THE CRYSTAL STRUCTURE OF SKINNERITE, P2₁/c-Cu₃SbS₃, FROM POWDER DATA

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ABSTRACT

The crystal structure of the room-temperature polymorph of skinnerite, Cu_3SbS_3, was determined by the Rietveld method from Guinier diffractometer X-ray powder data. The space group is $P2_1/c$; the cell parameters are a 7.814(1), b 10.242(1), c 13.273(1) Å, β 90.29(1)°, with $Z = 8$. The sulfur framework can be described as a (deformed) $(11\overline{2}2)_{hcp}$ twinned *hcp* array. Sb has trigonal pyramidal coordination in the bases of trigonal coordination prisms created by the unit-cell twinning of the S array. The Sb–S bond is between 2.44 and 2.47 Å in length. Most Cu sites have a triangular coordination, with <Cu–S> distances in the range 2.26–2.31 Å. Cu4 is split into two irregularly tetrahedral, [3 + 1] coordinations, with <Cu–S> in the range 2.40–2.46 Å. Cu3 and Cu4 are in triangular faces common to two tetrahedral voids of the S array, and the remaining Cu atoms are in such faces common to tetrahedral and octahedral voids. $P2_1/c$-skinnerite is a low-temperature polymorph of the ionic conductor Cu_3SbS_3. Differences in the distribution of Cu between $P2_1/c$-skinnerite and $P2_12_12_1$-wittichenite are caused by different sizes of Sb and Bi coordination polyhedra.

Keywords: skinnerite, room-temperature polymorph, crystal structure, Rietveld refinement.

SOMMAIRE

Nous avons affiné la structure cristalline du polymorphe de la skinnerite, Cu_3SbS_3, stable à température ambiante, au moyen de données diffractométriques (système de Guinier) obtenues sur poudre. Le groupe spatial est $P2_1/c$; les paramètres réticulaires sont a 7.814(1), b 10.242(1), c 13.273(1) Å, β 90.29(1)°, avec $Z = 8$. On pourrait décrire le réseau d'atomes de soufre comme un agencement *hcp* difforme maclé selon $(11\overline{2}2)_{hcp}$. Le Sb possède une coordinence trigonale pyramidale dans les bases de prismes de coordinence trigonaux, qui résultent des macles à l'échelle de la maille élémentaire de l'agencement des atomes de soufre. La longueur de la liaison Sb–S est entre 2.44 et 2.47 Å. La plupart des sites Cu ont une coordinence triangulaire, avec les distances <Cu–S> de 2.26 à 2.31 Å. L'atome Cu4 occupe un de deux sites à coordinence tétraédrique [3 + 1] irrégulière, les longueurs <Cu–S> étant dans l'intervalle 2.40–2.46 Å. Cu3 et Cu4 sont situés dans les faces triangulaires partagées par deux lacunes tétraédriques de l'agencement d'atomes S, et le reste des atomes Cu sont dans des faces semblables partagées entre lacunes tétraédrique et octaédrique. La skinnerite-$P2_1/c$ serait un polymorphe de basse température du conducteur Cu_3SbS_3. Les différences dans la distribution des atomes de Cu entre la skinnerite-$P2_1/c$ et la wittichenite-$P2_12_12_1$ seraient dues aux différences dans la taille des polyèdres de coordinence des atomes Sb et Bi.

(Traduit par la Rédaction)

Mots-clés: skinnerite, polymorphe stable à la température ambiante, structure cristalline, méthode de Rietveld.

INTRODUCTION

Cu_3SbS_3 was first prepared by Godovikov *et al.* (1971), and studied in detail by Skinner *et al.* (1972) and Makovicky & Skinner (1972). Karup-Møller & Makovicky (1974) described Cu_3SbS_3 as skinnerite. Further studies on the stability and crystallography of Cu_3SbS_3 were published by Whitfield (1980), Luce *et al.* (1977), Makovicky & Hyde (1983), and Makovicky & Skinner (1975).

Homeotypic Cu_3BiS_3 was named wittichenite by Hintze (1905). The X-ray crystallography of wittichenite was studied by Nuffield (1947); structure determinations at room temperature were made by Matzat (1972) and Kocman & Nuffield (1973). The crystallography of wittichenite between 25 and 300°C was investigated by Makovicky (1983). Studies by Makovicky & Skinner (1972, 1975) and Makovicky (1983) suggest that both Cu_3SbS_3 and Cu_3BiS_3 are ionic conductors, with Cu becoming mobile at moderate temperatures (120 – 190°C).

CRYSTALLOGRAPHY OF SKINNERITE

Skinner *et al.* (1972) showed that Cu_3SbS_3 is stable between 607.5 ± 3°C and 359 ± 2°C, below which it is

replaced in equilibrium conditions by $Sb + CuSbS_2 + Cu_{12+x}Sb_{4+y}S_{13}$. Cu_3SbS_3 can be readily quenched to room temperature and persists indefinitely. Contrary to Skinner *et al.* (1972), Bryndzia & Kleppa (1988) suggested that Cu_3SbS_3 is stable down to room temperature. Skinner *et al.* (1972) showed that Cu_3SbS_3 converts into a high-temperature, ion-conducting form above 122°C (*Pnma*; $Pn2_1a$ is excluded on the basis of the unpublished structure determination by Makovicky and Skinner at 170°C, with cell parameters *a* 7.81, *b* 10.25, and *c* 6.61 Å). Below 122°C, a metastable monoclinic form was found with space group $P2_1/c$ and unit-cell parameters *a* 7.815, *b* 10.252, *c* 13.270 Å and β 90.3° (Karup-Møller & Makovicky 1974). Whitfield (1980) stated that below –10°C, Cu_3SbS_3 transforms into a $P2_12_12_1$ polymorph with *a* 7.84, *b* 10.22, and *c* 6.60 Å.

