

CRYSTAL STRUCTURE OF COPPER-RICH UNSUBSTITUTED TENNANTITE, $\text{Cu}_{12.5}\text{As}_4\text{S}_{13}$

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ABSTRACT

The crystal structure of a Cu-rich tennantite from Cerro Atajo, province of Catamarca, northwestern Argentina, has been refined using single-crystal data [MoK α X-ray diffraction, CCD detector, $R_I = 0.03$]. It crystallizes in space group $I3m$, with $a = 10.1756(9)$ Å. The X-ray-diffraction analysis led to the formula $\text{Cu}_{12.5}(\text{As}_{0.98}\text{Sb}_{0.02})_{\Sigma 4}\text{S}_{13}$, in full agreement with the electron-microprobe data and the unit-cell parameter. Cu-rich tennantite shows all structural features of tetrahedrite and tennantite, but it contains a partly occupied triangular Cu2A position, accompanied by a new site, Cu2B, coordinated tetrahedrally to three S and one As atom. This finding is in contrast to Cu-rich tetrahedrite, where partial occupancy and redistribution of Cu are associated with the Cu1 site. Atoms Cu2A and Cu2B form, respectively, an octahedron and a Laves polyhedron around the S2 site, a situation similar to Te3 coordination in $\gamma\text{-Ag}_8\text{SiTe}_6$ and $\gamma\text{-Ag}_8\text{GeTe}_6$. On the basis of bond lengths, we contend that the Cu^{2+} necessary to balance the formula resides primarily at the Cu1 site. The electron density shows a dynamic disorder between closely separated Cu2A and Cu2B sites, which, together with available vacancies at these positions, suggests that Cu-rich tennantite is an ionic conductor even at room temperature. The Cu-rich tennantite is a rare case of formation from late hydrothermal solutions devoid of ubiquitous Fe, Zn and other divalent elements, which usually enter tennantite as electron donors.

Keywords: Cu-rich tennantite, crystal structure, tetrahedrite, copper disorder, solid electrolyte, bismuthian watanabeite, Cerro Atajo, Argentina.

SOMMAIRE

Nous avons affiné la structure cristalline de la tennantite riche en Cu avec un échantillon provenant de Cerro Atajo, province de Catamarca, dans le nord-ouest de l'Argentine, en utilisant les données prélevées sur monocristal [rayonnement MoK α , diffraction X, détecteur CCD, $R_I = 0.03$]. Ce matériau cristallise dans le groupe spatial $I3m$, avec $a = 10.1756(9)$ Å. L'analyse par diffraction X a mené à la formule $\text{Cu}_{12.5}(\text{As}_{0.98}\text{Sb}_{0.02})_{\Sigma 4}\text{S}_{13}$, ce qui concorde pleinement avec les données obtenues avec une microsonde électronique et avec le paramètre réticulaire. La tennantite riche en Cu présente toutes les caractéristiques structurales de la tétraédrite et la tennantite, mais elle contient une position triangulaire Cu2A partiellement occupée, ainsi qu'un nouveau site, Cu2B, en coordinence tétraédrique à trois atomes de S et un de As. Cette situation contraste avec le cas de la tétraédrite riche en Cu, où l'occupation partielle et la redistribution du Cu sont associées au site Cu1. Les atomes Cu2A et Cu2B forment, respectivement, un octaèdre et un polyèdre de Laves autour du site S2, situation semblable au cas de la coordinence de Te3 dans les composés $\gamma\text{-Ag}_8\text{SiTe}_6$ et $\gamma\text{-Ag}_8\text{GeTe}_6$. À la lumière des longueurs de liaison, nous croyons que le Cu^{2+} nécessaire servant à équilibrer les charges réside surtout au site Cu1. La densité d'électrons montre un désordre dynamique entre les sites voisins Cu2A et Cu2B; d'après cette évidence, considérée en tenant compte des lacunes disponibles à ces positions, la tennantite riche en Cu serait un conducteur ionique, même à température ambiante. La cristallisation de la tennantite riche en Cu résulterait d'un cas inhabituel où les solutions hydrothermales tardives sont dépourvues de Fe, de Zn et d'autres ions bivalents, généralement ubiquistes et incorporées dans la tennantite comme donateurs d'électrons.

(Traduit par la Rédaction)

Mots-clés: tennantite riche en Cu, structure cristalline, tétraédrite, désordre du Cu, électrolyte solide, watanabéite bismuthifère, Cerro Atajo, Argentine.

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INTRODUCTION

Although less common than the antimony end-member of the tetrahedrite–tennantite solid-solution series, tennantite is one of the most common sulfosalts. The crystal-chemical formula of this solid-solution series is $(\text{Cu, Ag})_{10}(\text{Fe, Zn, Hg, Cu, ...})_2(\text{As, Sb})_4\text{S}_{13}$. The majority of natural examples of tetrahedrite–tennantite are fully substituted by divalent elements, with only 10 (Cu, Ag) atoms per formula unit (*pfu*) and 2 atoms of Fe, Zn, Hg, ... distributed over the tetrahedral sites. This is the primary reason for the somewhat surprising fact that unsubstituted, pure copper tennantite has never been characterized structurally. We report here the results of a study of such material from Cerro Atajo, northern Argentina.

PREVIOUS WORK

From the point of view of charge balance, an ideal formula of members of the tetrahedrite family is $(\text{Cu, Ag})_{10}M^{2+}_2(\text{As, Sb})_4\text{S}_{13}$, but the existence of not-quite-fully-substituted samples with the formula $(\text{Cu, Ag})_{12-x}M^{2+}_x(\text{As, Sb})_4\text{S}_{13}$ requires an explanation for the apparent excess (up to two) of negative charges in partially substituted samples of tetrahedrite–tennantite, in which $0 < x < 2$. The same holds for the “unsubstituted” $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ and $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ (*i.e.*, $x = 0$) synthetic samples. At least two possible explanations exist: delocalization of electrons in the crystal toward the valence band of S (Jellinek 1968), or the presence of randomly distributed Cu^{2+} ions at one or both copper sites. The latter case involves possible indirect charge-transfer between adjacent Cu^+ and Cu^{2+} ions, mediated by intervening sulfur. Either situation can be described by the presence of *formally divalent* copper. On the basis of the change in the unit-cell parameter, Makovicky & Karup-Møller (1994) ascribed an effective radius of 0.51 Å to the formally divalent copper in the Cu1 sites of tetrahedrite, contrasting with the analogous radius of 0.635 Å determined for monovalent copper in sulfides (Shannon 1981).

