THE CRYSTAL STRUCTURE OF GABRIELITE, $Tl_2AgCu_2As_3S_7$, A NEW SPECIES OF THALLIUM SULFOSALT FROM LENGENBACH, SWITZERLAND

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ABSTRACT

The crystal structure of gabrielite has been refined using single-crystal data (X-ray diffraction, Mo$K\alpha$, CCD area detector) to a conventional R-factor R_1 of 0.0486. It crystallizes in space group $P\bar{1}$, with a 12.138(3), b 12.196(3), c 15.944(4) Å, α 78.537(5), β 84.715(4), γ 60.470(4)° and $Z = 2$. The chemical formula obtained from the structure analysis is $Tl_6Ag_{2.61}Cu_{6.39}As_{8.55}Sb_{0.45}S_{21}$, in good accordance with the results of the chemical analysis. It can be represented as $Tl_6(Ag,Cu)_3{}^{IV}(Cu,Ag)_6{}^{III}(As,Sb)_9S_{21}$, where IV denotes the tetrahedral, and III the trigonal planar coordinations. There are both isolated AsS_3 pyramidal groups and those forming four-membered rings. The Tl atom shows various coordinations, from trigonal prismatic and antiprismatic to square antiprismatic, and more complex arrangements with coordination numbers 7 and 9. A characteristic feature is the presence of many short contacts between those of Tl atoms, which have more strongly expressed lone-electron pair activity, and Cu atoms (Tl–Cu in the range 3.03–3.08 Å). There is also a short Tl–Tl contact of only 3.09 Å between atoms in flattened trigonal antiprismatic coordination. The same Tl atoms exhibit short Tl–As distances (3.11 Å) across the lone pairs of electrons of As. This Tl coordination is of the same type as that found in Li_5Tl_2. These are the shortest Tl–Cu, Tl–Tl and Tl–As contacts recorded in sulfosalts so far. The crystal structure is layered, with two types of sulfur layers, one with the $3^4.6$ mesh, and the other composed of triangles, squares and pentagons with idealized plane-symmetries $p3$ and $p31m$, respectively. The coordination polyhedra of cations form three main slabs, two with the idealized plane-symmetry $P\bar{3}$ and one with $C2/m$ symmetry. One of the two pseudotrigonal slabs is the starting member of a hypothetical homologous series of cyclically twinned sulfosalt structures. Internal symmetries of the slabs lead to a twin law with (100) as the twin plane, and make possible the existence of several potential OD polytypes.

Keywords: gabrielite, sulfides, sulfosalts, crystal structure, Tl–metal bond.

SOMMAIRE

Nous avons affiné la structure cristalline de la gabrielite au moyen de données en diffraction X (rayonnement Mo$K\alpha$, détecteur à aire de type CCD) obtenues sur monocristal, jusqu'à un résidu conventionnel R_1 de 0.0486. Ce minéral cristallise dans le groupe spatial $P\bar{1}$, avec a 12.138(3), b 12.196(3), c 15.944(4) Å, α 78.537(5), β 84.715(4), γ 60.470(4)°, et $Z = 2$. La formule chimique découlant de l'analyse structurale, $Tl_6Ag_{2.61}Cu_{6.39}As_{8.55}Sb_{0.45}S_{21}$, concorde assez bien avec les résultats de l'analyse chimique. On peut la représenter ainsi: $Tl_6(Ag,Cu)_3{}^{IV}(Cu,Ag)_6{}^{III}(As,Sb)_9S_{21}$; ici, IV indique la coordinence tétraédrique, et III, la coordinence trigonale planaire. Il y a des groupes pyramidaux AsS_3 isolés et en anneaux à quatre membres. L'atome Tl adopte plusieurs coordinences, allant de trigonale prismatique et antiprismatique à antiprismatique carrée, ainsi que des arrangements plus complexes à coordinence 7 et 9. Une caractéristique de cette structure est la présence de plusieurs contacts courts entre les atomes Tl possèdant un caractère fortement exprimé à paires d'électrons isolés, et les atomes de Cu (Tl–Cu allant de 3.03 à 3.08 Å). Il y a aussi un contact Tl–Tl court, seulement 3.09 Å, entre atomes dans une coordinence trigonale antiprismatique applatie.

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Les mêmes atomes Tl font preuve de courtes liaisons Tl–As (3.11 Å) traversant les paires d'électrons isolés de As. Cette coordinence du Tl est du même genre que dans le composé Li₅Tl₂. Il s'agit des contacts Tl–Cu, Tl–Tl et Tl–As les plus courts qui aient été signalés dans les sulfosels jusqu'à ce point. La structure est faite de couches, avec deux sortes de couches portant le soufre, une avec un réseau 3⁴.6, et l'autre composée de triangles, de carrés et de pentagones, avec des symétries planaires idéalisées de p3 et p31m, respectivement. Les polyèdres de coordinence des cations forment trois plaques, deux avec une symétrie planaire idéalisée P3̄ et une avec la symétrie C2/m. Une des deux plaques pseudotrigonales est en fait le point de départ d'une série hypothétique d'homologues de structures cycliquement maclées de sulfosels. Les symétries internes de ces plaques mènent à un loi de macle ayant (100) comme plan de macle, ce qui rend possible l'existence de plusieurs polytypes OD potentiels.

(Traduit par la Rédaction)

Mots-clés: gabrielite, sulfures, sulfosels, structure cristalline, liaison Tl–métal.

Introduction

Gabrielite is a new species of Tl sulfosalt from Lengenbach, Switzerland. It was found as pseudo-hexagonal tabular metallic black crystals associated with realgar, rathite, trechmannite, tennantite, hatchite and hutchinsonite, definitely restricted to a zone very rich in arsenic and thallium. Preliminary X-ray photographs showed crystals to be pseudohexagonal, the real symmetry being monoclinic or lower. A full description of paragenesis and properties of this new mineral species is presented in a companion article (Graeser *et al*. 2006). For the determination of crystal structure, two crystal fragments were chosen. The larger one showed fine-scale splitting of some diffraction spots, most probably owing to the twinning common in gabrielite, whereas the other one gave a satisfactory single-crystal pattern.

Experimental

The chemical formula of gabrielite was determined by electron-microprobe analysis before its extraction from a polished section. The average results for 11 points calculated on the basis of 45 atoms yielded the formula $Tl_6Ag_{2.58}Cu_{6.55}As_{8.29}Sb_{0.48}S_{21.14}$ (Graeser *et al*. 2006). No significant compositional variations were detected for any of the elements.

An irregular fragment of approximate dimensions 0.13 × 0.09 × 0.07 mm was used for crystal-structure analysis. Room-temperature data (298 K) were collected on a Bruker-AXS four-circle diffractometer equipped with a Smart1000 CCD area detector (6.25 × 6.25 cm active area with a resolution of 81.92 pixels cm⁻¹) and a flat graphite monochromator, using Mo$K\alpha$ radiation from a fine-focus sealed X-ray tube. The sample-to-detector distance was 4.0 cm. A total of 1780 exposures (frame width = 0.3°, time = 45 s) were collected. Of 11589 measured reflections, 7166 were unique and 4687 were stronger than $2\sigma(I)$.

The crystal-lattice parameters are very close to a monoclinic symmetry (a transformation 0,1̄,0/2,1̄,0/0,0,1 produces a *C* lattice with parameters *a* 12.196 Å, *b* 21.124 Å, *c* 15.944 Å, α 90.509°, β 101.463°, γ

89.374°); therefore, the refinement of the unit-cell parameters, as well as the structure solution, was attempted in both the monoclinic and the triclinic systems. The results suggested a triclinic symmetry for the crystals, because a significantly better goodness of fit was obtained when the monoclinic constraint was removed. Final unit-cell parameters were refined using 859 strong reflections (2θ from 7.5 to 55.8°) with $I > 10\sigma(I)$.

The software SMART was used for the lattice determination and data collection, SAINT for the integration of intensities, a Lorentz-polarization correction and calculation of the final unit-cell parameters. The empirical absorption-correction (program XPREP from the SHELXTL package) using 905 reflections and an ellipsoid approximation yielded merging R_{int} = 0.0341 compared to R_{int} = 0.0719 before the correction. Minimum and maximum transmission factors were 0.0867 and 0.1825, respectively. All software is produced by Bruker-AXS. Other crystal and measurement data are given in Table 1.

The structure was solved by direct methods (SHELXS97, Sheldrick 1997a) which revealed the

TABLE 1. CRYSTAL AND MEASUREMENT DATA FOR GABRIELITE

Empirical formula (XRD)		$Tl_6Ag_{2.61}Cu_{6.39}As_{8.53}Sb_{0.48}S_{21}$	
Formula weight, M_r	3282.40	Crystal system	Triclinic
Space group (no.)	P1̄ (2)	Z	2
a (Å)	12.138(3)	F(000)	2870
b (Å)	12.196(3)	μ (mm⁻¹)	36.822
c (Å)	15.944(4)	ρ_x (g cm⁻³)	5.416
α (°)	78.537(5)	Range for data	1.93–
β (°)	84.715(4)	collection, θ (°)	26.37
γ (°)	60.470(4)		
V (Å³)	2012.7(9)		
Limiting indices		−15 ≤ h ≤ 15, −14 ≤ k ≤ 15, −19 ≤ l ≤ 19	
Reflections collected / unique		11589 / 7166 (R_{int} = 0.0531)	
Data / restraints / parameters		7166 / 0 / 419	
Extinction coefficient, k ⁑		0.00032(3)	
Goodness-of-fit, S		0.909	
R indices [$I > 2\sigma(I)$]		R_1 = 0.0486, wR_2 = 0.0913 ‡	
R indices (all data)		R_1 = 0.0834, wR_2 = 0.0991	

⁑ $F_c^* = kF_c[1 + 0.001F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
‡ $w = 1/[\sigma^2(F_o^2) + (0.0363P)^2]$, where $P = (F_o^2 + 2 F_c^2)/3$

positions of Tl and Ag, as well as of some As and Cu atoms. The remaining atoms were found in difference-Fourier maps during the subsequent isotropic and finally anisotropic refinements of all atoms by full-matrix least-squares on F^2 (SHELXL97, Sheldrick 1997b). The refinement indicated six fully occupied Tl sites. According to their scattering power and coordinations, nine sites were identified as Ag, Cu or mixed [Ag,Cu] sites, while another nine were found to be As or mixed [As,Sb] sites. In the final least-squares cycles, all 18 sites were refined as mixed [Ag,Cu] or [As,Sb] sites, constraining each one to full occupancy. The results converged very closely on the values obtained by the chemical analysis (Table 1). The structure solution and refinement confirmed the true symmetry of the structure to be triclinic $P\bar{1}$.

The majority of [Cu,Ag] sites showed mixed occupancy. Only Cu3 refined to a single-element value (Table 2). In the case of [As,Sb] sites, the majority contained only As, with As3, As4, As6, and As8 showing a minor Sb content (5–15%). Attempts to refine the positional and displacement parameters for atoms at mixed sites independently failed because the refinement became unstable. Therefore, identical fractional coordinates and displacement parameters for both atoms were applied. Full and unique occupancies were assumed for all thallium and sulfur sites. The highest residual maximum and minimum in the last difference-Fourier map are 3.14 e Å^{-3} (0.94 Å from Tl4) and –1.61 e Å^{-3} (1.45 Å from Tl4).