EXPERIMENTAL

The material used in the present study was synthesized at 450°C from pure elements and recrystallized in a NH_4Cl solution at 375°C. The resulting Cu_3SbS_3 inevitably contains small amounts of tetrahedrite in intimate intergrowths. The *Pnma* → $P2_1/c$ polymorphic transformation causes intimate twinning of low skinnerite which, connected with the β angle of ~90°C, leads to severe overlap of reflections that hinders single-crystal structure determination.

Because of a need to achieve very high resolution, the X-ray powder diffraction pattern was measured using a Guinier diffractometer (Huber G600), $CuK\alpha_1$ radiation (wavelength 1.54051 Å), an incidence angle of 45°, in the range 15° < 2θ < 90°, with a step width 0.01° 2θ, and a counting time of 8 seconds. The powdered specimen was mounted between two layers of mylar in the specimen holder for transmission geometry. The measured pattern was converted to the Bragg–Brentano geometry required by the program for Rietveld refinement (Balić-Žunić 1992). The absorption factor was determined from the measurement of attenuation of the primary beam in the sample. The contribution of broad diffraction-peaks from the mylar at about 18, 21.5, 24 and 33° 2θ was subtracted using the appropriately scaled measurements on mylar-only specimen. To reduce the number of observations (the total accepted by the programme is 4096 data points), the recorded data were recalculated to a step width of 0.02° 2θ.

For Rietveld refinement, the LHPM1 computer programme was used (Wiles & Young 1981, Howard & Hill 1986). The Pearson VII function was used for the
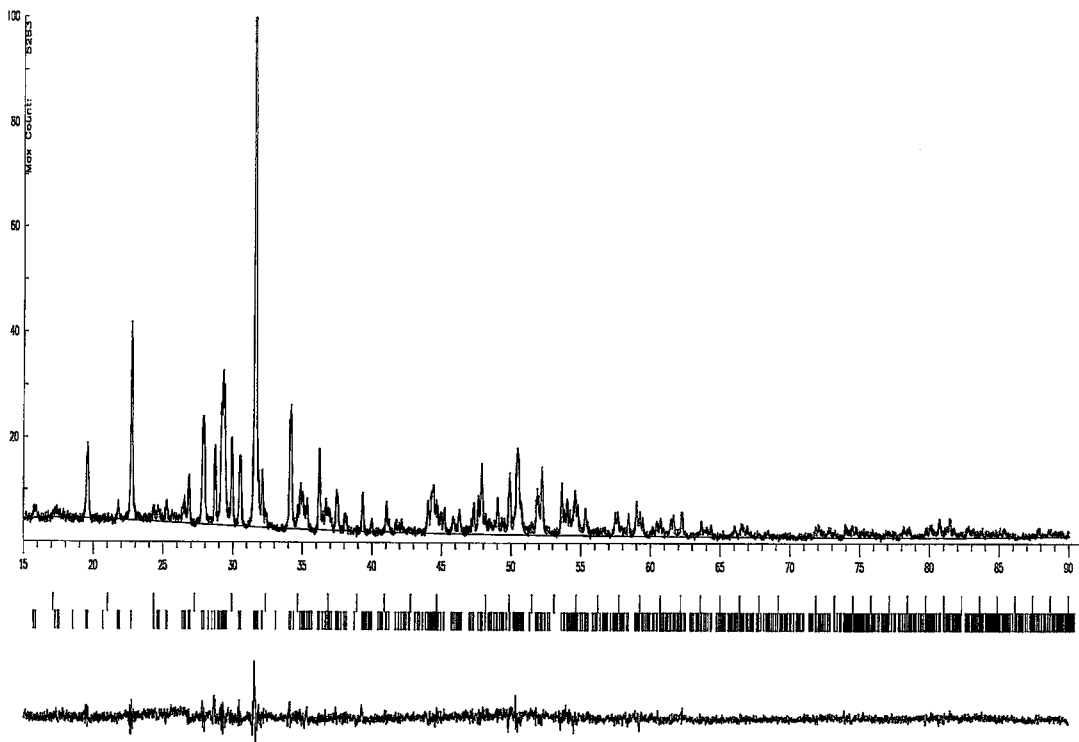

FIG. 1. Observed and calculated X-ray diffraction patterns for $P2_1/c$-skinnerite. The solid line is the calculated profile. The difference between the observed and calculated patterns is plotted underneath the pattern. The vertical bars mark all possible Bragg reflections of skinnerite and tetrahedrite.