Previous studies of synthetic tennantite revealed that the stoichiometry is more variable than the ideal formula for natural tetrahedrite–tennantite. In the system Cu–As–S, Maske & Skinner (1971) found an elongate field of compositions $\text{Cu}_{12+x}\text{As}_{4+y}\text{S}_{13}$ with $0 < x < 1.72$ and $0 < y < 0.08$; their diagrams show a virtually complete range of compositions between about $\text{Cu}_{12.3}\text{As}_4\text{S}_{13}$ and $\text{Cu}_{13.7}\text{As}_4\text{S}_{13}$, with a negligible width of the solid-solution field (*i.e.*, formal excess of As). The stoichiometrically simple compositions, $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ and $\text{Cu}_{14}\text{As}_4\text{S}_{13}$ (*i.e.*, formally $\text{Cu}^+_{10}\text{Cu}^{2+}_2\text{As}_4\text{S}_{13}$ and $\text{Cu}^+_{14}\text{As}_4\text{S}_{13}$), were not reached at synthesis temperatures of 300–660°C. The unit-cell edge *a* varies from 10.168 Å to 10.222 Å at the above experimental conditions. A linear fit to the data in Table 2 of Maske &

Skinner (1971) yielded the equation $a = 9.683(5) + 0.0393(4)*\text{Cu}$, from which the *a* values were extrapolated, equal to 10.155 Å for $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ and 10.233 Å for $\text{Cu}_{14}\text{As}_4\text{S}_{13}$. Therefore, we can assume that the tennantite series is an interstitial solid-solution.

The solid-solution field broadens for the compositions in which As is partly replaced by Sb (Luce *et al.* 1977); *x* and *y* in the analogous formula $\text{Cu}_{12+x}(\text{As, Sb})_{4+y}\text{S}_{13}$ reach the values of 1.99 and 0.37, respectively. Below 120°C, the tetrahedrite solid-solution $\text{Cu}_{12+x}\text{Sb}_{4+y}\text{S}_{13}$ exsolves into two low-temperature tetrahedrites, a Cu-rich one with the composition tending toward $\text{Cu}_{14}\text{Sb}_4\text{S}_{13}$, and a Cu-poor one, close to $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ (Makovicky & Skinner 1978). No such exsolution-induced phenomenon was observed for tennantite. Luce *et al.* (1977) suggested that the exsolution is limited to the compositions with between 0 and 8 mol.% of the tennantite component.

Phase relations (Maske & Skinner 1971) indicate a very pronounced drop in sulfur fugacity from the S-rich side of the tennantite solid-solution field, where tennantite is associated with Cu_3AsS_4 , toward the S-poor side of this field, associated with CuAsS and, for higher temperatures, with the As–S melt. This observation was useful for the interpretation of the natural association observed at Cerro Atajo.

The crystal structure of members of the tetrahedrite family was first proposed by Pauling & Neuman (1934) and later confirmed by the structure determinations for a natural, substituted tetrahedrite (Wuensch 1964) and “binnite”, a synonym of tennantite (Wuensch *et al.* 1966). Although these structure determinations were followed by several additional determinations on a similar material, the only structure determinations made on the unsubstituted tetrahedrite–tennantite are those of Cu-poor and Cu-rich synthetic tetrahedrite (Makovicky & Skinner 1979) and of another synthetic Cu-poor tetrahedrite, interpreted as being stoichiometric $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ (Pfitzner *et al.* 1997). Using only the reflections involving diffraction at higher angles and harmonic displacement coefficients, Makovicky & Skinner (1979) found fully occupied Cu2 sites in both varieties of tetrahedrite, but only 2/3 occupancy of the Cu1 site in the Cu-rich tetrahedrite $\text{Cu}_{13.8}\text{Sb}_4\text{S}_{13}$. This change in the occupancy was connected with the appearance of a highly disordered, partly occupied Cu3 position in the triangular spaces surrounding the base of the SbS_3 pyramid. A very small deficit of stationary Cu was found for the Cu1 position of $\text{Cu}_{12.3}\text{Sb}_4\text{S}_{13}$. The approach used did not allow refinement of the mobile and anharmonic portion of the copper. Pfitzner *et al.* (1997) described positional disorder of the three-coordinated Cu2 atom of the Cu-poor variety of tetrahedrite in detail. They found full occupancy of all atomic sites and no extra electron density in ΔF maps. Pfitzner (1997) found the same additional Cu3 maximum as Makovicky & Skinner (1979) in Cu-rich synthetic tetrahedrite.

LOCALITY, CHEMICAL COMPOSITION
AND MINERAL ASSOCIATION

The single sample of tennantite used for this study was discovered at Cerro Atajo, a subvolcanic Au and Cu deposit located in the Farallon Negro mining district, Department of Andalgala, Province of Catamarca, Argentina. The sample was collected from a small dump located in front of an adit providing access to the Triunfo vein. The exact position of that dump is 27°19' S (longitude) and 66°28' latitude; the altitude is 3005 m above sea level.

The most important veins, which are hosted by andesites, dacites and rhyolites of Upper Miocene age, are known as Carmen, Maria Eugenia, Grande and Triunfo, and were mined for copper, gold and silver. Widespread wallrock alteration includes silicification, argillitization and propylitization. The veins are mineralogically complex, and the assemblages differ. Hübnerite, scheelite, native gold, pyrite and chalcopyrite are typical of the Carmen vein, whereas a gold-bearing base-metal mineralization (chalcopyrite, tetrahedrite, galena and sphalerite) associated with colusite, mawsonite, luzonite, bournonite and chalcostibite are characteristic of the other veins.

The composition of the sample was determined by electron-microprobe analysis before its extraction from a polished section. A JEOL-8600 electron microprobe equipped with Link EXL software and on-line ZAF correction was used. Analytical conditions employed were 25 kV and 30 nA. Synthetic and natural sulfide standards were used.

An average of 13 point-analyses, made on different grains, gave the following results (in wt.%): As 19.5(1)[19.4], Cu 52.8(3)[52.5], S 26.5(1)[27.5], Sb 0.70(6)[0.6], Mn 0.2(1), Fe 0.08(1), total 99.8(3)[100]. The square brackets indicate the theoretical values calculated from the results of the structure analysis. If the minor percentage of Mn and Fe is neglected, the empirical formula calculated on the basis of 4 (As + Sb) atoms is $\text{Cu}_{12.5}(\text{As}_{0.98}\text{Sb}_{0.02})_4\text{S}_{12.4}$.