The final coordinates of the atoms are presented in Table 2. The full data with anisotropic displacement parameters, together with the list of observed and calculated structure-factors, are deposited in the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

DESCRIPTION OF THE STRUCTURE

The crystal structure of gabrielite (Fig. 1) has a distinct layered character, with the layers parallel to (001). Sulfur atoms form layers with two mesh-types. Type 1 hosts a $3^4.6$ mesh which, if idealized, corresponds to an Archimedean tiling with symmetry $p6$ (O'Keeffe & Hyde 1996), but in gabrielite, is reduced to $p3$ symmetry owing to ditrigonalization of the hexagons (Figs. 2a–b). Type 2 consists of four-connected triangles, tetragons and pentagons (Fig. 2c), and is similar to the oxygen layer found in the structure of $K_3V_5O_{14}$ (O'Keeffe & Hyde 1996). However, the latter compound is formed of a combination of coordination octahedra and trigonal bipyramids of V, whereas in gabrielite, quite different kinds of Tl coordination polyhedra are formed between two such layers. The plane-group symmetry of this layer is $p31m$.

The crystal structure can be divided into three types of regularly alternating (001) slabs, each of which shares layers of common S atoms with adjacent slabs:

I) The thickest slab comprises four sulfur layers of type 1. It is situated between z approximately –0.20 and 0.20, and hosts coordination polyhedra As4–9 and Tl5–6 (Fig. 3). II) A slab situated between the two different types of sulfur layers and composed of AsS$_3$ coordination pyramids combined with (Cu,Ag)S$_3$ coordination triangles and (Ag,Cu)S$_4$ tetrahedra (Fig. 4). Its boundaries lie between $z \approx 0.20$ and ≈ 0.36. III) A slab of pure Tl coordination polyhedra between $z \approx 0.36$ and ≈ 0.64, bordered by the two sulfur layers of type 2 (Fig. 5).

TABLE 2. ATOM COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS FOR GABRIELITE

Atom	x	y	z	U_{eq} (Å^2)	Occupancies
Tl1	0.38351(7)	0.48556(7)	0.43115(5)	0.0312(2)	1
Tl2	0.23349(7)	0.89114(8)	0.49914(6)	0.0388(2)	1
Tl3	0.62806(7)	0.84668(8)	0.46356(6)	0.0385(2)	1
Tl4	–0.00007(8)	0.27521(9)	0.46826(6)	0.0471(3)	1
Tl5	0.66667(7)	0.64355(8)	0.09277(6)	0.0389(2)	1
Tl6	0.98277(9)	–0.0079(1)	0.09798(6)	0.0502(3)	1
Cu1	0.1340(2)	0.6009(2)	0.2828(2)	0.0388(8)	0.62(2)
Ag1					0.38(2)
Cu2	0.1853(2)	0.0675(2)	0.2747(2)	0.0362(9)	0.86(2)
Ag2					0.14(2)
Cu3	0.6677(2)	0.1094(2)	0.2695(2)	0.0333(6)	1
Cu4	0.9877(2)	0.4746(2)	0.3155(2)	0.0320(9)	0.94(2)
Ag4					0.06(2)
Cu5	0.4554(2)	0.8991(2)	0.3143(2)	0.0349(9)	0.94(2)
Ag5					0.06(2)
Cu6	0.5796(2)	0.3587(2)	0.3002(2)	0.0410(1)	0.90(2)
Ag6					0.10(2)
Cu7	0.8453(2)	0.2692(2)	0.2835(1)	0.0335(8)	0.74(2)
Ag7					0.26(2)
Ag8	0.8334(1)	0.7523(2)	0.2846(1)	0.0311(6)	0.84(2)
Cu8					0.16(2)
Ag9	0.3348(1)	0.7544(2)	0.2806(1)	0.0318(6)	0.79(2)
Cu9					0.21(2)
As1	–0.0071(2)	0.9304(2)	0.2972(1)	0.0173(4)	1
As2	0.6726(1)	0.5751(2)	0.3357(1)	0.0144(4)	1
As3	0.3332(2)	0.2538(2)	0.2878(1)	0.0181(6)	0.95(1)
Sb3					0.05(1)
As4	0.6547(2)	0.3772(2)	0.0767(1)	0.0201(6)	0.87(1)
Sb4					0.13(1)
As5	0.3347(1)	0.5449(2)	0.1504(1)	0.0184(4)	1
As6	0.3920(1)	0.9315(2)	0.0763(1)	0.0190(6)	0.84(1)
Sb6					0.16(1)
As7	0.5890(2)	0.0339(2)	0.1548(1)	0.0183(4)	1
As8	0.9525(2)	0.6356(2)	0.0761(1)	0.0193(6)	0.89(1)
Sb8					0.11(1)
As9	0.0814(2)	0.2971(2)	0.1535(1)	0.0175(4)	1
S1	0.8184(4)	0.9306(4)	0.3576(3)	0.022(1)	1
S2	0.1479(4)	0.7430(5)	0.3627(3)	0.034(1)	1
S3	0.0106(4)	0.0724(5)	0.3581(3)	0.029(1)	1
S4	0.8221(4)	0.5819(4)	0.4070(3)	0.022(1)	1
S5	0.4915(4)	0.7057(4)	0.4014(3)	0.019(1)	1
S6	0.7016(4)	0.3778(4)	0.3975(3)	0.021(1)	1
S7	0.5071(4)	0.2152(4)	0.3599(3)	0.023(1)	1
S8	0.1863(4)	0.3989(5)	0.3657(3)	0.027(1)	1
S9	0.3171(4)	0.0807(4)	0.3621(3)	0.025(1)	1
S10	0.7640(4)	0.2076(4)	0.1805(3)	0.028(1)	1
S11	0.4630(4)	0.3752(4)	0.0821(3)	0.022(1)	1
S12	0.2807(4)	0.7213(4)	0.0406(3)	0.026(1)	1
S13	0.4834(4)	0.5567(4)	0.2135(3)	0.023(1)	1
S14	0.2332(4)	0.9487(5)	0.1691(3)	0.030(1)	1
S15	0.3998(4)	0.1179(4)	0.0861(3)	0.023(1)	1
S16	0.7330(4)	0.9695(5)	0.0454(3)	0.026(1)	1
S17	0.6114(4)	0.8430(4)	0.2160(3)	0.022(1)	1
S18	–0.0059(4)	0.7294(5)	0.1687(3)	0.026(1)	1
S19	0.1415(4)	0.4423(4)	0.0840(3)	0.022(1)	1
S20	0.9862(5)	0.2717(5)	0.0453(3)	0.028(1)	1
S21	0.9053(4)	0.4274(4)	0.2156(3)	0.024(1)	1

Slab I encompasses four S layers (including the bordering ones) of Type 1 with a $3^4.6$ mesh in a stacking sequence of A–B–A–B type. The meshes of the outer and inner S layers are not of a perfectly equal size owing to coordination requirements of cations (Fig. 3). The three-fold axes of subsequent layers superimpose, and the resulting symmetry of the slab is $P\bar{3}$, where one-third of the triad axes are rotoinverse ($\bar{3}$). The Tl atoms in this slab are situated in trigonal-prismatic coordinations on simple triad axes (Tl5), and antiprismatic coordinations on rotoinverse triad axes (Tl6). The slab contains additional trigonal prismatic and "lying" square-pyramidal voids. The arsenic atoms occupy prism faces of the trigonal prismatic voids, which are at the same time the bases of the "lying" square-pyramidal voids (Fig. 3).

Idealized and expanded infinitely perpendicular to the slab plane, the slab I would produce a structure with the $P6_3/m$ symmetry. It would be a hypothetical new member of the family of cyclically twinned sulfosalt structures (Makovicky 1985). The composition of this member would be XY_2S_4, where X and Y represent the large cations in trigonal channels, and small cations in square-pyramidal coordinations, respectively. In case of Y being a trivalent cation (like As^{3+}), the X cation should be divalent to satisfy the charge balance. This hypothetical structure represents the starting member of a hypothetical homologous series proposed by Makovicky (1985), with hexagonal rods of capped trigonal prisms, trigonal channels and intervening PbS-like rods (Fig. 6). In slab I in gabrielite, the rods of a PbS-like structure are missing, and hexagonal rings surrounding 6_3 channels (similar to those in the structure of zinkenite) are interconnected directly, forming the trigonal prismatic channels between them (Fig. 7).

The sulfur layers that border slab II (Fig. 4) are superimposed in such a way that the triangles or hexagons from the Type-1 layer come in inverted position over triangles from the Type-2 layer. The symmetry of slab II is trigonal, like that of slab I. Arsenic atoms in this slab occupy positions on triad axes forming AsS_3 pyramidal groups with As on apices, their lone-electron pairs pointing toward slab I. The Cu and Ag atoms occupy trigonal-planar and tetrahedral coordinations. Combinations of two coordination triangles and one tetrahedron make $[Ag,Cu]_3S_7$ rings. Three different configurations of these groups are formed around As coordination pyramids. Atoms labeled As1 is situated over Tl6 from the slab I, and on the intersection of three mirror planes of the plane group $p31m$ of the Type-2 sulfur layer. It is surrounded by three $[Ag,Cu]_3S_7$ groups, of which each one shares two marginal S atoms with two corners of the $As1S_3$ pyramid. Each of the pyramidal groups of As2 and As3 (both placed over Tl5) has three $[Ag,Cu]_3S_7$ rings attached, one ring to each corner of the pyramidal base, but in two different ways. Around As2, the $[Ag,Cu]_3S_7$ groups are mutually

interconnected, whereas those attached to As3 coordination pyramid do not share common S atoms. Owing to such arrangements, the As3 atom is not approached by additional S atoms in this slab, unlike the As1 and As2 atoms, which have three additional atoms of sulfur each, completing their coordination to distorted trigonal antiprisms. Three more distant S atoms, which form the smaller base of the Tl5 coordination prism and are situated inside slab I, complete the environment of As3 to make a distorted (skew) trigonal prism. The resulting idealized symmetry of the full II-I-II sandwich is $P\bar{3}$.

Slab III (Fig. 5) is sandwiched between two sulfur layers of Type 2. The mutual displacement of these layers is parallel to one of the mirror planes of their idealized $p31m$ symmetry, which closely approximates $C2/m$ symmetry, and which is reflected also in the arrangement of Tl atoms. Slab III contains four distinct Tl sites. Above each of pentagons from a Type-2 sulfur layer, one of the Tl1, Tl3, or Tl4 atoms is situated. These atoms are moved from the median plane of slab III toward the respective layer of sulfur. Two-thirds of the squares from a sulfur layer are superimposed over the squares of the other layer in antiprismatic orientation, with Tl2 atoms situated between them. Tl2 is positioned close to the median plane of the slab III. In the case of Tl1 and Tl3 coordination polyhedra, the pentagons of one sulfur layer are superimposed over an edge separating a triangle and a pentagon in the other layer. These two coordinations become equivalent in the idealized $C2/m$ symmetry of the slab. The pentagon from the Tl4 coordination lies over an edge separating a triangle and a square in the other Type-2 sulfur layer. It is the third, "empty" square that is not included in the coordination of Tl2.

A substantial difference in the internal symmetries of the II–I–II slab sandwich ($P\bar{3}$) and of the slab III ($C2/m$) leaves the centers of symmetry in both layer groups as the only common element of symmetry resulting in the overall triclinic symmetry of the structure. However, the underlying trigonal symmetry of all sulfur layers explains the pseudohexagonal habit of crystals. This fact, combined with the stacking direction of the neighboring Type-2 sulfur layers, which produces the monoclinic symmetry of slab III, explain the nearly monoclinic symmetry of the gabrielite lattice. The latter points to a probable mechanism of twinning in this structure.