profile fitting; the contribution of each reflection was calculated over ±8 FWHM (full width at half maximum). Atomic parameters, the scale factor, half-width parameter of the peaks, Pearson VII parameter, Rietveld asymmetry parameter, cell parameters and zero-2θ correction were refined. The background was refined using a six-parameter polynomial function. The small amount of tetrahedrite admixture could be accurately measured because the most prominent peak (222) of tetrahedrite does not overlap with any peaks attributed to skinnerite. The contribution of tetrahedrite was then subtracted using simultaneous two-phase refinement. The unit-cell parameter (10.336 Å) shows that this tetrahedrite corresponds to $Cu_{12+\delta}Sb_4S_{13}$ (Makovicky & Skinner 1976). Its crystal-structure parameters were kept constant; only the scale factor and the profile parameters were adjusted repeatedly during the refinement. The total number of calculated reflections was 938 (skinnerite) + 63 (tetrahedrite) (Fig. 1).

The starting set of atomic coordinates was derived from those of the high-temperature, ion-conducting $Pnma$ form of Cu_3SbS_3 (at 170°C: Makovicky &

Skinner 1975). The Cu distribution used for $P2_1/c$-skinnerite was suggested as a model by Makovicky & Hyde (1983). The refinement was started with two different settings having the same starting atomic coordinates but β > 90° or β < 90°, respectively. The first setting gave better R factors and was chosen for the final refinement.

Refinement of the Cu distribution scheme observed in low wittichenite also was attempted, but the agreement with observed data was found to be poor and could not be improved.

The Cu4 atomic position shows a very large isotropic displacement factor, about two times greater than that for the other Cu atoms. An anisotropic displacement factor was introduced, resulting in an elongate displacement-ellipsoid, with the principal axes (the half-lengths in Å and angles with crystal axes in degrees) as follows: 0.60, 23.1, 67.0, 89.9; 0.11, 109.4, 39.6, 56.9; 0.34, 78.0, 120.2, 33.1. This position was then split into two half-occupied Cu atoms (4A and 4B). Subsequent refinement gave the same R indices as before. There are good crystal-chemical reasons to suspect that Cu is statistically distributed over Cu4A and Cu4B positions and does not reside between them. The final refinement showed that the Cu4A and Cu4B atoms are indeed ~1 Å apart, and led to reasonable Cu–S coordinations. Final parameters are quoted in Table 1, with selected interatomic distances and angles in Table 2. A table of structure factors can be ordered from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S1.

TABLE 2.   SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (deg)

Sb1	S1	S3	S5		Cu4A	S6	S2	S1	S2
S1	2.42(4)	99(1)	100(1)		S6	2.16(6)	129(2)	111(2)	105(2)
S3	3.69(6)	2.45(3)	100(1)		S2	3.98(4)	2.24(5)	109(2)	97(2)
S5	3.74(4)	3.76(4)	2.46(3)		S1	3.86(5)	3.85(4)	2.50(6)	100(2)
					S2	3.88(5)	3.72(4)	3.99(4)	2.70(6)

Sb2	S6	S4	S2		Cu4B	S2	S6	S1	S5
S6	2.41(3)	102(1)	99(1)		S2	2.29(5)	120(2)	113(2)	108(2)
S4	3.79(5)	2.47(6)	96(1)		S6	3.98(4)	2.31(6)	112(2)	105(2)
S2	3.76(4)	3.72(6)	2.53(3)		S1	3.85(4)	3.86(5)	2.33(6)	97(2)
					S5	4.18(4)	4.16(5)	3.96(5)	2.92(6)

Cu1	S3	S6	S2		Cu5	S1	S2	S5
S3	2.25(3)	129(1)	114(1)		S1	2.25(4)	126(1)	118(1)
S6	4.05(4)	2.26(4)	115(1)		S2	4.10(4)	2.34(3)	114(1)
S2	3.86(4)	3.88(5)	2.34(3)		S5	3.96(5)	3.93(5)	2.34(4)

Cu2	S4	S5	S3		Cu6	S3	S6	S4
S4	2.16(4)	135(2)	107(1)		S3	2.23(3)	117(1)	125(1)
S5	4.08(5)	2.27(4)	117(1)		S6	3.88(5)	2.33(4)	118(1)
S3	3.64(5)	3.94(5)	2.36(3)		S4	4.07(4)	4.03(6)	2.36(4)

Cu3	S1	S4	S5
S1	2.20(3)	117(2)	127(1)
S4	3.78(5)	2.24(5)	113(2)
S5	4.01(4)	3.77(6)	2.28(4)

Matrix diagonals contain M–S distances, left-hand lower halves S–S distances, and right-hand upper halves S–M–S angles.