Compact aggregates of tennantite (Fig. 1) contain locally irregular grains of luzonite. Analysis of five grains yielded (in wt.%): Cu 48.69(9), Sb 0.44(5), As 19.13(9), and S 32.48(5), for a total of 100.30(17) wt.%, equivalent to $\text{Cu}_{3.01}\text{Sb}_{0.01}\text{As}_{1.00}\text{S}_{3.98}$. Along former zones of weakness, tennantite in aggregates is replaced by *bismuthian watanabeite*, too fine-grained and impure for analysis by X-ray diffraction. Twenty-one point-analyses made on different grains gave (in wt.%): Cu 42.95(65), Mn 0.12(6), Bi 7.65(2.41), Sb 3.24(1.54), As 20.02(0.95), and S 26.39(39), for a total of 100.37(60) wt.%, and a formula $\text{Cu}_{4.06}\text{Mn}_{0.01}\text{Bi}_{0.22}\text{Sb}_{0.16}\text{As}_{1.61}\text{S}_{4.94}$, which is closest to the formula of watanabeite, $\text{Cu}_4(\text{As,Sb})_2\text{S}_5$ as published by Shimizu *et al.* (1993). The principal compositional variations observed in watanabeite involve Bi (from 0.15 to 0.44 atoms per formula unit, *apfu*), Sb (0.02–0.30 *apfu*), and As (1.50–

1.72 *apfu*). The Cu content is practically constant (4.03–4.10 *apfu*). Luce *et al.* (1977) described the synthetic “compound C”, $\text{Cu}_4(\text{Sb,As})_2\text{S}_5$ with the ratio As/(As+Sb) varying from 0.74 to 0.455. This “synthetic watanabeite” differs from “compound A”, $\text{Cu}_{24}(\text{As,Sb})_{12}\text{S}_{31}$, to which Shimizu *et al.* (1993) compared watanabeite. Contained in these replacement aggregates are irregular grains of *aikinite* $\text{Cu}_{4.02}\text{Pb}_{4.04}\text{Bi}_{3.98}\text{S}_{12.01}$ (Paar *et al.* 2002).

A powder diffractogram of the tennantite (Siemens diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation) showed the diffraction maxima of luzonite (Cu_3AsS_4) in addition to those of tennantite.

STRUCTURE DETERMINATION

A silver-grey fragment of irregular shape (size: 0.108 × 0.072 × 0.054 mm) was extracted from a polished section for structure analysis. Data were collected at room temperature (25°C) on a Bruker SMART CCD diffractometer, using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), a crystal-to-detector distance of 3.85 cm and collimator size of 0.5 mm. The data collection covered slightly more than a hemisphere of reciprocal space (2200 frames), by a combination of ω and φ scans and four sets of exposures; each 60-second exposure covered an angular step of 0.2°. Unit-cell parameters were determined from 1065 strong ($I > 8\sigma_I$) reflections. The software SMART (Bruker 1998) was used for data collection, SAINT (Bruker 1996) for integration of intensi-

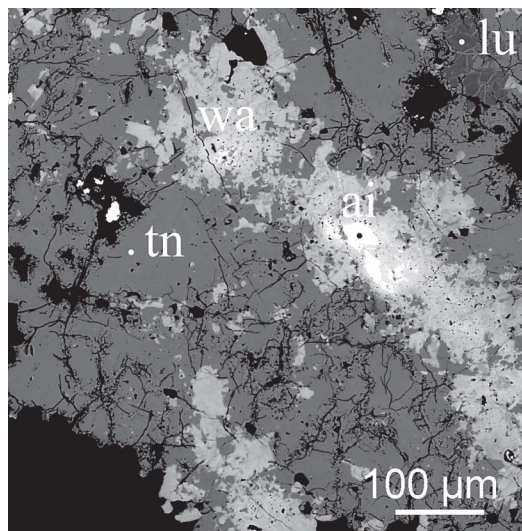


FIG. 1. Back-scattered electron image of a polished surface showing a massive aggregate of tennantite (tn) with sporadic grains of luzonite (lu) and replacement aggregates of watanabeite (wa) with aikinite (ai).

ties, *XPREP* in *SHELXTL* (Bruker 1997) for empirical (Ψ -scan, ellipsoid) absorption correction (with merging R_{int} equal to 0.086 and 0.052 before and after correction, respectively) and *SHELXL97* (Sheldrick 1997) for structure refinement. Crystal data and refinement parameters are listed in Table 1.

TABLE 1. CRYSTAL DATA AND DETAILS OF STRUCTURE REFINEMENT OF Cu-RICH TENNANTITE

Empirical formula	Cu _{3.13} As _{0.96} Sb _{0.07} S _{3.25}
Formula weight	378.35
Crystal system, space group (No.)	Cubic, <i>I</i> $\bar{4}3m$ (217)
<i>a</i> (Å)	10.1756(9)
<i>V</i> (Å ³)	1053.61(16)
<i>Z</i>	8
<i>D_x</i> (Mg m ⁻³)	4.770
μ (mm ⁻¹)	19.800
<i>F</i> (000)	1407
Range for data collection, θ (°)	2.83–31.51
Limiting indices	$-14 \leq h \leq 14, -14 \leq k \leq 13, -14 \leq l \leq 14$
Reflections collected / unique	3991 / 331 [$R_{\text{int}} = 0.0651$]
Completeness to full θ range	99.5%
Transmission coefficients	$T_{\text{min}} = 0.0881, T_{\text{max}} = 0.1591$
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	331 / 0 / 26
Goodness-of-fit, <i>S</i>	1.039
<i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0295, wR_2 = 0.0706$ [‡]
<i>R</i> indices (all data)	$R_1 = 0.0392, wR_2 = 0.0750$
Absolute structure-parameter †	-0.01(4)
Extinction coefficient, <i>k</i> [#]	0.00028(10)
($\Delta\rho$) _{max} , ($\Delta\rho$) _{min} (eÅ ⁻³)	0.680 (1.64 Å from S2), -0.544 (1.25 Å from Cu1)

[‡] $w = 1/[\sigma^2(F_o^2) + (0.0278P)^2 + 8.9857P]$, where $P = (F_o^2 + 2F_c^2)/3$

[†] Flack (1983)