TWINNING AND POTENTIAL POLYTYPY

The two sides of a sulfur layer of Type 1 ($3^4.6$ net) are enantiomorphs (Figs. 2a–b). Because of this, a II–I–II slab sandwich turned upside-down is a mirror image of the same sandwich in the starting orientation. Slab III contains the mirror symmetry of the layer group $C2/m$ and has no such property. Therefore, attachment of a slab III to an inverted II–I–II sandwich induces
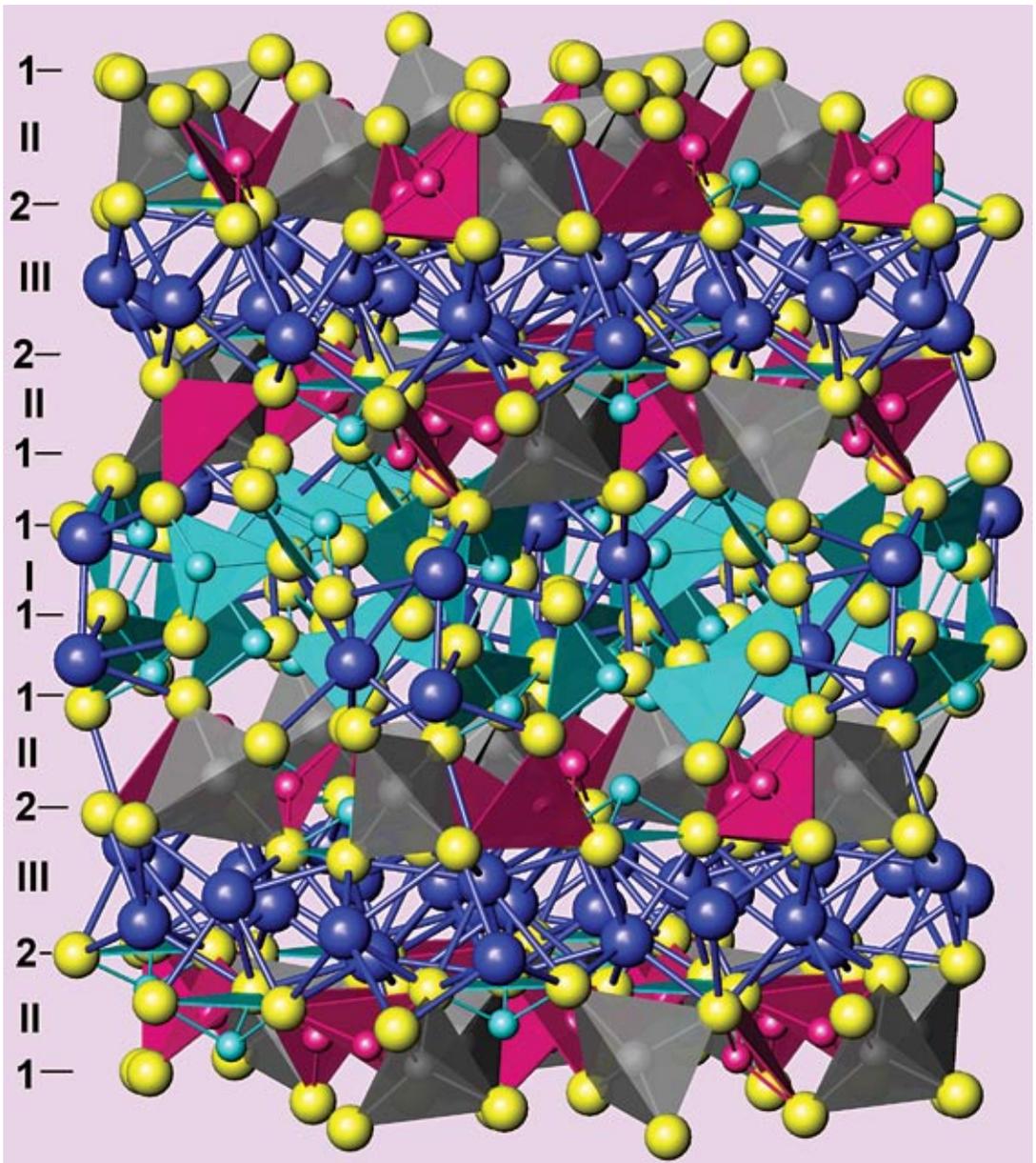
FIG. 1.   The crystal structure of gabrielite, with the characteristic structural slabs and sulfur layers indicated. The c axis is approximately vertical. Symbols: Tl blue, S yellow, Ag grey, Cu red and As(Sb) green. Coordinations of Ag, Cu and As are colored semi-transparent. For mixed Ag and Cu sites, the colors are determined by the predominant cation except for Cu7, which is grey like all tetrahedraly coordinated cations, but smaller in size than Ag atoms.

no changes in the idealized structure among either the first- or the second-coordination neighbors if compared to the attachment to a II–I–II sandwich in its initial orientation. Such an event is the equivalent of twinning, with the mirror plane from the layer group of slab III taking the role of the twin plane, which is parallel to the (100) plane of gabrielite. In the real structure, the twinning would produce only very small displacements

of atoms from ideal "monoclinic" values (deviations of α and γ from right angles are only up to 0.5°). This kind of twinning is therefore very probable and is assumed to be common in crystals of gabrielite.

The gabrielite structure shows features that rank among the class of order–disorder (OD) structures (Dornberger-Schiff 1956). The OD character of gabrielite becomes understandable when the structure is described as a stacking of three non-polar OD layers: the II–I–II layer with layer symmetry $P\bar{3}$, the sheet of type-2 sulfur with layer symmetry $P\bar{6}2m$, and the layer III with layer group $C2/m$. There are three possible positions of the layer III on the trigonal layer of Type-2 sulfur, and two possible positions for the II–I–II slab on the latter. This results in six possible positions of

the layer III relative to the II–I–II slab; the twin law described above is a part of this set.

Whereas the symmetrical Sb–As distribution in the interior of slab I (see below) does not seem to influence the polytypism (or its absence), the distribution of Cu–Ag in slab II violates its idealized trigonal symmetry (a desymmetrization of the polytype layer) and can be regarded as responsible both for the deviation of the crystal's lattice parameters from ideal pseudosymmetric values, and for the stabilization of the simplest polytype represented by the present structure. With a different Ag:Cu ratio, a negligible deviation from the idealized symmetry in slab II could be achieved, and both two-layer polytypes with two alternating stacking vectors at 120° [in projection on (001)] to each other
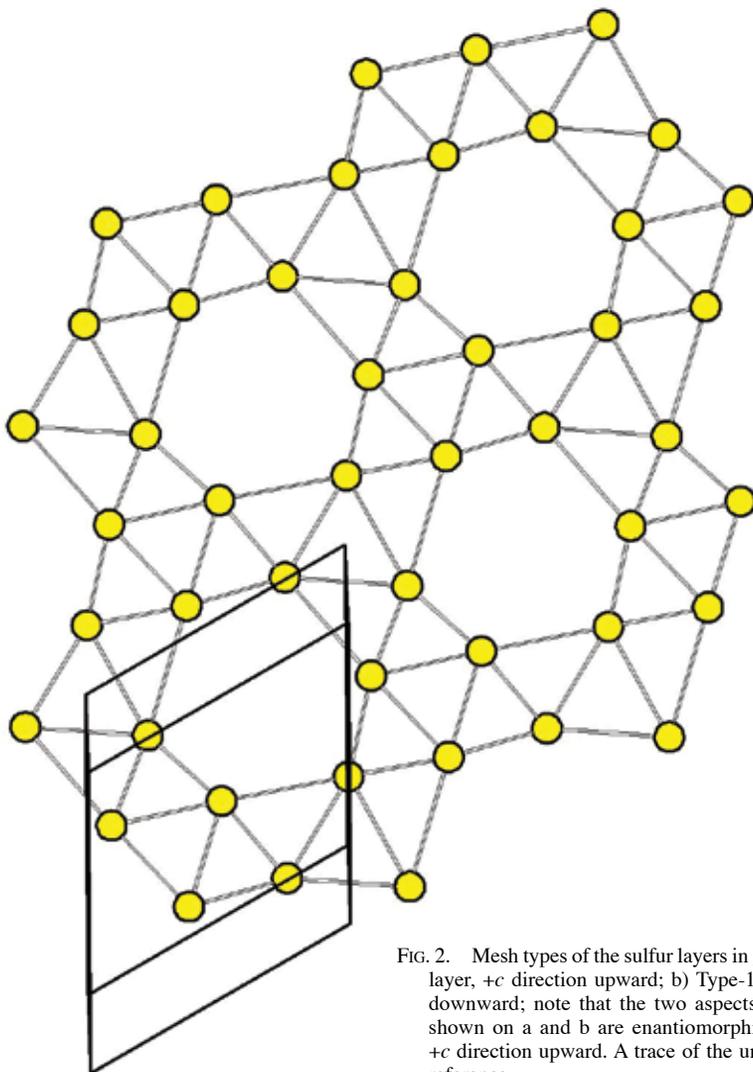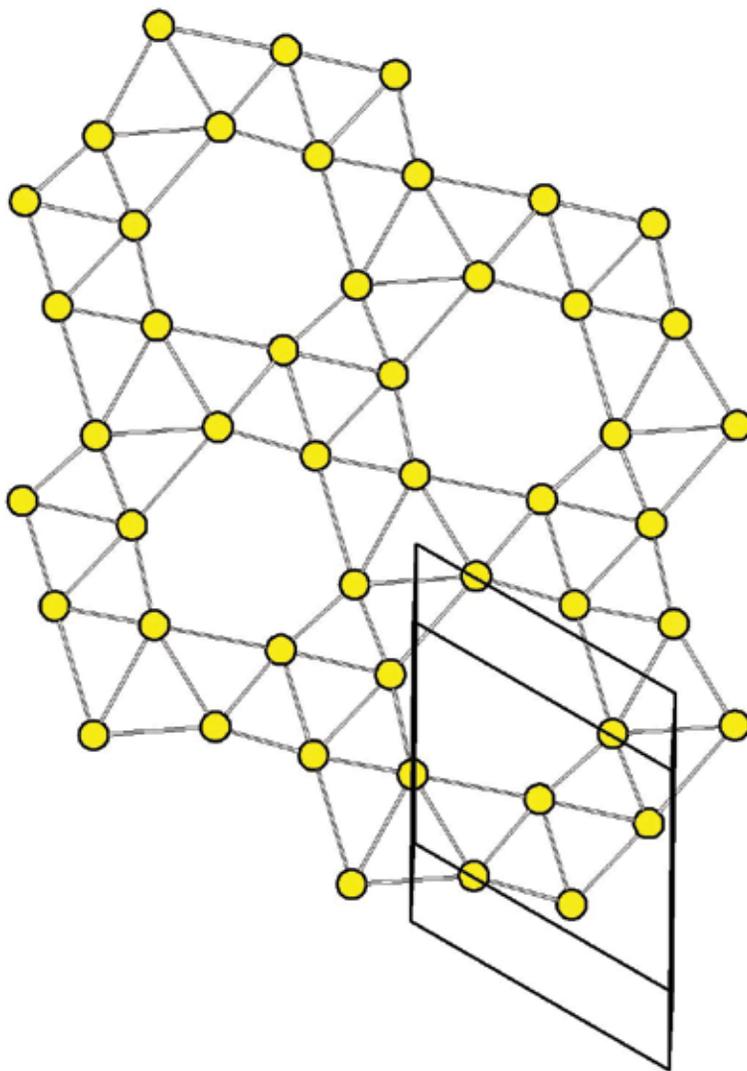