TABLE 1. FINAL RESULTS OF RIETVELD REFINEMENT OF $P2_1/c$ SKINNERITE

a	7.8142(3)Å	c	13.2726(5)Å
b	10.2424(4)Å	β	90.294(3)deg

Atom	x	y	z	B
Sb(1)	0.2819(9)	0.247(1)	0.0591(5)	3.5(2)
Sb(2)	0.7788(9)	0.254(1)	0.1949(5)	3.5(2)
Cu(1)	0.653(2)	0.902(2)	0.202(1)	4.9(5)
Cu(2)	0.847(2)	0.108(2)	0.456(1)	4.9(5)
Cu(3)	0.203(2)	0.102(3)	0.327(1)	6.0(6)
Cu(4A)	0.383(5)	0.923(4)	0.082(3)	5.7(11)
Cu(4B)	0.268(5)	0.888(4)	0.080(3)	4.1(10)
Cu(5)	0.933(2)	0.976(2)	0.106(1)	5.1(5)
Cu(6)	0.567(2)	0.037(2)	0.364(1)	3.9(4)
S(1)	0.172(4)	0.073(4)	0.164(2)	3.6(9)
S(2)	0.665(3)	0.073(3)	0.085(2)	1.4(7)
S(3)	0.815(3)	0.933(3)	0.341(2)	0.9(6)
S(4)	0.311(4)	0.936(5)	0.417(3)	4.9(10)
S(5)	0.937(3)	0.751(4)	0.075(2)	2.7(6)
S(6)	0.560(3)	0.258(3)	0.322(2)	1.7(5)

Half-occupancies for Cu(4A) and Cu(4B)

Refined Pearson VII function gamma parameter	1.42(4)
Peak full width at half-maximum	0.12(2)
Asymmetry parameter	-1.4(2)
Scale factor x 10⁴	0.468(6)
R exp	6.8
Profile R factor (R_p)	12.5
Weighted profile R factor (R_{wp})	16.4
Bragg R factor (R_B)	10.2
Goodness-of-fit	5.87
Number of parameters	75
Bragg reflections	938 (skinn.) + 63 (tetr.)

[1] Standard errors given in terms of the last digit as yielded by refinement program LHPM1

DESCRIPTION OF THE STRUCTURE

General features

The crystal structure of skinnerite is based on an *hcp* array of sulfur atoms twinned on a unit-cell scale on $(11\bar{2}2)_{hcp}$ (Andersson & Hyde 1974). Sb resides in the trigonal prism formed on the composition plane. The thickness of the unit *hcp* lamellae is one S_6 coordination octahedron. In the following section, all comparisons with wittichenite are based on the refinement of Kocman & Nuffield (1973).

The coordination of copper atoms is predominantly triangular, with the exception of Cu4. The copper sites Cu3 and Cu4 are in the triangular face common to two tetrahedral voids, and both correspond to the Cu2 site of Kocman & Nuffield (1973) in low wittichenite. The remaining Cu sites are on triangular interfaces of octahedral and tetrahedral voids. Cu1 and Cu2 are located in those triangles that are inclined to (001); they correspond to Cu1 in wittichenite. Cu5 and Cu6 correspond to Cu3 in wittichenite and reside in triangles nearly parallel to (001) of skinnerite.

In each *hcp* lamella parallel to (010) of skinnerite, S_6 octahedra are occupied by two Cu atoms in three different Cu configurations: (1) two Cu5 atoms occur in a *trans* position (Cu–Cu = 3.05 Å), and (2) two Cu2 atoms occur in a *trans* position (Cu–Cu = 3.44 Å); (1) and (2) are situated on every second level $(004)_{skn}$, and

they mutually alternate both along the *c* direction and over adjacent *hcp* lamellae on the same (004) level (Figs. 2, 3). Finally, (3) Cu1 and Cu6 occur in *cis* position (Cu–Cu = 2.64 Å).

The Cu1–Cu6 octahedra are related by inversion on adjacent (002) levels. The same is true for adjacent *hcp* lamellae. These layers of octahedra and tetrahedra are equivalent to (002) layers in wittichenite ($c_{wit} = \frac{1}{2}c_{skn}$), where they are related by a 2_1 operation along [001] (Fig. 4).

Along the *c* direction of skinnerite, every Cu site is occupied only once and is met by a corresponding vacant coordination triangle at $\Delta z = 0.5$. Across the plane of unit-cell twinning, the mirror-equivalent occupied position is vacant as well. In the high-temperature form, *Pnma*, all these triangles were statistically occupied with equal probabilities (Makovicky & Skinner 1975).