[#] $F_c^* = kF_o[1 + 0.001F_o^2/\lambda^3/\sin(2\theta)]^{-1/4}$

Refinement was initiated using the atom parameters reported for tennantite by Wuensch *et al.* (1966). Scattering factors for neutral atoms were employed. In the

TABLE 2. FRACTIONAL COORDINATES OF ATOMS, AND EQUIVALENT DISPLACEMENT AND OCCUPATION PARAMETERS FOR Cu-RICH TENNANTITE

Atom †	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>	Occupancy
Cu1 (12d)	0.25	0.5	0	0.0238(4)	1
Cu2A (12e)	0.2174(3)	0	0	0.046(2)	0.75(2)
Cu2B (24g)	0.075(2)	0.075(2)	-0.2139(9)	0.050(5)	0.17(1)
As (8c)	0.2586(1)	0.2586(1)	0.2586(1)	0.0180(3)	0.98 [‡]
Sb (8c)	0.2586(1)	0.2586(1)	0.2586(1)	0.0180(3)	0.02 [‡]
S1 (24g)	0.1184(2)	0.1184(2)	0.3570(2)	0.0183(4)	1
S2 (24a)	0	0	0	0.020(1)	1

[†] With Wyckoff position in parentheses. [‡] Fixed according to the results of the chemical analysis. *U_{eq}* is defined as one third of the trace of the orthogonalized *U_i* tensor.

TABLE 3. ANISOTROPIC DISPLACEMENT PARAMETERS (Å²) FOR Cu-RICH TENNANTITE

Atom	<i>U₁₁</i>	<i>U₂₂</i>	<i>U₃₃</i>	<i>U₂₃</i>	<i>U₁₃</i>	<i>U₁₂</i>
Cu1	0.0309(9)	0.0202(5)	0.0202(5)	0.000	0.000	0.000
Cu2A	0.0175(12)	0.060(3)	0.060(3)	-0.032(4)	0.000	0.000
Cu2B	0.057(7)	0.057(7)	0.035(5)	0.018(3)	0.018(3)	0.025(7)
As,Sb	0.0180(3)	0.0180(3)	0.0180(3)	-0.0002(4)	-0.0002(4)	-0.0002(4)
S1	0.0195(6)	0.0195(6)	0.0158(12)	0.0019(5)	0.0019(5)	-0.0001(8)
S2	0.0205(12)	0.0205(12)	0.0205(12)	0.000	0.000	0.000

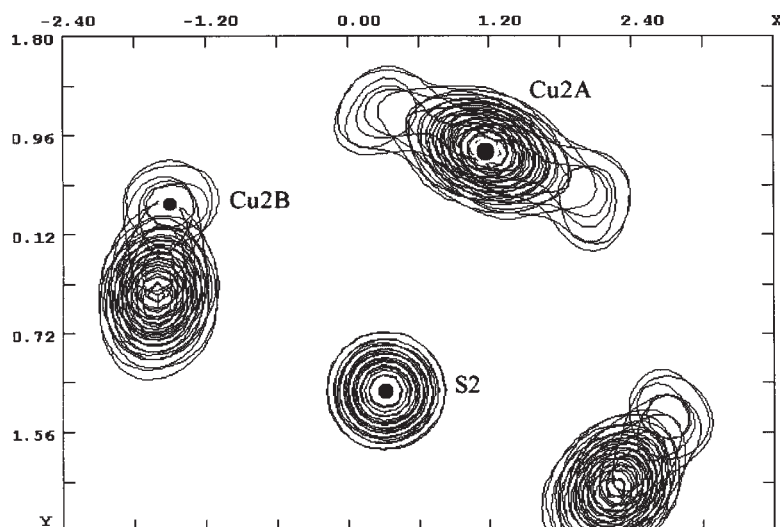


FIG. 2. Fourier map of a diagonal XY section 1.8 Å thick of the unit cell through Cu2A, Cu2B and S2 atoms. Black dots indicate positions of atoms; contours are drawn at 5 e Å⁻³; *z* from -0.9 to 0.9 Å.

last stages of isotropic refinement ($R_1 \approx 0.12$), a relatively strong peak ($7.5 e\text{\AA}^{-3}$) at approximately 1\AA from Cu2A appeared in ΔF maps, which also suggested only partial occupancy of the Cu2A site. After introducing Cu2B at a new position (Table 2, Fig. 2) and further isotropic refinement with free occupancy-factors for Cu2A and Cu2B, a significant drop of all R values (*e.g.*, $R_1 = 0.072$) was observed.

Since almost full occupancy of other sites was confirmed in separate refinements, the occupancies were fixed during the last stage of refinement. The ratio As/Sb was fixed to that determined from the chemical analysis and, because of a very low content of Sb, their positional and displacement parameters were kept equal. As expected, in the case of Cu2A and Cu2B, a strong correlation (coefficients approaching 0.9) was observed between the displacement factors and occupancies.

Cu2A and Cu2B show very elongate ellipsoids oriented with their axes of elongation approximately along a line connecting two Cu2B positions with a Cu2A between them (Fig. 3). This finding suggests a statistical disorder and movement of Cu atoms between these neighboring sites, with Cu2A and Cu2B coordinates representing just the average values for the most common positions. The very elongate ellipsoid of Cu2A (principal mean square displacements of atoms, U : 0.0926, 0.0280, 0.0175 \AA^2) also indicates a potential split of this position, which would move the atom out of the plane formed by the three coordinating S atoms (Table 3). However, attempts to split the Cu2A position invariably resulted in an unstable refinement or increased R factors.

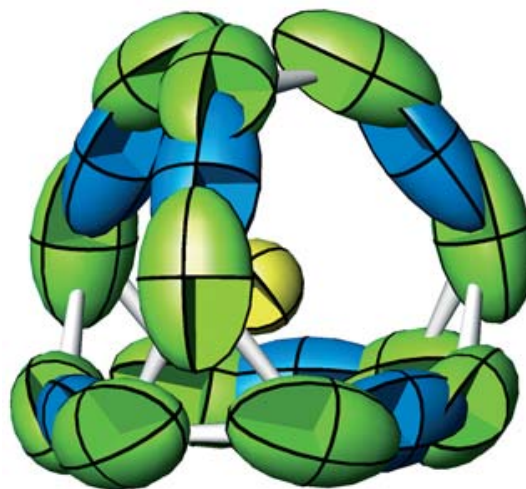


FIG. 3. Environment of S2 (central yellow atom) showing the atom-displacement parameters of Cu2A (blue) and Cu2B (green). Ellipsoids are drawn at 99% probability level.