FIG. 2.   Mesh types of the sulfur layers in gabrielite. a) Type-1 layer, +c direction upward; b) Type-1 layer, +c direction downward; note that the two aspects of the same layer shown on a and b are enantiomorphic. c) Type-2 layer, +c direction upward. A trace of the unit cell is drawn for reference.
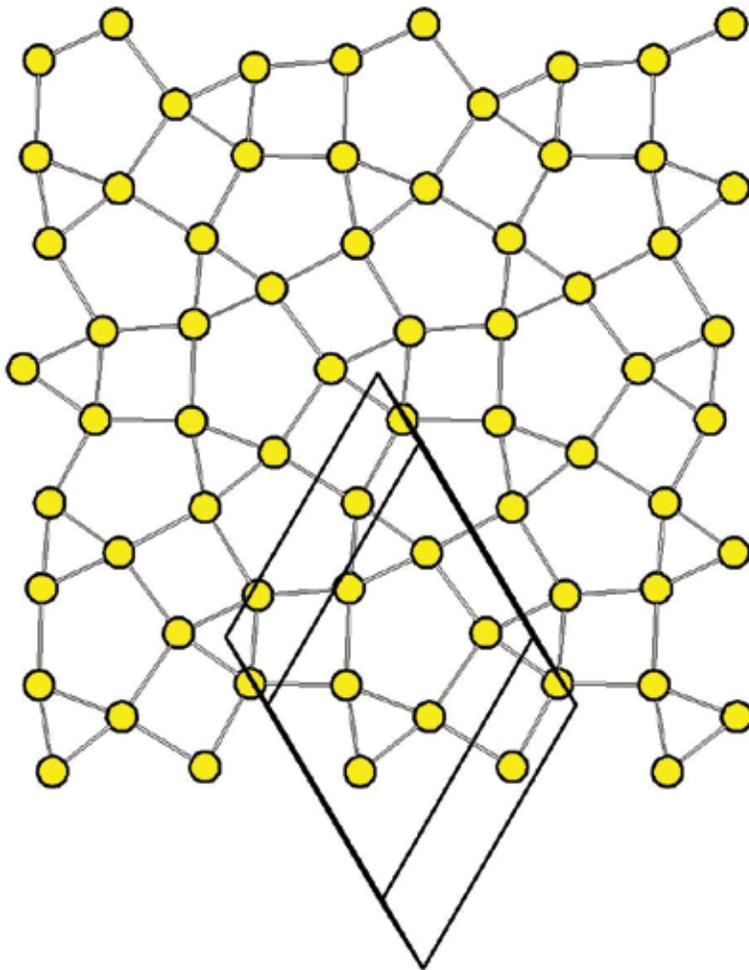
can be expected, along with the trigonal three-layer polytypes with all three stacking vectors applied in a spiral sequence.

COORDINATION POLYHEDRA OF ARSENIC, COPPER AND SILVER

As is usual in sulfosalts, all As atoms have three short bonds to sulfur in a form of a trigonal pyramid. There are isolated AsS_3 groups (involving As1–3) in slab II, and As_4S_8 rings in slab I (involving As4–9). The four-fold rings with a chair conformation are formed by a regular alternation of S and As and four additional S atoms oriented toward the ring exterior. All As–S–As angles in the rings are in the range 101–103°, whereas S–As–S angles are either 92–93° or 102–103°, depending on the extent of As-for-Sb substitution (see below). Median planes of these puckered rings are perpendicular to (001) and are grouped with three rings forming narrow channels around Tl5, and six rings forming broad channels around Tl6 atoms (Fig. 3). The former channels are plugged on one side by As3, and on the other by the As2 coordination pyramid, whereas As1 pyramids plug both ends of the broader channels. Apices of the pyramids (and the lone pairs of electrons of As1–3) point into the channels, toward the Tl6 atoms. The lone pairs of electrons of the ring As atoms point into the trigonal prismatic voids that surround coordination prisms of Tl5 (Fig. 3). Rings and isolated AsS_3 pyramids are interconnected by the Cu and Ag coordina-

tions, which form the slab II. Slab III, with the rest of Tl coordination polyhedra, is formed between the planes defined by the bases of the isolated AsS_3 pyramids. Based on As_nS_m complex anions, the general formula of gabrielite can be written as $X_2Y_3[AsS_3][As_2S_4]$, where X represents the large monovalent cation (Tl), and Y, the small monovalent cation (Cu or Ag).

Refinement of site occupancies shows a 11–16% substitution of Sb for As in the As_4S_8 rings on sites As4, As6 and As8, which lie closer to the central plane of the slab I (Table 2, Fig. 8). To a lesser extent, Sb occupies the As3 site in slab II. This is reflected in an increase in bond distances and a decrease in bond angles due to the increased Sb content (Table 3). If the full surroundings of As1 and As2 in slab II is considered, they have distorted trigonal antiprismatic coordinations (with the base comprising three short bonds, and thus having a smaller area than the opposite one). As(Sb)3 has a

somewhat skewed trigonal prismatic coordination, with the three more distant S atoms situated deeper in slab I. Volume distortions (Makovicky & Balić-Žunić 1998) of these polyhedra (Table 4) show that all three deviate significantly from a regular octahedron (which has the largest volume-capacity for the coordination number 6, and consequently no distortion). The coordination of As3 has the largest distortion (20%), which is still better than the volume capacity of a regular trigonal prism (25% volume distortion compared to a regular octahedron).

The bases of square pyramids "lying flat" in the slab I occupied by [As,Sb]4, [As,Sb]6 and [As,Sb]8 (all with 10–15% Sb in the site) have a clearly defined trapezoidal character. Considering only the short bonds, these As(Sb) atoms are side-bonded to two sulfur atoms of the pyramidal base. The bases of pyramids of top- (or bottom)-bonded As5, As7 and As9, situ-
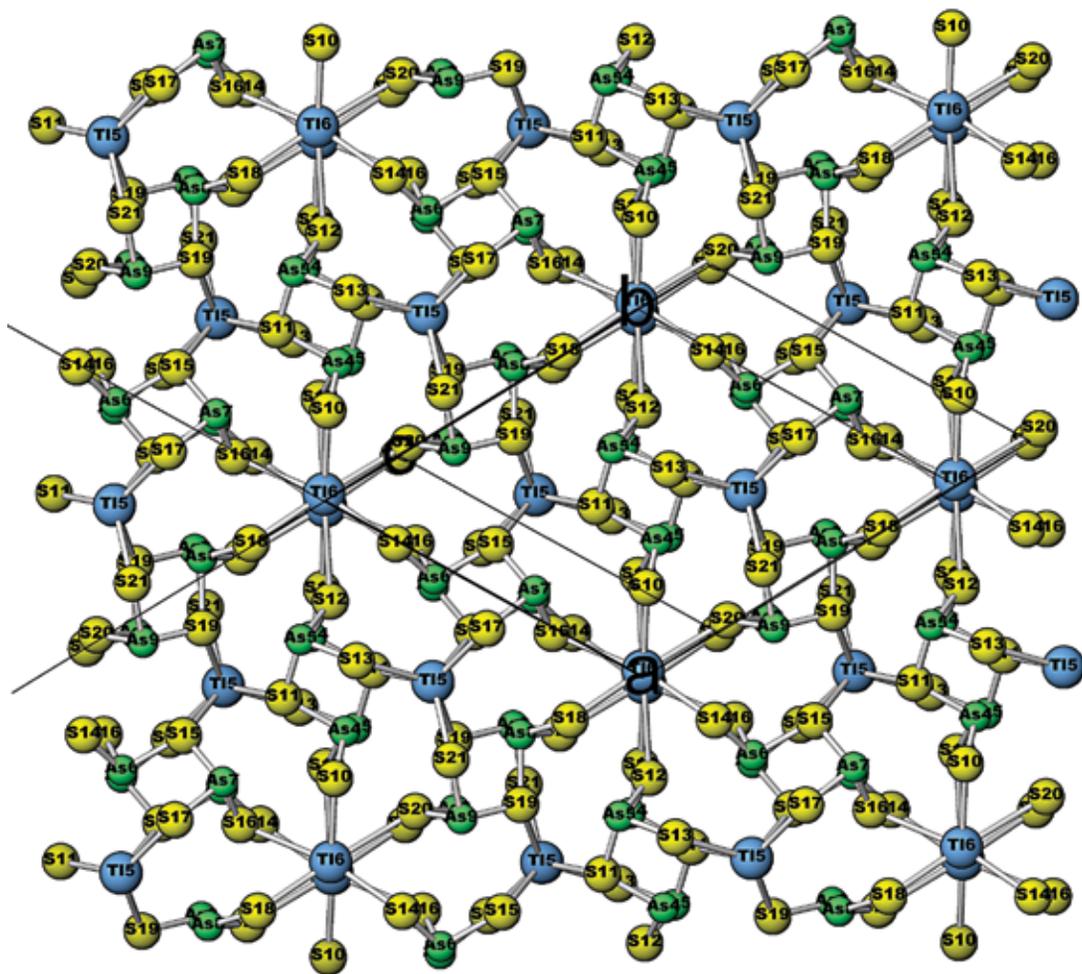
FIG. 3. The thick slab I is composed of Tl and As(Sb) coordination polyhedra, between $z \sim$ –0.20 and 0.20 comprising four sulfur layers of Type 1. A trace of the unit cell is drawn for reference.

ated in the pyramidal columns below or, alternatively, above the former, reach with two of their sulfur atoms the boundary between the slabs II and III and are exceedingly drawn out, "dissolved" by the coordination requirements of other cations in slab II. The fragments of crankshaft chains of strong [As,Sb]–S bonds (Berlepsch *et al.* 2001) on the opposite sides of a double column of square pyramids run parallel to each other and form the above-mentioned As_4S_8 rings (Fig. 8). As all these atoms occupy the faces of bicapped trigonal prismatic voids in slab I, the full coordination-number is effectively 8. As can be seen from Table 4, the full coordinations of these sites show important differences between the Sb-free and the partly substituted sites. Both the average interatomic distances and volumes of

the polyhedra are lower for the partly substituted sites, whereas their sphericities and volume distortions are larger. Volume distortions are compared to a bisdisphenoid (O'Keeffe & Hyde 1996), which has the largest volume-capacity for a coordination number 8. By comparison, a bicapped trigonal prism with the largest volume has 7% distortion related to a bisdisphenoid. It is apparent that the coordinations deviate significantly from that of an ideal bicapped trigonal prism. Those around pure As sites have lower volume-distortions than the prism itself, whereas those around mixed sites have much higher distortions. Average (As,Sb)–S distances in the full coordination are shorter than As–S distances, which is just the opposite of what is observed for the averages of the three shortest bonds. Although arsenic

forms shorter strong bonds to sulfur than antimony, owing to a larger activity of its lone pair of electrons, more space is needed for its accomodation, and a larger coordination-volume results when the whole coordination environment is taken in consideration.