Geometry of the structure

Distortion of the sulfur framework of skinnerite and wittichenite can be measured by the distortion and tilt of copper configuration octahedra (Table 3). The octahedra are distended in the direction closest to [100]. The 2–3° difference between the octagonal tilt in skinnerite and wittichenite, respectively, appears significant for their geometry.
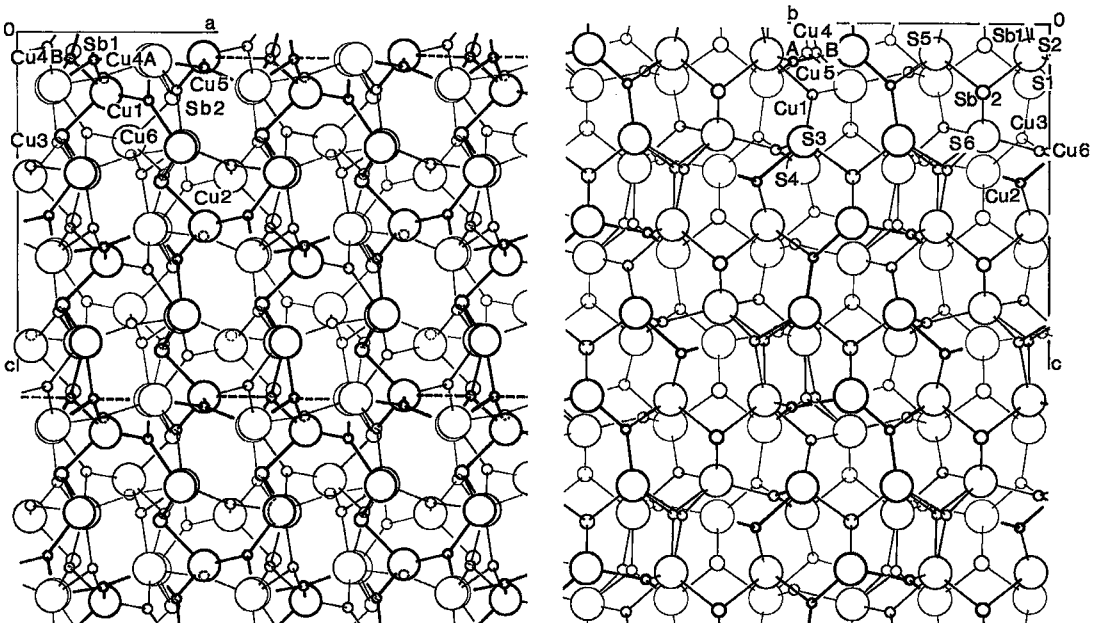
The geometry of Cu_3XS_3 can be compared with that

FIG. 2. The crystal structure of $P2_1/c$-skinnerite projected on (010) and (001), respectively. In order of increasing size, circles denote Cu, Sb and S. Line thicknesses denote four height-intervals above the projection plane.
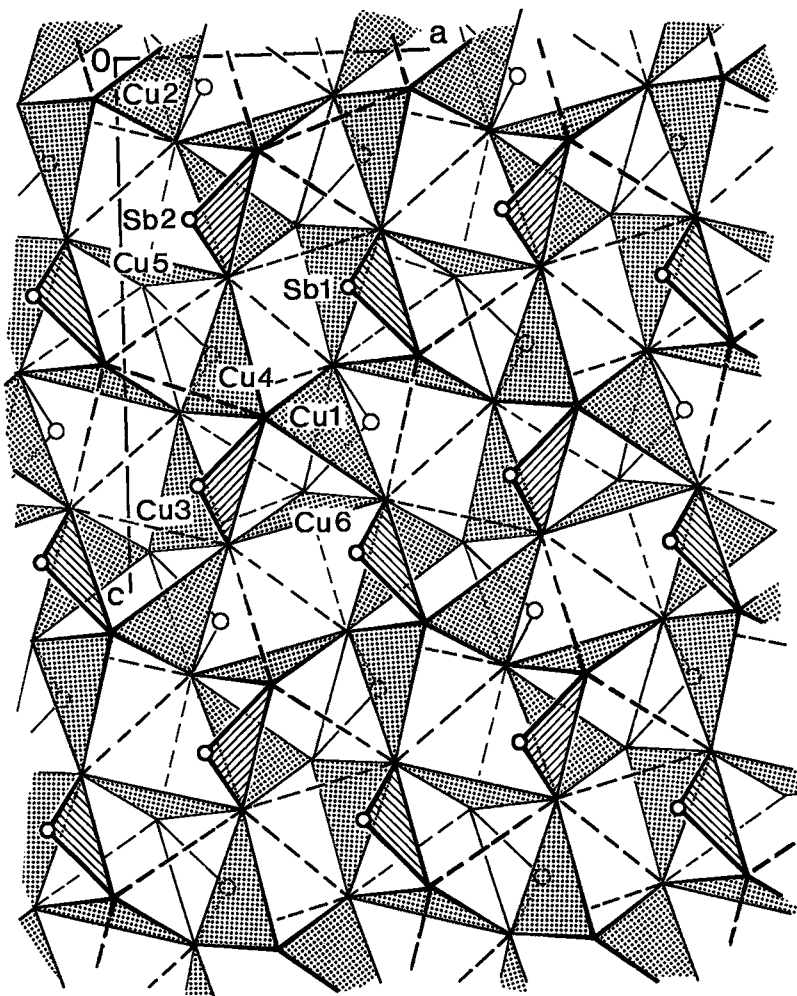
FIG. 3. A twin lamella $(11\bar{2}2)_{hcp}$ [$i.e.$, $(020)_{skn}$] from the structure of $P2_1/c$-skinnerite. Circles denote Sb atoms in SbS_3 pyramids at the front and rear planes of this lamella; Cu-occupied coordination triangles are shaded, and the splitting of the Cu4 position is ignored.

of an ideal hcp array twinned on $(11\bar{2}2)$ and that of chalcocite and other Cu sulfides. The XS_6 prisms in Cu_3XS_3 are more slender than in the ideal unit-cell-twinned hcp array; puckering of [100] chains of these prisms deviates substantially from that in the ideal array (Table 3). In the ideal twinned hcp array, the "trigonal" prisms are flattened about $(010)_{wit}$ (Table 3); those in Cu_3XS_3 show only a small departure from a regular trigonal prism. The a/c ratio of the wittichenite-like cell is 1.1057 for the ideal hcp, it is 1.150 for wittichenite and 0.5×1.178 for intermediate skinnerite. If we base the ideal hcp model on the observed b values [which are $6d(11\bar{2}2)_{hcp}$ for both phases], we obtain "ideal" a 7.78 Å and

c 7.04 Å values for wittichenite, and a 7.67 Å and c 13.87 Å for skinnerite. In the real phases, the c parameters are strongly compressed compared to ideal hcp; such differences are much smaller along the a axis.

A comparison of Cu_3XS_3 with chalcocite and djurleite, hcp Cu–S sulfides with 3-, 4- and 2-fold coordinated copper, leads to very interesting parallels. The crystal structures of high chalcocite, low chalcocite and djurleite all have that diameter of octahedra, which is parallel to [001] equal to 3.36–3.37 Å (Djurle 1958, Evans 1979), whereas the inclined diameters can be estimated as approximately 3.23, 3.22–3.23 and 3.17–3.21 Å, respectively, using some-
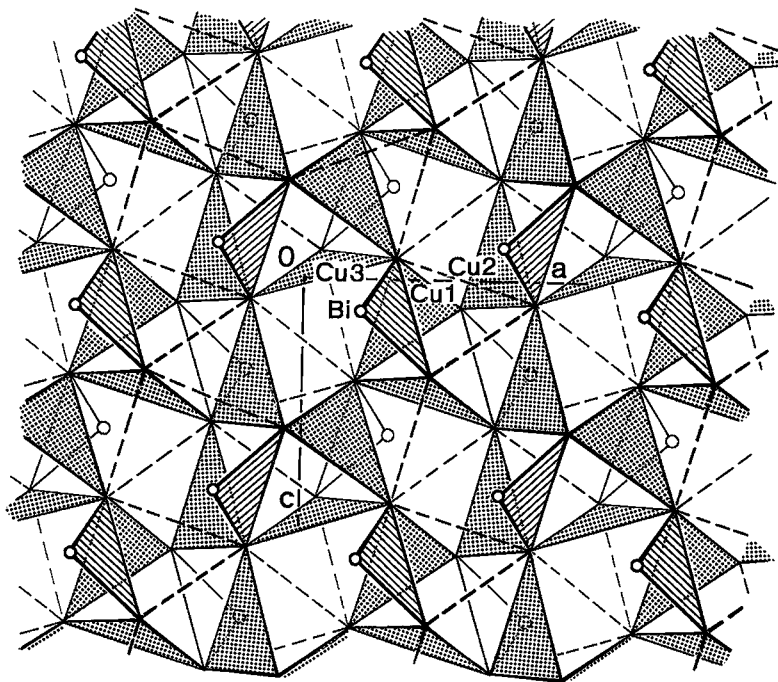
FIG. 4. A twin lamella $(11\bar{2}2)_{hcp}$ [*i.e.*, $(020)_{wit}$] from the structure of $P2_12_12_1$ wittichenite (Kocman & Nuffield 1973). Circles denote Bi atoms in BiS_3 coordination pyramids; Cu-occupied coordination triangles are shaded.

what idealized geometry of the octahedra.

The (0002) planes of *hcp* slabs in Cu_3XS_3 are parallel to [001] and make an angle of approximately 30.5° with [010] in the Cu_3XS_3 lattice. Their mean spacing is 3.33 Å for wittichenite and 3.38 Å for skinnerite; it influences the *a* axis of Cu_3XS_3, and the *b* axis less so. Other diameters of the octahedra are much smaller (Table 3). Therefore, the twinned *hcp* array in skinnerite and wittichenite *inherited the metrics of copper sulfides* based on *hcp* packing with predominantly triangular coordination of copper.

The coordination states of copper

The accuracy of the Rietveld refinement is best described by a plot of bond-length variations that compares Cu–S and Sb(Bi)–S distances in $P2_1/c$ skinnerite and $P2_12_12_1$ wittichenite (Fig. 5). The half-occupied Cu positions Cu4A and Cu4B, 0.97 Å apart, assume highly skewed tetrahedral coordinations [3 + 1] (Tables 2, 4, Fig. 2). The position Cu4A has a near-two-coordinated character [average Cu4A–S bond length is 2.20(6) Å] because a more regular non-planar three-fold coordination would bring Cu4A too close to Sb1. No such problem arises for Cu4B. In wittichenite, the corresponding position, Cu2, has an average Cu–S

distance of 2.27 Å for three-fold coordination; the nearest additional sulfur is at 3.18 Å. It exhibits the largest anisotropic displacement ellipsoid; its *rms* displacement and orientation parameters are (in Å and degrees) 0.30, 29.3, 62.5, 80.6; 0.17, 119.2, 36.9, 69.6; 0.13, 88.3, 112.6, 22.7. A larger split of the Cu4 position in skinnerite (see Experimental) correlates with its smaller coordination triangle [average S–S distance = 3.89(6) Å *versus* 3.92(15) Å for Cu2 in wittichenite]. Split Cu positions in Cu_3XS_3 are comparable to those in other Cu sulfosalts. Based on *rms* displacement values, in substitution-free tetrahedrites $Cu_{12.3}Sb_4S_{13}$ and $Cu_{13.8}Sb_4S_{13}$ (Makovicky & Skinner 1979), this split site gives a Cu–Cu distance of 0.82 and 0.88 Å, respectively, leading to corrected Cu–S distances equal to 2.28–2.30 Å, and <S–S> equal to 3.85(44) and 3.88(45) Å, respectively. A split Cu position was refined in $Cu_4Bi_4S_9$ (Bente & Kupčík 1984), with Cu–Cu equal to 0.59 Å and <S–S> equal to 3.99(8) Å.

Sb coordination

The Sb–S bonds are all in the range 2.42–2.46 Å (Sb1) and 2.41–2.53 Å (Sb2); the bond angles fall in the range 96–102° (Tables 2, 4). The SbS_3 triangular pyramids occupy one of the bases of the triangular

TABLE 3. GEOMETRY OF SELECTED COORDINATION POLYHEDRA IN SKINNERITE AND WITTICHENITE

Octahedra	Wittichenite Cu1/Cu3		Cu1/Cu6		Skinnerite Cu5/Cu5		Cu2/Cu2	
Octahedral faces	Octahedral diameter (Å) and its inclination to the indicated axis (deg)							
Face pair ⊥ a	3.34(2)	32°	3.36(8)	31°	3.41(8)	33°	3.38	31°
Face pair ⊥ b	3.13(5)	35°	3.13(4)	33°	3.15(4)	32°	3.02	34°
Face pair ⊥ c	3.14(3)	22°	3.14(3)	19°	3.15	19°	3.08	18°
Remaining face pair	3.19(5)		3.14(4)		3.16		3.11	
Cu-Cu distance	2.74		2.64		3.05		3.44	

Prisms	Wittichenite Bi	Sb1	Skinnerite Sb2	Unit-cell twinned ideal *hcp*
Base inclination to [001]				
base occupied by Sb (Bi)	73.2°	74.3°	73.6°	73.24°
unoccupied base	74.4°	75.8°	75.3°	
Base/base angle	1.5°	1.9°	2.3°	0°
Base-base distance (Å)	4.07(4)	4.06(5)	4.08(6)	
Mean face-to-base inclination				
base occupied by Sb (Bi)	89.2(4)°	89.0(6)°	88.1(3)°	90°
unoccupied base	88.4(3)°	88.4(4)°	89.3(7)°	
Angle of normals to occupied prism bases for adjacent prisms				
in zig-zag "chains" of prisms	32.4°	30.6°		33.53°
Mean face-to-opposite edge distance (Å)				
	3.40(11)	3.31(14)	3.33 (14)	
Prism axis inclination to [100]				
	17.2°	14.8°	14.8°	16.76°
Prism length to prism diameter ratio in (010)				
	1.197	1.227	1.225	1.170
Straddling edge-to-(mean) inclined S-S edge ratio (in the occupied bases)				
	0.986	0.985	0.986	0.853

¹Parthé (1976), Hyde et al.(1979)

prisms that straddle the original mirror planes of the unit-cell twinning (Fig. 2); the long Sb–S distances lie between 3.50 and 3.84 Å. Wittichenite contains corresponding Bi coordination polyhedra; its pyramidal bonds are longer (Bi–S in the range 2.57–2.61 Å, angles in the range 94.2–98.7°), and the long Bi–S distances are somewhat shorter than for Sb, from 3.43 to 3.77 Å. The width of the coordination prisms of Sb and Bi varies significantly, whereas their length varies little (Table 3).

Structure metrics

The more slender character of the trigonal coordination prisms of Sb, and their smaller inclination to [100], in comparison to Bi, agree well with the differences between the unit-cell parameters of $P2_1/c$ skinnerite and $P2_12_12_1$ wittichenite. In the (002) levels of skinnerite with *cis* configuration octahedra, the average Sb2–S bond is 2.47(5) Å; in those with *trans* occupied octahedra, the average Sb1–S bond is 2.44(2) Å.

Splitting of the Cu4 position occurs on the levels of flattened *trans* octahedra as a response to the overall reduction in the height of the level; the analogous position Cu3 in *cis* layers is not split.

The length of the zig-zag sequence of octahedra along the *c* direction of skinnerite is 3.15 + 3.14 + 3.08 + 3.14 Å. It involves all types of octahedra defined on page 658. If we relate this sequence of octahedra to the *c* parameter of skinnerite, 13.273 Å, the [001] sequence of two *cis* octahedra in wittichenite results in the model *c* parameter equal to 6.66 Å instead of 6.72 Å. In wittichenite, the configuration octahedra have bases at ~68° to [001]; in skinnerite, the corresponding Cu1–Cu6 octahedra have them at ~71°. Correcting the calculated *c* value of 6.66 Å for this difference gives the right answer for wittichenite, 6.78 Å. On the other hand, the *c* parameter of the lowest form of Cu_3SbS_3 (Whitfield 1980), 6.60 Å, compares favorably with the analogous value for the [001] sequence of alternating type (1) and type (2) *trans* octahedra, 6.61 Å.

In the plane (010), the concordant inclination of all *trans* octahedra of Cu2 and Cu5 and of all *cis* octahedra, respectively, leads to the monoclinic character of the structure of $P2_1/c$-skinnerite (Fig. 3), which is impossible for wittichenite, in which all octahedra have the same *cis* configuration and are inclined in opposite directions in consecutive (002) structure layers (Fig. 4).

Short Cu–Cu contacts

The framework of Cu–Cu distances, typically 2.6–2.9 Å, between tetrahedrally or trigonally coor-

TABLE 4. AVERAGE Cu-S AND Sb(Bi)-S BOND DISTANCES (Å) IN SKINNERITE AND WITTICHENITE

$P2_1/c$ skinnerite		$P2_12_12_1$ wittichenite	
Sb_1-S	2.44	Bi-S	2.592
Sb_2-S	2.47		
Cu1-S	2.28	Cu1-S	2.292
Cu2-S	2.26		
Cu3-S	2.24	Cu2-S	2.274
Cu4A-S	$2.30^1 (2.40)^2$		
Cu4B-S	$2.31^1 (2.46)^2$		
Cu5-S	2.31	Cu3-S	2.289
Cu6-S	2.31		

¹⁾ split, flat-pyramidal coordination; other CuS_3 coordinations are triangular

²⁾ average of four Cu-S distances in irregular tetrahedral coordination [3+1]
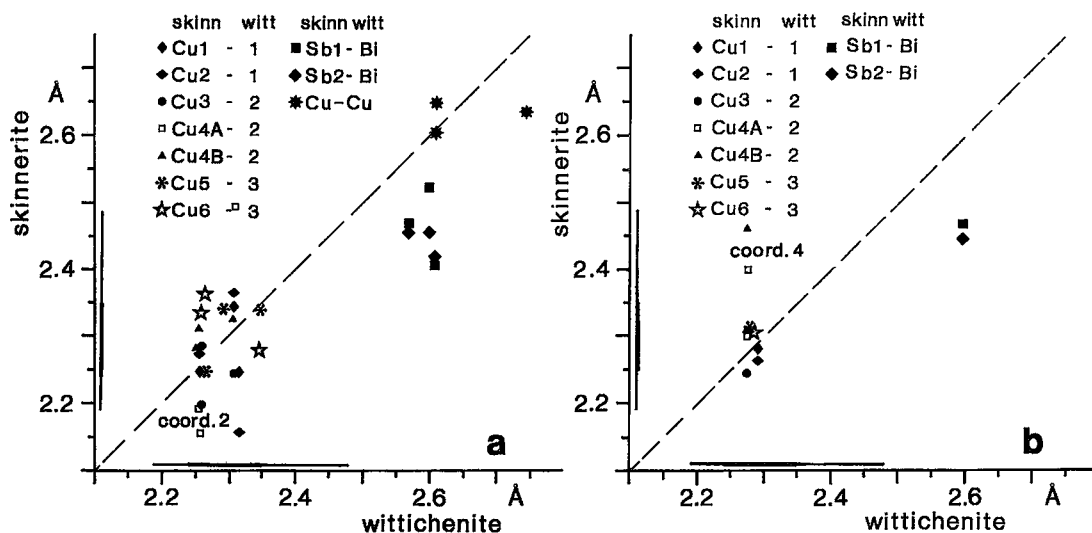
FIG. 5. The bond-length variation for Cu–S and Sb–S bonds in skinnerite correlated with the corresponding Cu–S and Bi–S bonds in wittichenite. (a) Individual bonds; (b) bond averages for individual coordination-polyhedra. Solid intervals along the axes denote ranges of Cu–S distances observed in sulfides and sulfosalts (Evans 1981, Makovicky & Skinner 1979). Most frequently encountered intervals are denoted by increased thickness of the lines.

dinated Cu atoms, is typical for many sulfides and sulfosalts (summaries in Makovicky & Skinner 1979, Evans 1981). In wittichenite (Table 5), Cu1 and Cu3 form a spiral of short Cu–Cu distances parallel to [001]. The average Cu2 position stands much more isolated; however, the Cu2–Cu3 distance will be shortened to 2.74 Å, and the fourth Cu2–S contact to 2.88 Å, when the *rms* displacement of Cu2 is taken into account.

In $P2_1/c$-skinnerite, Cu–Cu distances are modified both by the distribution of Cu atoms in the structure and by the Cu4A–Cu4B split (Table 5). The Cu1–Cu3 spiral from wittichenite is replaced by a finite chain fragment Cu5 · 2.65 Å · Cu1 · 2.64 Å · Cu6 · 2.60 Å · Cu2. Cu1 in skinnerite has an additional short Cu–Cu contact to Cu4A (2.66 Å). Cu3 simulates the average, "stationary" Cu2 position in wittichenite. Cu4A and B gained one short contact (2.66–2.77 Å) in the process of splitting, similar to Cu2 of wittichenite at *rms*

displacement. Cu–Cu contacts for Cu6 and Cu5 are listed in Table 5.

CONCLUSIONS

(1) Rietveld refinement of the crystal structure of the $P2_1/c$ polymorph of skinnerite confirms the model derived from crystal-chemical considerations and results in a reasonable set of interatomic distances.
(2) Sb forms SbS_3 coordination pyramids, situated at the bases of S_6 coordination prisms. Cu is in triangular coordination, except for Cu4, which is split into two statistically occupied, distorted tetrahedral coordinations. Atoms of S form an *hcp* array periodically twinned on $(11\bar{2}2)_{hcp}$.
(3) