affected by temperature; consistent with the model developed here, the framework rotation was greater. Studies in the Cu-As-S and Cu-Sb-S systems (Maske and Skinner, 1971; Skinner et al., 1972) have shown that the thermal stability of tetrahedrite is increased by As. This is inconsistent with the model, as substitution of As increases the framework rotation, which should then decrease the thermal stability. Although the tetrahedrite model does provide some insight into the effects of substitution, it is clear that the usefulness of modeling in determining the effects of *P-T-X* on the tetrahedrite framework is limited and that there is room for a great deal more research on such effects.

REFERENCES CITED

Beagley, B., Henderson, C.M.B., and Taylor, D. (1982) The crystal structures of aluminosilicate-sodalites: X-ray diffraction studies and computer modeling. Mineralogical Magazine, 46, 459–464.

Belov, N.V., and Pobedimskaya, E.A. (1969) Covelline (klockmannite), chalcocite (acanthite, stromeyerite, bornite), fahlerz. Soviet Physics Crystallography, 13, 843–847.

Dempsey, M.J., and Taylor, D. (1980) Distance least squares modelling of the cubic sodalite structure and of the thermal expansion of Na₈(Al₆Si₆O₂₄)I₂. Physics and Chemistry of Minerals, 6, 197–208.

Depmeier, W. (1984) Tetragonal tetrahedra distortions in cubic sodalite frameworks. Acta Crystallographica, B40, 185–191.

Edenharter, A. (1976) Fortschritte auf dem Gebiete der Kristallchemie der Sulfosalze. Schweizerische Mineralogische und Petrographische Mitteilungen, 56, 195–217.

Hassan, I., and Grundy, H.D. (1984) The crystal structures of sodalite group minerals. Acta Crystallographica, B40, 6–13.

Hawthorne, F.C. (1983) Graphical enumeration of polyhedral clusters. Acta Crystallographica, A39, 724–736.

Hazen, R.M. (1977) Temperature, pressure and composition: Structurally analogous variables. Physics and Chemistry of Minerals, 1, 83–94.

Hellner, E., and Koch, E. (1981) Cluster or framework considerations for the structures of Tl₇Sb₂, α-Mn, Cu₅Zn₈ and their variants Li₂₂Si₅₁, Cu₄₁Sn₁₁, Sm₁₁Cd₄₅, Mg₆Pd and Na₆Tl with octuple unit cells. Acta Crystallographica, A37, 6–11.

Henderson, C.M.B., and Taylor, D. (1978) The thermal expansion of synthetic aluminosilicate sodalites, M₈(Al₆Si₆O₂₄)X₂. Physics and Chemistry of Minerals, 2, 337–347.

Johnson, M.L. (1982) The effect of substitutions on the physical properties of tetrahedrite. Ph.D. thesis, Harvard University, Cambridge, Massachusetts.

Johnson, M.L., and Burnham, C.W. (1985) Crystal structure refinement of an arsenic-bearing argentian tetrahedrite. American Mineralogist, 70, 165–170.

Johnson, N.E., Craig, J.R., and Rimstidt, J.D. (1986) Compositional trends in tetrahedrite. Canadian Mineralogist, 24, 385–397.

——— (1987) Substitutional effects on the cell dimension of tetrahedrite. Canadian Mineralogist, 25, 237–244.

Kalbskopf, R. (1972) Strukturverfeinerung des freibergits. Tschermaks Mineralogische und Petrographische Mitteilungen, 18, 147–155.

——— (1974) Synthese und Kristallstruktur von Cu₁₂₋ₓTe₄S₁₃, dem Tellur-endglied der Fahlerze. Tschermaks Mineralogische und Petrographische Mitteilungen, 21, 1–10.

Kaplunnik, L.N., Pobedimskaya, E.A., and Belov, N.V. (1980) Crystal structure of schwatzite (Cu₄.₄Hg₁.₆)Cu₆Sb₄S₁₂. Soviet Physics Doklady, 25, 506–507.

Koch, E., and Hellner, E. (1981) The frameworks of sodalite-like structures and of tetrahedrite-like structures. Zeitschrift für Kristallographie, 154, 95–114.

Machatschki, F. (1928a) Formel und Kristallstruktur des tetraedrites. Norsk Geologische Tidsskrift, 10, 23–32.

——— (1928b) Präzisionsmessungen der Gitterkonstanten verschiedener Fahlerze. Formel und struktur derselben. Zeitschrift für Kristallographie, 68, 204–222.

Makovicky, E., and Skinner, B.J. (1979) Studies of the sulfosalts of copper. VII. Crystal structures of the exsolution products Cu₁₂.₃Sb₄S₁₃ and Cu₁₃.₈Sb₄S₁₃ of unsubstituted synthetic tetrahedrite. Canadian Mineralogist, 17, 619–634.

Maske, S., and Skinner, B.J. (1971) Studies of the sulfosalts of copper. I. Phases and phase relations in the system Cu-As-S. Economic Geology, 66, 901–918.

Nowacki, W. (1969) Zur Klassifikation und Kristallchemie der Sulfosalze. Schweizerische Mineralogische und Petrographische Mitteilungen, 49, 109–156.

Nyman, H., and Hyde, B.G. (1981) The related structures of α-Mn, sodalite, Sb₂Tl₇, etc. Acta Crystallographica, A37, 11–17.

O'Leary, M.J., and Sack, R.O. (1987) Fe-Zn exchange reaction between tetrahedrite and sphalerite in natural environments. Contributions to Mineralogy and Petrology, 96, 415–425.

Pattrick, R.A.D., and Hall, A.J. (1983) Silver substitution into synthetic zinc, cadmium and iron tetrahedrites. Mineralogical Magazine, 47, 441–450.

Pauling, L. (1930) The structure of sodalite and helvite. Zeitschrift für Kristallographie, 74, 213–225.

Pauling, L., and Neumann, E.W. (1934) The crystal structure of binnite, (Cu,Fe)₁₂As₄S₁₃, and the chemical composition and structure of minerals in the tetrahedrite group. Zeitschrift für Kristallographie, 88, 54–62.

Peterson, R.C., and Miller, I. (1986) Crystal structure and cation distribution in freibergite and tetrahedrite. Mineralogical Magazine, 50, 717–721.

Ross, V. (1957) Geochemistry, crystal structure and mineralogy of the sulfides. Economic Geology, 52, 755–774.

Sack, R.O., and Loucks, R.R. (1985) Thermodynamic properties of tetrahedrite-tennantites: Constraints on the interdependence of the Ag = Cu,Fe = Zn and As = Sb exchange reactions. American Mineralogist, 70, 1270–1289.

Shannon, R.D. (1981) Bond distances in sulfides and a preliminary table of sulfide crystal radii. In M. O'Keeffe and A. Navrotsky, Eds., Structure and bonding in crystals, vol. II, p. 53–70. Academic Press, New York.

Shannon, R.D., and Prewitt, C.T. (1969) Effective ionic radii in oxides and fluorides. Acta Crystallographica, B25, 925–945.

Skinner, B.J., Luce, F.D., and Makovicky, E. (1972) Studies of the sulfosalts of copper. III. Phases and phase relations in the system Cu-Sb-S. Economic Geology, 67, 924–938.

Smith, J.V., and Bennett, J.M. (1981) Enumeration of 4-connected 3-dimensional nets and classification of framework silicates: The infinite set of ABC-6 nets; the Archimedian and σ-related nets. American Mineralogist, 66, 777–788.

——(1984) Enumeration of 4-connected 3-dimensional nets and classification of framework silicates: Linkages from the two $(5^2.8)_2(5.8^2)_1$ 2D nets. American Mineralogist, 69, 104–111.

Taylor, D. (1972) The thermal expansion behavior of the framework silicates. Mineralogical Magazine, 38, 593–604.

Taylor, D., and Henderson, C.M.B. (1978) A computer model for the cubic sodalite structure. Physics and Chemistry of Minerals, 2, 325–336.

Wuensch, B.J. (1964) The crystal structure of tetrahedrite, $Cu_{12}Sb_4S_{13}$. Zeitschrift für Kristallographie, 119, 437–453.

——(1974) Determination, relationships, and classification of sulfide mineral structures. Mineralogical Society of America Reviews in Mineralogy 1, W1–W20.

Wuensch, B.J., Takéuchi, Y., and Nowacki, W. (1966) Refinement of the crystal structure of binnite, $Cu_{12}As_4S_{13}$. Zeitschrift für Kristallographie, 123, 1–20.