It should be noted that the coordinations of the mixed sites are confined completely to slab I, whereas the most distant sulfur atoms in the coordination of the pure As sites (the top of the trigonal prism) belong to the Type-2 sulfur layer and the boundary between slabs II and III. These pure As sites also have the shortest arsenic–copper distances in the structure [As7–Cu3 = 2.64 Å, As9–(Cu,Ag)2 = 2.82 Å, As5–(Cu,Ag)1 = 2.97 Å]. It is evident that Sb shows a preference for the sites with a smaller full-coordination radius, and at the same time avoids short contacts with copper. The position of the centroid of coordination calculated for the entire

coordination indicates the direction of displacement of the lone pair of electrons (Balić-Žunić & Makovicky 1996). For the sites As4–9, the lone pairs of electrons at pure As sites 5, 7, and 9 point into the slab II, whereas the lone pairs of electrons of atoms at mixed sites 4, 6, and 8 point toward Tl5.

Cu and Ag are found in three tetrahedral sites, [Cu,Ag]7, [Ag,Cu]8 and [Ag,Cu]9, and six sites with trigonal-planar coordinations, [Cu,Ag]1–6. Whereas Ag dominates in the tetrahedral sites, except for [Cu,Ag]7, it substitutes only in minor amounts in trigonal-planar sites [Cu,Ag]1, [Cu,Ag]2 and [Cu,Ag]6, and is entirely or nearly absent from the Cu3, [Cu,Ag]4 and [Cu,Ag]5 sites. The low eccentricities (0.025–0.029) and low volume-distortions (0.018–0.044) (Table 4) reflect the regularity of the tetrahedra. The most regular is the smallest Cu-rich site [Cu,Ag]7. In the
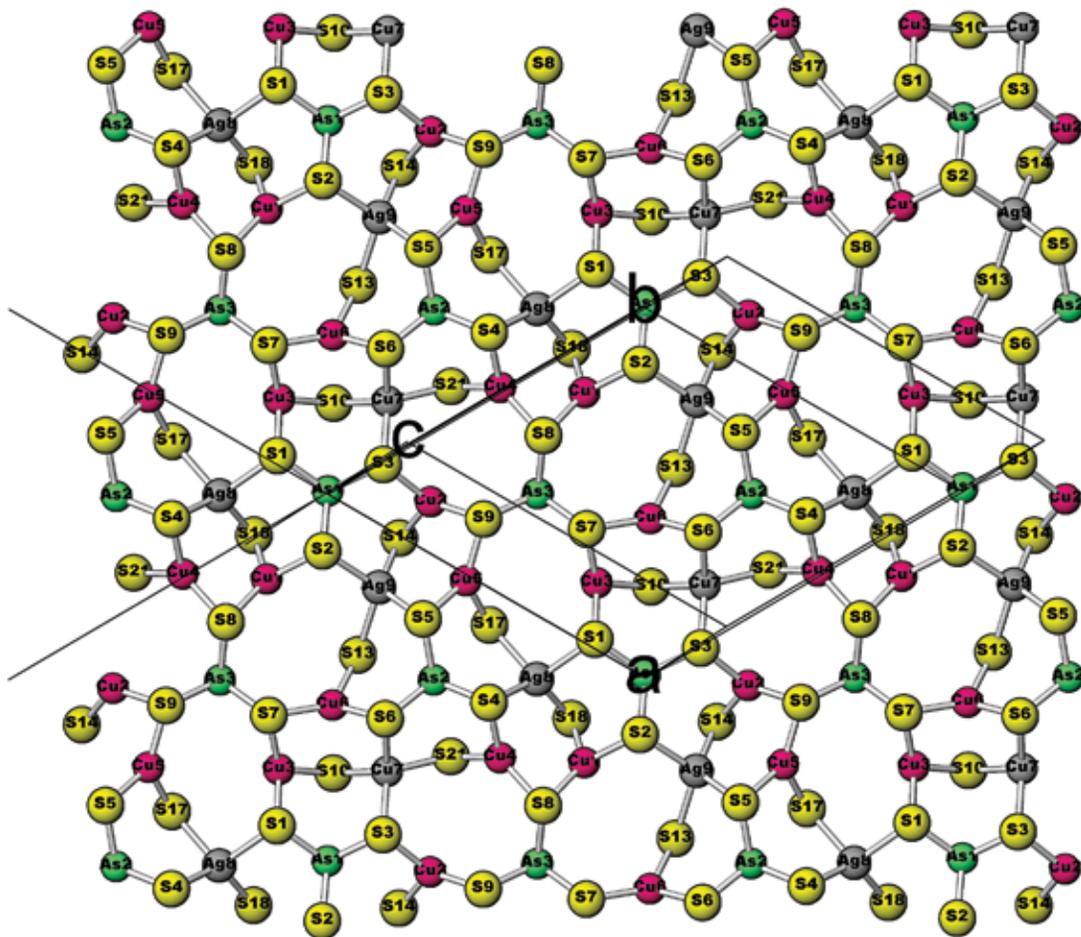

FIG. 4.   Slab II is composed of AsS$_3$ pyramids combined with (Cu,Ag)S$_3$ triangles and (Ag,Cu)S$_4$ tetrahedra. It is bordered by the two different types of sulfur layers and situated between $z \approx 0.20$ and ≈ 0.36.

trigonal-planar coordinations, the eccentricities are lowest for [Cu,Ag]4 and [Cu,Ag]5, with only minor Ag substitution, and larger for the sites with more Ag. However, the pure Cu site, Cu3, has the highest eccentricity of all. This is likely related to distortion of the approximate trigonal symmetry of slab II in the triclinic structure, with a consequent restriction in the size for the Cu3 site and a reversal of Ag:Cu substitution ratio for the pair Cu3,[Cu,Ag]6 as compared to the pairs [Cu,Ag]2,[Cu,Ag]5 and [Cu,Ag]1,[Cu,Ag]4.

The [Ag,Cu]$_3$S$_7$ groups in the slabs II, mentioned already, come in three crystallographic non-equivalent situations, differing by their positions in the triclinic unit-cell. The [Ag,Cu]8–[Cu,Ag]1–[Cu,Ag]4 group contains the largest Ag tetrahedron and the largest ([Cu,Ag]1) coordination triangle, in agreement with the largest Ag content for each of these coordination types (Tables 2, 4). The [Ag,Cu]9–[Cu,Ag]2–[Cu,Ag]5 group displays average polyhedra, with [Cu,Ag]2 more eccentric than [Cu,Ag]1. Finally, in the third such group, the mixed tetrahedral site [Cu,Ag]7 has the smallest tetrahedral volume, [Cu,Ag]6 an average, but more eccentric triangular site, and the pure copper site Cu3 displays the smallest and the most eccentric Cu coordination. With four of their sulfur atoms, those that belong to the boundary between slabs II and III, the Ag–Cu coordination groups form tetragons in the type-2 sulfur layer. In this way, the [Cu,Ag]7–Cu3–[Cu,Ag]6 and [Ag,Cu]9–[Cu,Ag]2–[Cu,Ag]5 groups occupy the opposite bases of the square-antiprismatic coordination of Tl2, whereas the [Ag,Cu]8–[Cu,Ag]1–[Cu,Ag]4 group with the highest Ag content forms the "empty" square, and is attached to the coordination polyhedron of Tl4.
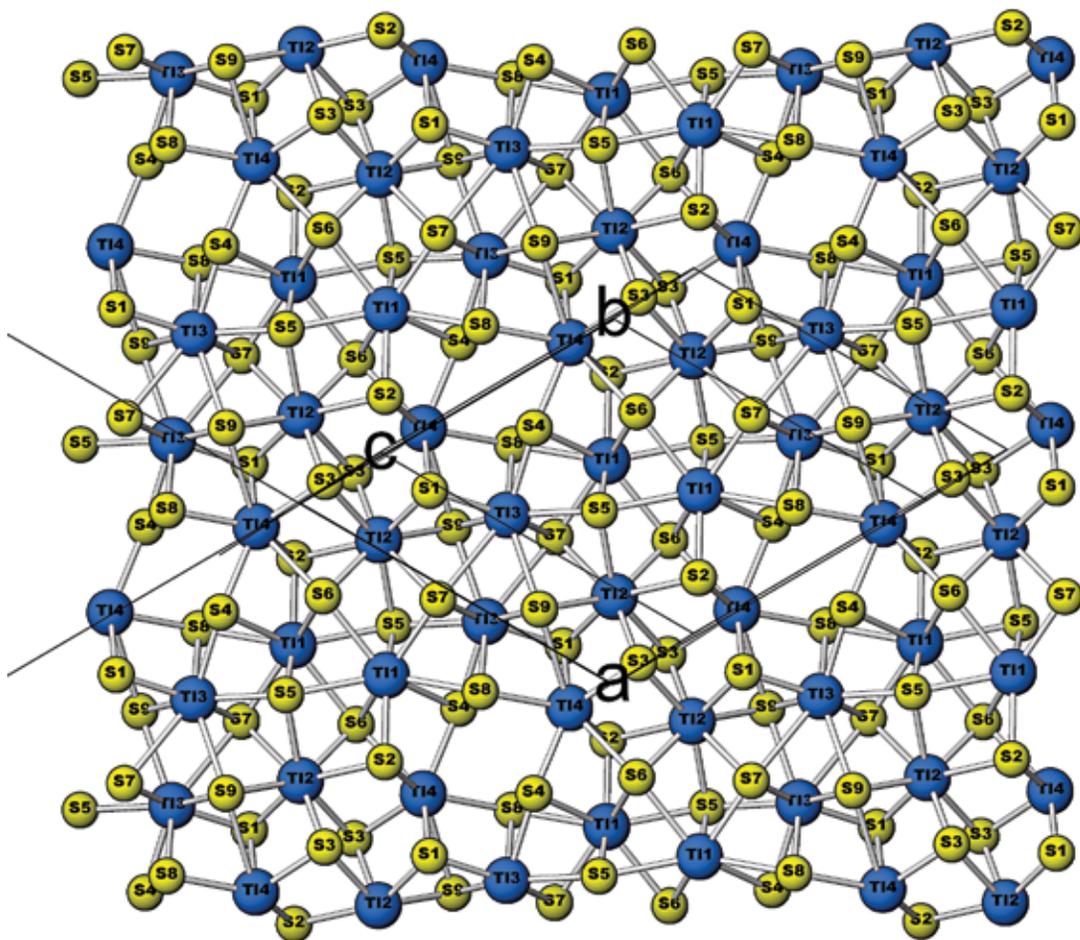

FIG. 5. Slab III, consisting of pure Tl coordination polyhedra, is situated between $z \approx 0.36$ and ≈ 0.64, and bordered by the two sulfur layers of Type 2.
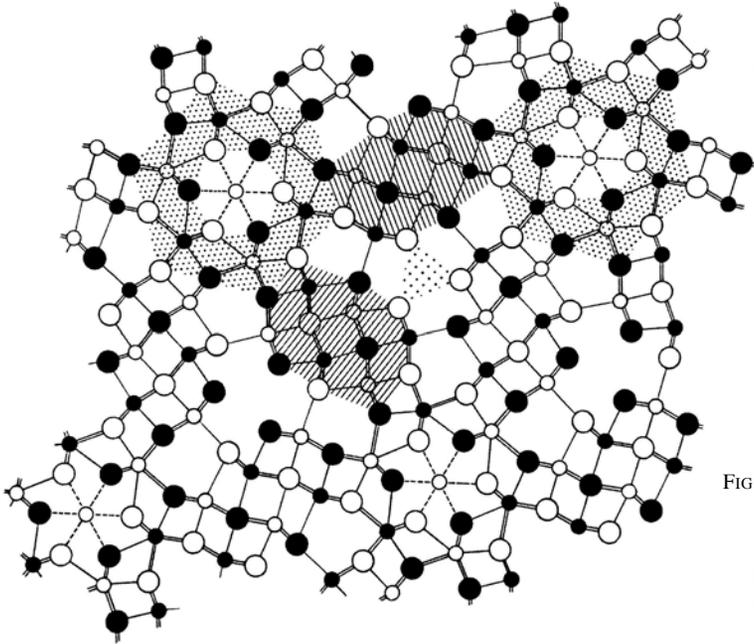
FIG. 6.   A hypothetical *P6/m* sulfosalt structure composed of circular walls of bicapped trigonal prisms (stippled) arranged around hexagonal channels, lozenge-like rods of PbS-like arrangement (hatched) and trigonal channels (stippled) (Makovicky 1985).
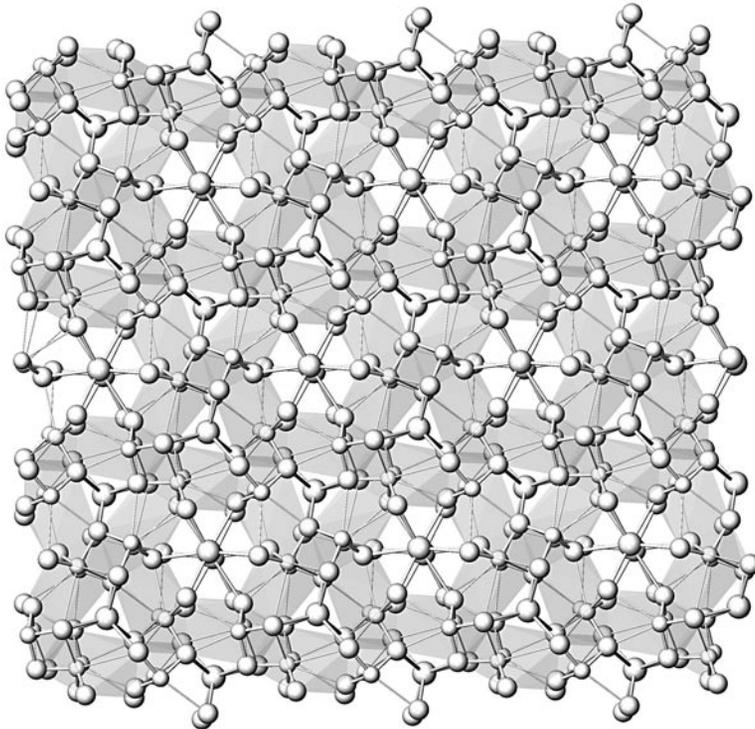

FIG. 7.   A 3D-infinite structure based on slab I of the gabrielite structure drawn for comparison with the structure in Figure 6. The rods of the PbS-like structure are removed, and hexagonal rings surrounding 6_3 channels (shaded) are interconnected directly, with the trigonal prismatic channels between them occupied by additional cations.

TABLE 3. SELECTED DISTANCES (Å) AND ANGLES (°) FOR GABRIELITE

Tl(1) - S(2)	3.097(5)	Tl(2) - S(6)[#1]	3.104(4)
Tl(1) - S(5)[#1]	3.108(4)	Tl(2) - S(3)[#2]	3.242(5)
Tl(1) - S(7)	3.273(5)	Tl(2) - S(1)[#3]	3.271(5)
Tl(1) - S(6)[#1]	3.302(5)	Tl(2) - S(5)	3.298(4)
Tl(1) - S(8)	3.367(5)	Tl(2) - S(9)[#2]	3.324(4)
Tl(1) - S(6)	3.437(4)	Tl(2) - S(3)[#4]	3.466(5)
Tl(1) - S(5)	3.464(4)	Tl(2) - S(7)[#1]	3.573(5)
Tl(1) - S(13)	3.652(5)	Tl(2) - S(2)	3.592(6)
Tl(1) - S(4)[#1]	3.682(4)		
		Tl(4) - S(2)[#4]	3.130(5)
Tl(3) - S(4)	3.171(4)	Tl(4) - S(4)[#5]	3.253(5)
Tl(3) - S(1)	3.189(4)	Tl(4) - S(3)	3.254(5)
Tl(3) - S(5)	3.237(5)	Tl(4) - S(6)[#5]	3.418(4)
Tl(3) - S(7)[#1]	3.272(4)	Tl(4) - S(8)	3.430(5)
Tl(3) - S(9)[#1]	3.294(5)	Tl(4) - S(1)[#1]	3.431(5)
Tl(3) - S(8)[#1]	3.564(5)	Tl(4) - S(9)	3.835(4)
Tl(3) - S(9)[#2]	3.698(5)		
Tl(3) - S(17)	3.979(5)	Tl(6) - S(14)[#8]	3.101(5)
Tl(3) - S(7)[#2]	4.005(5)	Tl(6) - S(18)[#8]	3.116(5)
		Tl(6) - S(20)	3.367(5)
Tl(5) - S(17)	3.206(5)	Tl(6) - S(16)[#6]	3.369(5)
Tl(5) - S(13)	3.240(4)	Tl(6) - S(12)[#8]	3.694(4)
Tl(5) - S(21)	3.262(5)	Tl(6) - S(12)[#7]	3.814(5)
Tl(5) - S(11)[#7]	3.423(5)		
Tl(5) - S(19)[#7]	3.467(4)	Cu(2) - S(14)[#6]	2.287(5)
Tl(5) - S(15)[#7]	3.473(5)	Cu(2) - S(9)	2.300(5)
		Cu(2) - S(3)	2.379(5)
Cu(1) - S(18)	2.338(5)	Cu(4) - S(21)	2.256(5)
Cu(1) - S(8)	2.353(5)	Cu(4) - S(8)[#9]	2.274(5)
Cu(1) - S(2)	2.420(6)	Cu(4) - S(4)	2.346(4)
Cu(3) - S(10)	2.283(5)	Cu(6) - S(13)	2.302(5)
Cu(3) - S(7)	2.298(5)	Cu(6) - S(7)	2.334(5)
Cu(3) - S(1)[#6]	2.323(5)	Cu(6) - S(6)	2.357(5)
Cu(5) - S(9)[#2]	2.253(5)		
Cu(5) - S(17)	2.262(5)	Ag(9) - S(14)	2.479(5)
Cu(5) - S(5)	2.340(5)	Ag(9) - S(2)	2.563(5)
Cu(7) - S(10)	2.398(6)	Ag(9) - S(13)	2.569(5)
Cu(7) - S(3)[#9]	2.401(5)	Ag(9) - S(5)	2.604(5)
Cu(7) - S(21)	2.415(5)		
Cu(7) - S(6)	2.490(5)	As(2) - S(4)	2.272(5)
Ag(8) - S(18)[#9]	2.511(5)	As(2) - S(6)	2.275(5)
Ag(8) - S(1)	2.587(5)	As(2) - S(5)	2.292(4)
Ag(8) - S(4)	2.602(5)	S(4) - As(2) - S(6)	100.1(2)°
Ag(8) - S(17)	2.609(5)	S(4) - As(2) - S(5)	101.2(2)°
		S(6) - As(2) - S(5)	101.6(2)°
As(1) - S(2)	2.242(5)		
As(1) - S(1)[#5]	2.243(4)	As(4) - S(10)	2.261(5)
As(1) - S(3)[#2]	2.250(5)	As(4) - S(12)[#7]	2.291(5)
S(2) - As(1) - S(1)	102.3(2)°	As(4) - S(11)	2.333(4)
S(2) - As(1) - S(3)	102.2(2)°	S(10) - As(4) - S(12)	99.9(2)°
S(1) - As(1) - S(3)	103.3(2)°	S(10) - As(4) - S(11)	100.1(2)°
		S(12) - As(4) - S(11)	92.1(2)°
As(3) - S(8)	2.282(5)		
As(3) - S(9)	2.292(5)	As(6) - S(14)	2.268(4)
As(3) - S(9)	2.295(5)	As(6) - S(16)[#11]	2.310(5)
S(8) - As(3) - S(7)	96.3(2)°	As(6) - S(15)[#2]	2.358(5)
S(8) - As(3) - S(9)	96.0(2)°	S(14) - As(6) - S(16)	96.4(2)°
S(7) - As(3) - S(9)	96.5(2)°	S(14) - As(6) - S(15)	100.4(2)°
		S(16) - As(6) - S(15)	92.3(2)°
As(5) - S(13)	2.222(5)		
As(5) - S(11)	2.303(5)	As(8) - S(18)[#9]	2.263(5)
As(5) - S(12)	2.333(5)	As(8) - S(20)[#10]	2.296(5)
S(13) - As(5) - S(11)	99.0(2)°	As(8) - S(19)[#9]	2.333(4)
S(13) - As(5) - S(12)	98.2(2)°	S(18) - As(8) - S(20)	96.5(2)°
S(11) - As(5) - S(12)	102.7(2)°	S(18) - As(8) - S(19)	100.8(2)°
		S(20) - As(8) - S(19)	92.7(2)°
As(7) - S(17)[#6]	2.228(5)		
As(7) - S(15)	2.284(5)	As(9) - S(21)[#5]	2.228(4)
As(7) - S(16)[#6]	2.311(5)	As(9) - S(19)	2.289(5)
S(17) - As(7) - S(15)	99.5(2)°	As(9) - S(20)[#5]	2.310(5)
S(17) - As(7) - S(16)	98.3(2)°	S(21) - As(9) - S(19)	99.6(2)°
S(15) - As(7) - S(16)	102.3(2)°	S(21) - As(9) - S(20)	97.6(2)°
		S(19) - As(9) - S(20)	102.4(2)°

Symmetry transformations used to generate equivalent atoms:
[#1] -x + 1, -y + 1, -z + 1; [#2] x, y + 1, z; [#3] -x + 1, -y + 2, -z + 1; [#4] -x, -y + 1, -z + 1, [#5] x - 1, y, z; [#6] x, y - 1, z; [#7] -x + 1, -y + 1, -z; [#8] x + 1, y - 1, z; [#9] x + 1, y, z; [#10] -x + 2, -y + 1, -z; [#11] -x + 1, -y + 2, -z.

The occupancies of Ag and Cu and the sizes of coordination polyhedra dependent on them show a pronounced deviation from the idealized trigonal symmetry of slab II. Primarily, the difference occurs between the [Cu,Ag]7–[Cu,Ag]6–Cu3 group and the other two Cu–Ag triplets. In the former, Cu dominates in the tetrahedral site [Cu,Ag]7, the [Cu,Ag]6 site has a larger amount of Ag than its pseudosymmetrical equivalents [Cu,Ag]4 and [Cu,Ag]5, whereas Cu3 is substantially a pure Cu site in contrast to the pseudo-equivalent [Cu,Ag]2 and [Cu,Ag]1 sites, with a sizable amount of Ag.

Three of the trigonally coordinated (Cu,Ag) sites show very short distances to the three of the Tl sites in slab III [Tl1–(Cu,Ag)6 = 3.03 Å, Tl4–(Cu,Ag)4 = 3.04 Å, Tl3–(Cu,Ag)5 = 3.08 Å]. In fact, these distances are shorter than any Tl–S contact of the corresponding Tl atoms (Table 3). The Cu(Ag) atoms are displaced from the centers of the trigonal planar coordinations. The direction of displacement depends on the environment (as explained below), whereas its extent (measured by the eccentricity of coordination, Table 4) depends on the degree of Ag-for-Cu substitution, but in a different way for the two groups of coordinations (Cu1–3 *versus* Cu4–6). In the case of Cu1, Cu2, and Cu3, the displacement

TABLE 4. COORDINATION NUMBERS AND SELECTED PARAMETERS OF COORDINATION POLYHEDRA[#]

Atom site	Substitution scheme	C.N.	Average bond-distance (Å)	Sphericity	Circumscribed sphere volume V_s	Eccentricity	Volume distortion	Polyhedron volume V_p (Å³)
[Cu,Ag]1	$Cu_{62}Ag_{38}$	3	2.370	1	53.8	0.146	–	–
[Cu,Ag]2	$Cu_{86}Ag_{14}$	3	2.321	1	49.4	0.190	–	–
Cu3		3	2.302	1	45.0	0.294	–	–
[Cu,Ag]4	$Cu_{94}Ag_6$	3	2.293	1	49.6	0.096	–	–
[Cu,Ag]5	$Cu_{94}Ag_6$	3	2.285	1	49.2	0.082	–	–
[Cu,Ag]6	$Cu_{90}Ag_{10}$	3	2.331	1	50.1	0.192	–	–
[Cu,Ag]7	$Cu_{74}Ag_{26}$	4	2.426	1	59.8	0.027	0.018	7.19(6)
[Ag,Cu]8	$Ag_{84}Cu_{16}$	4	2.577	1	71.3	0.025	0.037	8.41(6)
[Ag,Cu]9	$Ag_{79}Cu_{21}$	4	2.554	1	69.5	0.029	0.044	8.14(6)
As1		6	2.856	0.996	109.3	0.403	0.133	30.2(1)
As2		6	2.750	0.992	91.6	0.317	0.067	27.2(1)
[As,Sb]3	$As_{95}Sb_5$	6	3.045	0.991	109.8	0.356	0.202	27.9(1)
Tl5		6	3.345	0.994	154.8	0.048	0.282	35.4(2)
Tl6		6	3.289	0.976	161.0	0.182	0.340	33.8(1)
Tl4		7	3.393	0.955	163.0	0.074	0.265	45.3(2)
[As,Sb]4	$As_{87}Sb_{13}$	8	3.211	0.944	140.5	0.453	0.160	51.1(2)
As5		8	3.364	0.899	145.3	0.437	0.041	60.4(2)
[As,Sb]6	$As_{84}Sb_{16}$	8	3.236	0.947	142.2	0.450	0.151	52.3(2)
As7		8	3.338	0.901	139.2	0.422	0.030	58.5(2)
[As,Sb]8	$As_{89}Sb_{11}$	8	3.239	0.944	144.2	0.463	0.162	52.4(2)
Ag9		8	3.331	0.907	139.9	0.429	0.029	58.9(2)
Tl2		8	3.359	0.949	158.6	0.009	0.050	65.3(2)
Tl1		9	3.375	0.940	161.3	0.019	0.058	74.1(3)
Tl3		9	3.491	0.925	178.6	0.092	0.103	78.1(3)

[#] The distortion parameters are defined in Balić-Žunić & Makovicky (1996) and Makovicky & Balić-Žunić (1998) and calculated with the program IVTON (Balić-Žunić & Vicković 1996). The volume of the circumscribed sphere V_s is expressed in Å³.

is toward the adjacent As5, As9, and As7, respectively. The lone pairs of electrons of the latter point toward the Cu atoms. The displacement of Cu(Ag) decreases with the increasing Ag content because Ag has a larger atomic radius and cannot approach As as much. As seen from the increasing radius of the circumscribed sphere (Table 4), replacement of Cu by Ag in these sites causes broadening of the triangles of S atoms where Ag is pushed away from As toward their plane. Cu4, Cu5, and Cu6 show, on average, smaller eccentricities than the former sites. Their displacement is determined by the very close Tl atoms (see above), and is directed away from the latter. Therefore, the eccentricity of coordination in this case increases with a larger Ag content. As the radius of the circumscribed sphere shows, there is almost no change in the size of the S triangle, and Ag is moved further both from the sulfur atoms and Tl, again in accordance with its larger radius.

The average bond-distance, radius of circumscribed sphere and volume of the Ag(Cu) tetrahedron all increase non-linearly with Ag content. Unfortunately, there are too few data to properly fit a higher-order function to this trend.

COORDINATION POLYHEDRA OF THALLIUM

Atoms Tl1, Tl2, Tl3 and Tl4, which belong to slab III, have their coordinations shaped by superposition of two identical type-2 nets of S atoms (Fig. 2c), consisting of 4-connected triangles, tetragons and pentagons. As mentioned in connection with the description of the structure, the coordinations of Tl1, Tl3, and Tl4 are formed between a pentagon and two opposing sulfur atoms. Atoms Tl1 and Tl3 occupy the voids formed between a pentagon and an edge separating a triangle and a pentagon, whereas Tl4 occupies a void bounded by a pentagon and an edge separating a triangle and a tetragon.

Atom Tl1 (Fig. 9a) is displaced toward the plane of the pentagon and binds to all of its S atoms. It also bonds to all three S atoms from a triangle on the opposite layer, and with a ninth S atom below the pentagon, at the boundary between slabs II and I. They all lie closer than 3.7 Å.

Atom Tl3 (Fig. 9b) has a coordination similar to that of Tl1. As mentioned before, they are symmetry-equivalents in the idealized $C2/m$ layer group of slab III. The differences in coordination are reflected in relatively small displacements of atoms, caused by the different
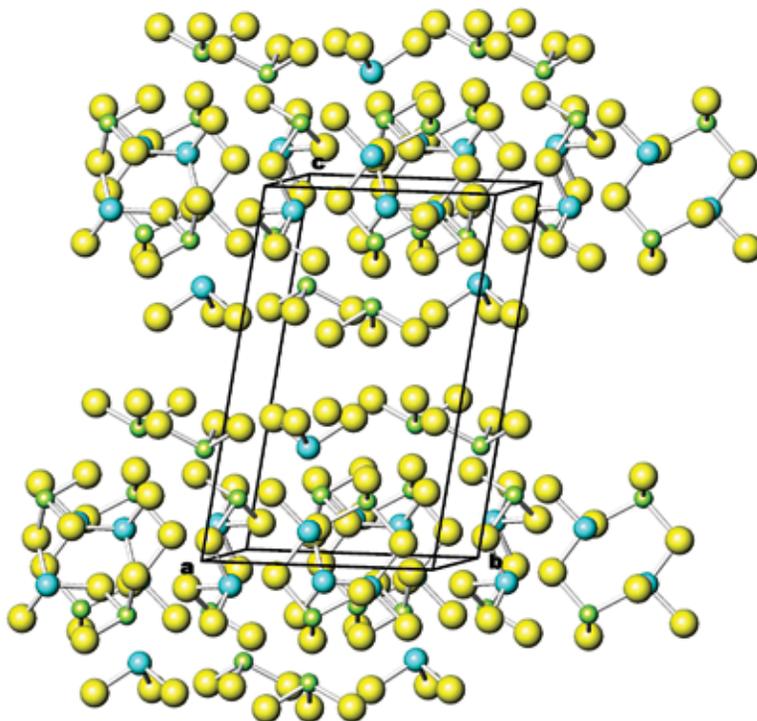

FIG. 8. The distribution of short As(Sb)–S bonds in the structure of gabrielite. S atoms are yellow, As, yellow-green (smaller), and mixed As–Sb positions, turquoise (larger).

Cu–Ag order in the secondary coordination sphere, and the obliquity of the structure. Atom Tl3 is less displaced from the median plane of the slab III toward the pentagonal side of its coordination than is Tl1. On the other hand, it is more displaced from the center of the pentagon, and two of its longest distances to the surrounding nine sulfur atoms exceed 3.7 Å (Table 3).

Apart from the S atoms forming the pentagon, and the opposing edge, Tl4 does not have any other sulfur atoms at distances less than 4 Å. It has coordination number 7, with the largest distance equal to 3.83 Å (Fig. 9c). Its displacement from the median plane of slab III equals that of Tl3, but is less than that of Tl1.

As mentioned earlier, each of the previously described Tl sites has one Cu atom closer than any of the sulfur atoms.

The coordination of Tl2, which lies in the same slab as Tl1, Tl3, and Tl4, is unique. It is square-antiprismatic, with all S atoms closer than 3.6 Å (Fig. 9d). The nearest cation is Cu2 at 3.72 Å.

Tl5 and Tl6 reside inside slab I, in channels with trigonal and hexagonal cross-sections. The coordination polyhedron of Tl5 (Fig. 9e) is a slightly distorted trigonal prism, with the Tl atom displaced toward the broader of the bases. Atom Tl6 occupies a much flattened trigonal antiprism. The antiprisms are stacked in pairs above each other and related by a center of symmetry between two adjacent bases (Fig. 10a). The latter bases are larger than the opposing triangular bases at the mouth of the channel.

SHORT METAL–METAL AND METAL–SEMIMETAL CONTACTS

One of the main characteristics of the structure of gabrielite is the presence of remarkably short Tl–Cu, Tl–Tl and Tl–As contacts. The Tl–Cu distances (3.03–3.08 Å) for Tl1, Tl3, and Tl4 are even shorter than the shortest Tl–S bonds for these atoms. These contacts are comparable to the Tl–Cu contact (3.126 Å) in Tl_2CuAsO_4 (Moser & Jung 1998). In this structure, which exhibits a strong activity of a lone pair of electrons in Tl, bidentate arsenate anions bridge two Cu^+ ions to form complex $[Cu_2(AsO_4)_2]^{4-}$ anions. Among ordered structures having Tl^+ and Cu^+ ions, no other examples with similar short Tl–Cu contacts have been found in the Inorganic Crystal Structure Database (Bergerhoff et al. 1983). In the increasing order, Tl1, Tl3 and Tl4 display the most pronounced activity of a lone pair of electrons among the thallium atoms in gabrielite.

Short Tl–Tl and Tl–As contacts (Tl6–Tl6: 3.09 Å, Tl6–Asl: 3.11 Å) are concentrated in slab I, around the center of symmetry at 0,0,0 (Fig. 10a). The fact that Tl–Tl distance in the hexagonal metal (coordination number 12) is 3.4 Å (Lipson & Stokes 1941), whereas the sum of covalent radii of Tl is 3.10 Å (i.e., very close to our value), indicates a strong Tl–Tl interaction in gabrielite.

Calculation of the Tl6–Tl6 distance corrected for thermal motion (Busing & Levy 1964) shows that this distance cannot be shorter than 3.094, or longer than 3.177 Å. A so-called riding motion distance has the value of 3.094 Å, whereas a non-correlated motion distance (which is probably the most realistic one for gabrielite) is 3.136 Å. Although the corrected distances are slightly longer than the ones calculated directly, they are still unusually short for sulfides and sulfosalts. The only known sulfosalt with a very short apparent Tl–Tl distance (2.94 Å) is jankovicite (Libowitzky et al. 1995), but as the Tl position in this structure is split and shared with Sb in a 1:1 occupancy, the authors considered the distance and the short Tl–Tl contacts in the structure unrealistic.

The same type of coordination as observed for the Tl6–Tl6 pair is found in Li_5Tl_2 (Stöhr & Schäfer 1979). In the Li_5Tl_2 structure (Fig.10b), the pair of Tl atoms, with a Tl–Tl contact even shorter than in gabrielite, is surrounded by Li atoms at short distances. Twelve Li atoms play the same role as S in gabrielite, whereas the two at the shortest distance are on sites occupied by As1 in gabrielite. The coordination in gabrielite is less regular, with distances from thallium atoms to the sulfur atoms at the antiprismatic bases topped by As shorter than those to the sulfur atoms closer to the median plane of the coordination. The overall centrosymmetric configuration (Fig. 10a) can be described as a cage created by 8 As and 12 S atoms. Six AsS_2 groups interconnect the two Tl6 atoms. Two additional As1 atoms from the slabs II enclose the cage in the [001] and [00$\bar{1}$] directions. Atom As1 is coordinated by 3 S atoms at short distances (2.24–2.25 Å) and 3 S atoms at long distances (3.44–3.49 Å), making an irregular trigonal antiprism. Atom Tl6 lies approximately on the 3-fold axis of this antiprism, on the side of the long As–S contacts. The lone pair of electrons of As1 thus points toward Tl6. In addition, the As1–Tl6–Tl6′–As1′ group, where Tl6′ and As1′ are generated by the center of symmetry, is very close to being linear. It is possible that the lone pair of electrons in As1 exerts influence on the Tl6–Tl6 contact. The displacement ellipsoid of Tl6 is oblate perpendicular to the Tl6–Tl6 join, and it appears that Tl6 atoms are being forced by pairs of lone electrons on As to approach each other to the closest tolerable distance in this environment. The pairs of lone electrons are probably placed between the two Tl atoms, as suggested by the position of the centroid of coordination (Fig. 10a). In the case of Li_5Tl_2, the centroid is at a distance of only 0.06 Å from the Tl atom compared to 0.6 Å in gabrielite.

Short Tl–Tl contacts are not rare among the Tl compounds, as they can be found in various polyanionic Tl clusters in "neat salts" of Tl with alkali metals (Corbett 2000). In some simple Tl salts (e.g., TlF and $TlNO_3$), even shorter distances are observed. In TlF, two independent Tl atoms form columns with an inter-columnar distance of 4.12 Å, whereas the intracolumnar
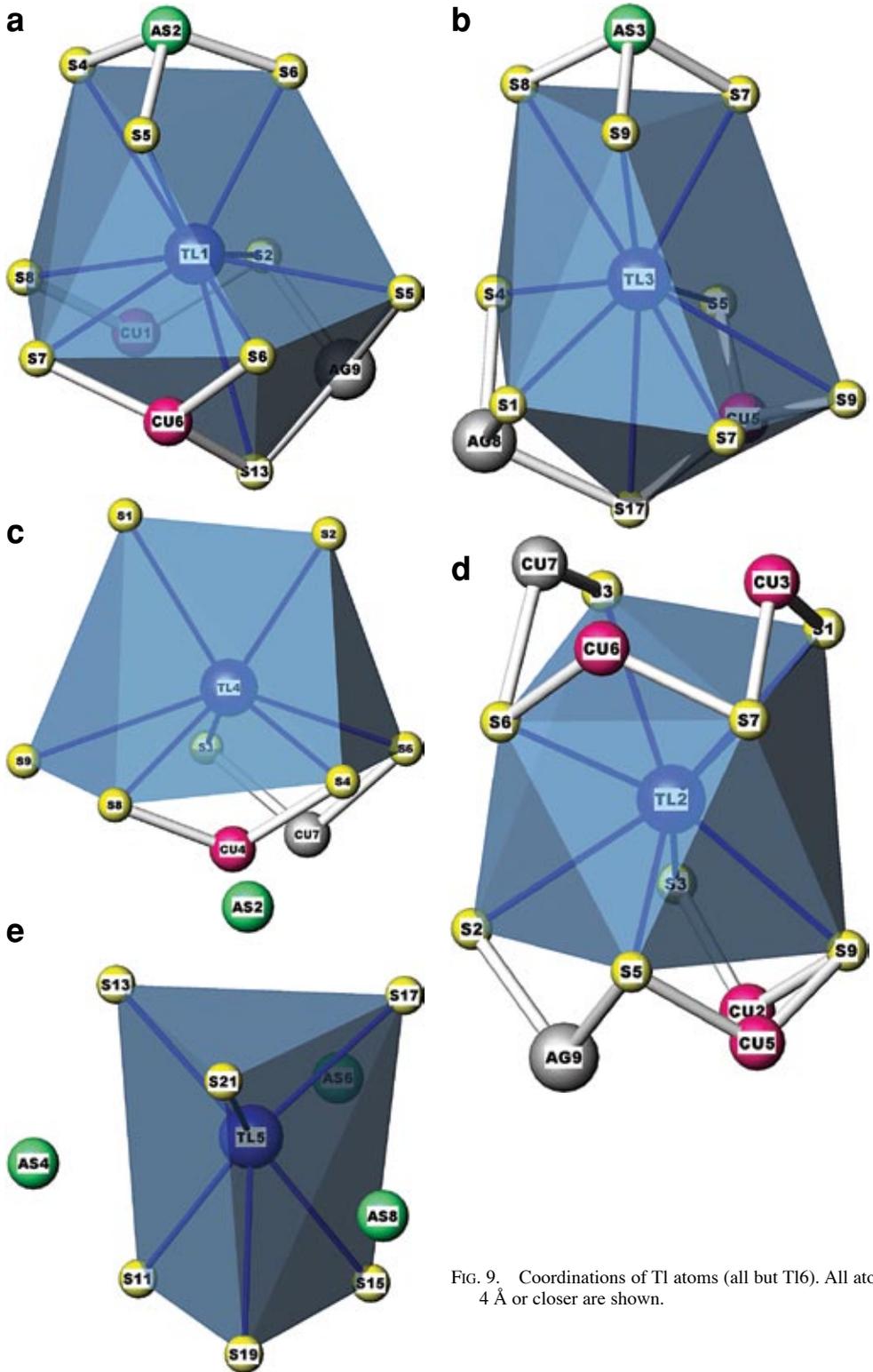
FIG. 9. Coordinations of Tl atoms (all but Tl6). All atoms at 4 Å or closer are shown.
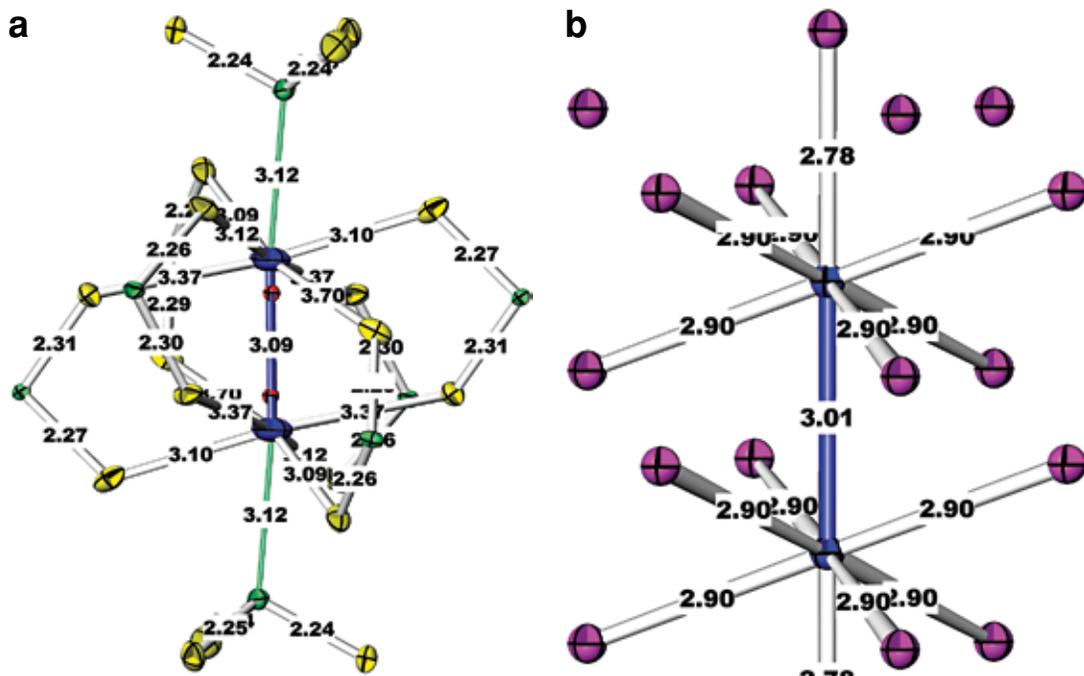
FIG. 10.   a) A coordination pair Tl6–Tl6 with ellipsoidal displacement parameters drawn at 50% probability. The coloring of atoms is like that in Figure 1. Red spheres mark positions of the Tl coordination centroids. Atoms of As surrounding the channel occupied by thallium atoms in slab I are illustrated as well, together with the As1 sites (connected to Tl) from slab II, plugging the channel from above and below. b) A coordination pair Tl–Tl from the structure of Li_5Tl_2 (Stöhr & Schäfer 1979). Atoms of Tl (blue) refined to a slightly anisotropic displacement factor, and those of Li (violet) refined to an isotropic one.

distance is only 2.59 Å (Alcock 1969). In $TlNO_3$, thallium is at the center of unit-cell faces, forming a regular octahedral cluster with a Tl–Tl distance of 3.05 Å (Sastry & Sequeira 1997).

Interaction of two close Tl^+ ions was theoretically treated by Janiak & Hoffmann (1992) and Beck (1992). The former authors used the extended Hückel framework to calculate this interaction for separations from 3.05 to 3.70 Å. They demonstrated that the repulsive Tl–Tl interaction alters to an attractive one when instead of pure s^2–s^2 interaction, s–p mixing is allowed. Ligands have a very pronounced influence on overlap population. At a Tl–Tl distance of 3.70 Å, they should deviate from the Tl–Tl line by at most 120° in order to facilitate the binding situation, whereas at 3.05 Å, they should preferably follow this line (both cases were modeled for hydrogen as a ligand).

Basing his arguments on the calculations of potentials, Beck (1992) suggested that the presence of lone-electron-pair elements lowers the ionicity of the structure, and the accumulation of lone pairs into micelles between such cations further stabilizes the structure by a screening effect of ns^2 pairs (for Tl in his example). This all is in accordance with the situation observed in gabrielite.

It appears that the shortest Tl–As distances reported so far are found in $Rb_5TaAs_4Tl_2$ (Huang & Corbett 1998), a transition-metal Zintl phase containing the polyanion $TaAs_4Tl_2^{5-}$. The distances range from 2.74 to 2.88 Å. This may be a typical situation for a compound in which As plays a role of anion. The shortest Tl–As distance in gabrielite is between Tl6 and As1. Its value corrected for thermal motion (Busing & Levy 1964) shows that this distance cannot be shorter than 3.120, or longer than 3.161 Å [riding motion: 3.130, non-correlated motion: 3.140 Å]. Although this is significantly longer than distances in $Rb_5TaAs_4Tl_2$, it is so far the shortest value observed for sulfosalts. The shortest Tl–As distance reported earlier (3.259 Å) was that in erniggliite (Graeser et al. 1992).

The closest As neighbors to the Tl5 site in gabrielite are considerably more distant (Tl–As ≈ 3.4 Å). Those are [As,Sb]4, [As,Sb]6 and [As,Sb]8, respectively. Again, they have their lone pairs of electrons oriented toward Tl5, but owing to a relatively large distance, only a very weak interaction is expected. Tl atoms in slab III have only relatively distant As neighbors (Tl–As > 3.7 Å), with lone pairs of electrons pointing out of the slab, so that no Tl–As interaction is expected for them.

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