Refinement results are summarized in Table 2 and 3, with characteristic bond-lengths and angles in Table 4. A table of structure factors has been sent to CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

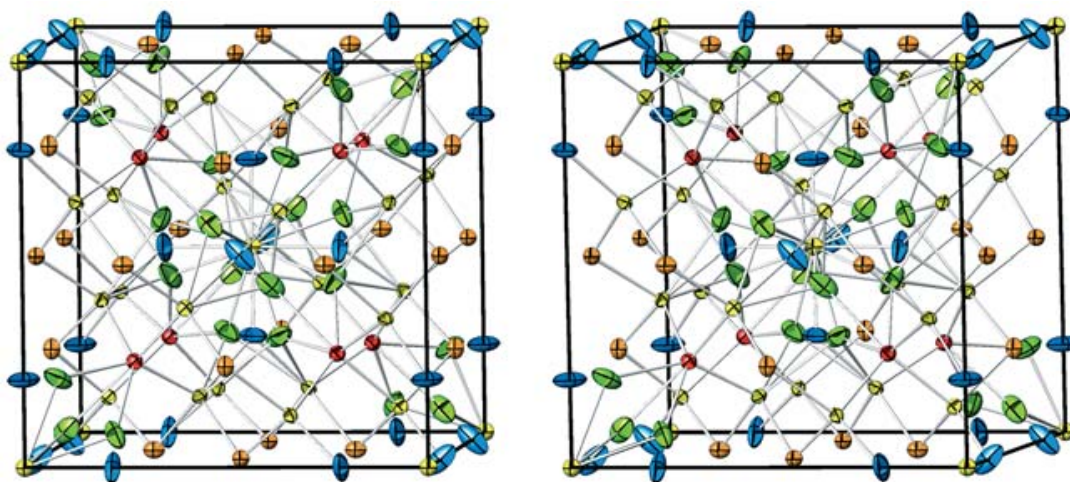


FIG. 4. Stereoview of Cu-rich unsubstituted tennantite. Red: As, yellow: S, orange: Cu1, blue: Cu2A, green: Cu2B. Displacement ellipsoids are drawn at 50% probability level.

DISCUSSION OF RESULTS

Occupancy factors and chemical composition

In the Cu-rich tennantite (Fig. 4), Cu atoms occupy three sites (Table 2): the 12*d* position was found to be fully occupied by Cu1 and subsequently fixed at 100% occupancy, and the other two, Cu2A and Cu2B, fill up 75 and 17% of the 12*e* and 24*g* positions, respectively. This is close to one Cu atom per one Cu2A site plus the two neighboring Cu2B, which suggests that it is mostly only one atom that occupies one of the closely associated sites of this triplet. However, about a 10% surplus of copper is suggested by both structure and chemical analysis. This surplus can be explained by the fact that it is possible to have two Cu atoms at two Cu2B sites flanking a central Cu2A at the same time. At about 10% of sites, therefore, the Cu2B atoms are hindered from moving to and from the Cu2A site because of the other Cu2B atom present on the opposite side of the Cu2A site. The formula obtained by the structural analysis is $\text{Cu}_{12.54}(\text{As}_{0.98}\text{Sb}_{0.02})_{\Sigma 4}\text{S}_{13}$, which is very close to the formula $\text{Cu}_{12.5}(\text{As}_{0.98}\text{Sb}_{0.02})_{\Sigma 4}\text{S}_{12.4}$ calculated from the results of the chemical analysis.

Some attention was given to the fact that the Cu:S ratio obtained by X-ray structure analysis is somewhat lower than that obtained by electron-microprobe analysis. The final ΔF map showed no unusual features or spurious peaks around the refined positions of the atoms. Actually, the highest peak ($0.68 \text{ e}\text{\AA}^{-3}$) in the ΔF map is found 1.64 Å from S2. Therefore, the discrepancy is ascribed to well-known difficulties encountered in electron-microprobe analyses of Cu-rich tetrahedrite, $(\text{Cu}_{12+x}\text{Sb}_4\text{S}_{13})$, and similar tennantite (Lind & Makovicky 1982, Makovicky & Karup Møller 1994). As the structure determination and the electron-microprobe analysis gave the same ratio of Cu to (As + Sb), the problem lies with the determination of S content. Correctness of the structural formula adopted above was further confirmed by comparing the unit-cell parameter of our phase with that of the complete solid-solution field $\text{Cu}_{12+x}\text{As}_4\text{S}_{13}$ in the experiments of Maske & Skinner (1971).

In order to find a possible pattern of order for copper vacancies, we tried to refine the structure in a cubic unit-cell with the same lattice parameter, but in space group *P1*, and with a cubic cell with a triple cell parameter ($a' = 3 \times a$) and the original space-group of tennantite $I\bar{4}3m$. Results of these refinements did not differ from the ones reported above.

Overall features

Primary building units of Cu-rich tennantite are regular Cu1S_4 tetrahedra, $\text{Cu2A-S1}_2\text{-S2}$ triangles and regular (As,Sb) S_3 trigonal pyramids. S1 is surrounded by an As, two Cu1 and a Cu2A atom in a distorted tet-

rahedral arrangement, whereas S2 is coordinated by six Cu2A atoms, making a regular octahedron. Thus, the basic arrangement of atoms in Cu-rich tennantite is the same as that in substituted tennantite ("binnite") and in various samples of tetrahedrite (Pauling & Neuman 1934, Wuensch *et al.* 1966, Wuensch 1964, Johnson & Burnham 1985, Johnson *et al.* 1987, 1988, Makovicky & Karup-Møller 1994, Pfitzner *et al.* 1997, Karup-Møller & Makovicky 1999).

The unique feature of the structure of Cu-rich tennantite is the presence of disordered Cu atoms resulting in the appearance of two partly occupied Cu2 sites, denoted as Cu2A and Cu2B, separated by a distance of only 1.08(2) Å (Table 4, Figs. 3, 4). This situation is similar to that found in so-called copper-rich tetrahedrite, $\text{Cu}_{13.8}\text{Sb}_4\text{S}_{13}$ (Makovicky & Skinner 1979), where Cu disorder also is observed. However, in $\text{Cu}_{13.8}\text{Sb}_4\text{S}_{13}$, it is the Cu1 position that is partly occupied (67%), and an additional Cu3 atom of very low occupancy (*ca.* 10%) is located in the center of the hexagonal SbCu_2S_3 ring (SbS1Cu1S1Cu1S1) that has a chair conformation. Moreover, copper-rich tetrahedrite contains about 28% of total Cu as the mobile portion that could not be located in a harmonic-displacements model used by Makovicky & Skinner (1979).

The published unit-cell parameter of Zn-Fe-bearing tennantite is $10.232 \pm 0.005 \text{ \AA}$ (Wuensch *et al.* 1966), but the sample examined by them contains some Sb (chemical formula: $\text{Cu}_{10.40}\text{Zn}_{1.20}\text{Fe}_{0.40}\text{As}_{3.48}\text{Sb}_{0.52}\text{S}_{13}$). An extrapolated value for a pure As specimen is about 10.20 Å, which is close to the value, 10.19(2) Å, reported by Pauling & Neumann (1934) for $\text{Cu}_{10}\text{Fe}_2\text{As}_4\text{S}_{13}$.

The unit-cell parameter of our Cu-rich tennantite is significantly smaller, more in agreement with the data of Maske & Skinner (1971) for unsubstituted tennantite. From the above-mentioned linear fit, for a composition $\text{Cu}_{12.5}\text{As}_4\text{S}_{13}$, the value of 10.1755 Å is to be expected, compared with the measured value of 10.1756 Å.

These conclusions about unit-cell size apply to unsubstituted tetrahedrite as well. A similar shrinkage of the unit cell was observed: unsubstituted, Cu-poor tetrahedrite $\text{Cu}_{12.3}\text{Sb}_4\text{S}_{13}$ has an *a* of 10.323 Å, which contrasts with an *a* of 10.3908 Å for the partially substituted tetrahedrite $(\text{Cu}_{10.40}\text{Zn}_{1.20}\text{Fe}_{0.33}\text{Pb}_{0.07})(\text{Sb}_{3.94}\text{Bi}_{0.06})\text{S}_{13}$. As noted by Makovicky & Karup-Møller (1994), these variations are primarily a function of the $\text{Cu}^+:\text{Cu}^{2+}$ ratio; this argument will be further elaborated in the discussion of the Cu1-S distances.

The other notable difference between Cu-rich tennantite and the substituted tennantite described by Wuensch *et al.* (1966) is the length of Cu2A-S1 bonds, which are also significantly shorter in Cu-rich tennantite (Table 4). This shortening could primarily be a consequence of the reduced size of the tetrahedral cage composed of pure Cu1 and As polyhedra [the sample investigated by Wuensch *et al.* (1966) displayed 80%

of the maximum allowed substitution by Zn and Fe in the Cu1 position] and partly due to the positional disorder and partial occupancy of the Cu2A site.

Disorder in the Cu2 site

The effect of Cu2 disorder on the structure of tennantite was further tested by calculation of geometrical parameters for Cu2B. In Table 5, these parameters are compared with those of unsubstituted tetrahedrite (Pfitzner *et al.* 1997) and substituted tennantite (Wuensch *et al.* 1966) obtained after a dummy Cu atom was added at the Cu2B position. In Table 5, we demonstrate that the presence of Cu2B atoms does not increase the volume of the S1S1S2(As or Sb) tetrahedron in which Cu2B resides; it actually is smaller in Cu-rich tennantite.

In a static model, and assuming that S2 atoms are preferentially surrounded by Cu atoms at equivalent sites, the S2 atoms are surrounded by six Cu2A atoms in a regular octahedral arrangement in 75% of the cases (Fig. 4). If the large displacement-factors of Cu2A are ignored, the Cu2A–S2 bond distances are equal to 2.212(3) Å. The rest of S2 in the structure has 12 Cu2B neighbors at a longer distance [2.428(9) Å] forming a truncated tetrahedron, also known as a Laves polyhedron (Johnson *et al.* 1988).

In the truncated tetrahedron, clusters of three close Cu2B atoms form a regular triangle (Fig. 5) with edges 2.00(3) Å long. The next shortest Cu2B–Cu2B distance, along the remaining edge of the hexagonal face, is

2.15(5) Å. Both of these distances preclude simultaneous occupancy of two adjacent static Cu2B sites. Figures 4 and 5 illustrate that Cu2A atoms are almost exactly situated on the longer Cu2B–Cu2B edges of the Laves polyhedron, with two equal Cu2A–Cu2B distances of 1.08(2) Å, Cu2B–Cu2B distances of 2.15(5) Å, and the Cu2B–Cu2A–Cu2B angle of 176(1)°. The overall shape and volume of Cu2 clusters are thus largely determined by positions of Cu2B atoms.

If we assume, as above, that S2 atoms are coordinated by either Cu2A or Cu2B at a time, 25% of S2 is coordinated by Cu2B. As the occupancy of the latter site shows, one can conclude that only 68% of Cu2B positions is occupied in the Cu2B polyhedron or, in other words, four of the vertices of a Laves polyhedron are vacant on average. Alternatively, one can propose that Cu2B vacancies correspond to completely vacant coordination-polyhedra (including the central S2 atom). This would result in 8% of vacancies in S2 positions, which is below the sensitivity of both the structure refinement and the chemical analysis (the deficit of S in the EMP analysis obtained is ten times larger than this value). The whole-polyhedron vacancies are unlikely, however, because this would leave relatively large holes in the structure and disturb the local balance of valence.

Comparison with the canfieldite-type structures

There are far-reaching similarities between the configurations of the cage content in the sample of tennantite studied and in cubic γ -Ag₈SiTe₆ and γ -Ag₈GeTe₆ (Boucher *et al.* 1992, 1993), which are canfieldite-type structures. In both cases, the sites and pathways occupied by Cu and Ag are Laves tetrahedra (Figs. 6a, b) with the corners defined by the Cu2B and Ag1* sites, respectively, and six long edges occupied by the Cu2A and Ag2* site (the latter is further split into two positions along each edge). Differences between the two structures pertain to the lack of a visible,

TABLE 4. SELECTED BOND-DISTANCES (Å) AND ANGLES (°) FOR Cu-RICH TENNANTITE

	This work	Wuensch <i>et al.</i> (1966)
Cu1–S1 × 4	2.316(1)	2.337 ± 0.008
Cu2A–S1 × 2	2.219(2)	2.258 ± 0.009
Cu2A–S2 × 1	2.212(3)	2.204 ± 0.008
Cu2A–Cu2B × 2	1.08(2)	
Cu2B–Cu2B [†]	2.00(3)	
Cu2B–S1 × 2	2.486(1)	
Cu2B–S2	2.428(9)	
Cu2B–(As,Sb)	2.41(2)	
(As,Sb)–S1 × 3	2.252(2)	2.246 ± 0.005
S1–Cu1–S1 × 2	109.4(1)	110°58' ± 18'
S1–Cu1–S1 × 4	109.53(6)	108°44' ± 15'
S1–Cu2A–S1 × 1	100.4(2)	101°12' ± 28'
S1–Cu2A–S2 × 2	129.8(1)	129°24' ± 9'
S1–Cu2B–S1	86.6(6)	
S1–Cu2B–S2	109.5(6)	
S1–(As,Sb)–S1 × 3	99.34(7)	98°22' ± 28'
Cu2A–S1–Cu1 × 2	115.70(9)	115°1' ± 24'
Cu2B–S1–Cu1	93.4(4)	
Cu2B–S1–Cu1	137.0(4)	
Cu1–S1–Cu1 × 1	101.95(8)	101°25' ± 19'
Cu2A–S1–(As,Sb) × 1	113.8(1)	114°57' ± 22'
Cu2B–S1–(As,Sb)	110.7(2)	
Cu1–S1–(As,Sb) × 2	104.06(7)	104°25' ± 17'

[†]Symmetry code: y, -z, -x.

TABLE 5. SELECTED GEOMETRICAL PARAMETERS FOR THE Cu2B SITE IN TENNANTITE AND TETRAHEDRITE*

Structure	Mean Cu2B–X bond (Å)	Sphere radius (Å)	Sphere volume (Å ³)	Tetrahedron volume (Å ³)	Reference
Unsubstituted tetrahedrite	2.458	2.445	61.219	7.158	Pfitzner <i>et al.</i> (1997)
Fe,Zn-substituted tennantite	2.466	2.458	62.185	7.333	Wuensch <i>et al.</i> (1966)
Cu-rich tennantite	2.454	2.447	61.405	7.170	This work

* Data describe a coordination tetrahedron S2S1₂(As,Sb) enclosing an observed or hypothetical Cu2B site. Sphere radius and volume refer to the geometrical properties of a sphere, least-squares-fitted to the vertices of tetrahedron (Balić-Zunić & Makovicky 1996).

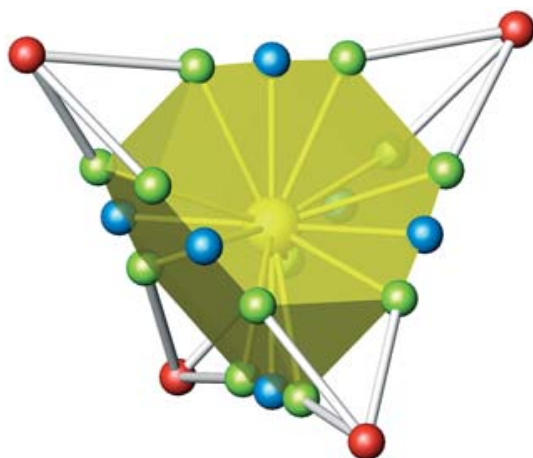


FIG. 5. The coordination polyhedron of S2, with the As atoms (red spheres) at the corners of a slightly distorted tetrahedron. The Laves polyhedron around S2 is indicated in yellow. The color coding for the atoms is the same as in Figure 4.

and occupied, path between the three immediately adjacent Cu2B sites at the tip of the Laves tetrahedron, contrasted by the indirect interconnection of such Ag1* sites *via* the additional Ag3* sites that are situated in adjacent tetrahedra, above the small triangular faces Ag1*–Ag1*–Ag1* of the Laves polyhedron. The distances between Ag1* and Ag3* are very short (0.7 Å) (Fig. 6b).

The occupancy of these sites was refined as Ag1*:Ag2*:Ag3*=17:26:12 in Ag₈SiTe₆ at 20°C (Boucher *et al.* 1992), whereas in the present refinement of tennantite, the occupancy scheme is Cu2B:Cu2A:□ = 17:75:0. However, there are twice as many Ag2* sites as Cu2A; the latter are not split. The similarities of the cage contents are related to similarities in cage configuration. The similarities between the cages of tennantite and Ag₈SiTe₆ are as follows: the icosahedral cage of Ag₈SiTe₆ is outlined by (1) triangular groups of Te atoms that belong to individual SiTe₄ tetrahedra [these Te atoms are analogous to the three S atoms on the “back” side of the AsS₃ pyramids in tennantite] and (2) by isolated Te atoms, which correspond to As atoms involved in interaction with Cu2B. The Ag1*Te₄ tetrahedra correspond completely to the tetrahedra about Cu2B, formed by S2, two S1 and one As atom.

Inspection of atom-displacement parameters (Table 3) and electron-density maps (Figs. 2, 3) shows that Cu2A and Cu2B positions are overlapped. However, it should be remembered that details of Figure 3 are somewhat distorted by the limitation of the refinement to quadratic displacement terms instead of anharmonic

ones. Nevertheless, the overlaps suggest a dynamic character of Cu2 disorder. In the current model, electron density concentrates in linear segments that are organized in a tetrahedron-like framework. The resulting Laves polyhedron is “open” at the positions of Cu2B atoms owing to the above-mentioned lack of direct Cu2B–Cu2B paths (Fig. 3).

The As or Sb atoms lie beyond the missing corners of the truncated Cu2B tetrahedra. The As,Sb–Cu2B distance is 2.41(2) Å, the Cu2B–As,Sb–Cu2B angle is 49.0(4)°, and the As,Sb–Cu2B–Cu2A angle is equal to 171.5(8)° (Fig. 5). The orientation of the (As,Sb)S₁₃ pyramids indicates that the lone-electron pairs of As or Sb are directed along the three-fold axes toward the missing tetrahedron corners. The short As–Cu2B distance suggests that the As,Sb lone-electron pairs *engage in direct interaction* with the valence shells of copper.

The valence of copper

In unsubstituted tennantite or tetrahedrite, charge balance in the formula Cu₁₂X₄S₁₃ shows an excess of two electrons. As already mentioned, this phenomenon can be explained by delocalization of electrons over the crystal toward the valence band of S (Jellinek 1968) or by presence of Cu²⁺ ions statistically distributed over the Cu1 site. Delocalization of electrons is in agreement with the calculations of Pfizner *et al.* (1997), who suggested that Cu₁₂Sb₄S₁₃ can be regarded as metallic.

With increasing Cu content (12 + *x* Cu *apfu*), like in copper-rich tetrahedrite (Makovicky & Skinner 1979) and Cu-rich tennantite, the need for formally divalent copper decreases [*ca.* 0.2 atoms of Cu²⁺ *apfu* in Cu_{13.8}Sb₄S₁₃ and *ca.* 1.5 Cu²⁺ *apfu* in Cu_{12.5}(As_{0.98}Sb_{0.02})₄S₁₃]. The diminishing number of delocalized electrons is accompanied by the increasing presence of excess, disordered Cu atoms. In nature, in almost all instances, divalent elements present in the environment are incorporated instead.

From Cu1–S bond distances (2.316 Å; Table 3) and Shannon’s radius of the S²⁻ ion (1.70 Å; Shannon 1981), it follows that the radius of ¹⁴Cu1 in Cu-rich tennantite is 0.616 Å. Taking into account Cu⁺ and Cu²⁺ radii (0.635 and 0.51 Å, respectively; Shannon 1981, Makovicky & Karup-Møller 1994), one can calculate that Cu1 site contains 85% of formal Cu⁺ and 15% of Cu²⁺. For 6 Cu1 atoms present in the formula unit, this population gives 6.9 positive charges, or 13.4 Cu charges in all assuming that all Cu2 atoms are Cu⁺. This estimate is not too far from 14.0 positive charges necessary to balance negative charges that are not neutralized by As or Sb atoms. If at all significant, this difference might also indicate the presence of a small amount of mobile copper that remains unlocated in the structure determination based on harmonic approximation and in results of the electron-microprobe analyses (see above).

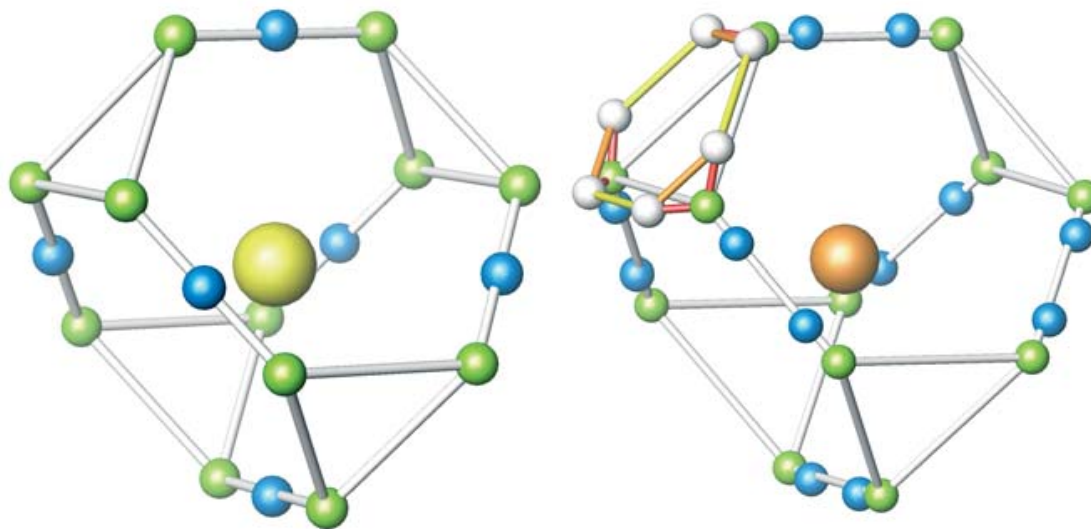


FIG. 6. (a) The Laves polyhedron of copper sites around S2 in $\text{Cu}_{12.5}\text{As}_4\text{S}_{13}$. Cu2A and Cu2B are blue and green, respectively. (b) The Laves polyhedron of silver sites around Te3 in Ag_8SiTe_6 . Ag2* and Ag1* are indicated by blue and green color, respectively; the Ag3* sites (depicted only in the upper left-hand corner) are white.

SOLID-ELECTROLYTE CHARACTER

Copper-rich tetrahedrite (Makovicky & Skinner 1979) and, very possibly, copper-rich tennantite belong to the group of room-temperature solid electrolytes. We ascribe the differences in the positions of diffuse Cu electron-density peaks along the conduction paths in these two compounds to the predominance of As or Sb in the structure, which influences the size of different sites available in the anion framework. Thus, according to the available evidence, copper diffusion in $\text{Cu}_{12+x}\text{Sb}_4\text{S}_{13}$ involves primarily the Cu1 and triangular Cu3 sites, whereas in $\text{Cu}_{12+x}\text{As}_4\text{S}_{13}$, it involves Cu2 and tetrahedral Cu2B sites described here. Crystal-chemical differences are also reflected in the different behavior of these compounds on cooling or quenching: separation of Cu-poor and Cu-rich compositions in tetrahedrite (Makovicky & Skinner 1978) *versus* the absence of such separation in tennantite (Maske & Skinner 1971). By analogy with the ionic conductor $\text{Cu}_{12+x}\text{Sb}_4\text{S}_{13}$, which seems not to be completely “frozen” even at room temperature, $\text{Cu}_{12+x}\text{As}_4\text{S}_{13}$ might not be a fully “frozen” conductor as well.

From the mineralogical point of view, the observed association of unsubstituted, Cu-enriched tennantite, luzonite and an unnamed Cu–As–Sb–Bi sulfide is a rare case of late hydrothermal solutions devoid of ubiquitous Fe, Zn and other divalent elements, which usually enter tennantite as electron donors, keeping its stoichiometry at the classical 12:4:13 composition.

ACKNOWLEDGEMENTS

This study was supported financially by Danish Natural Science Research Council, project “Complex Sulphides”, No. 9901772 (KU 56347). W.H.P. is especially grateful for the support of the Austrian Research Council through grants P11987 and P13974 to cover the field and laboratory work in Argentina and Austria. The authors are indebted to Dr. D. Topa for carrying out the electron-microprobe analyses and to Mrs. Camilla Sarantaris for the assistance with the manuscript. Helpful comments of the referees, Professors Arne Pfitzner and Franklin Foit Jr., as well as the editorial assistance of Professors Nigel J. Cook and Robert F. Martin, are gratefully acknowledged.

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Received November 28, 2003, revised manuscript accepted February 10, 2005.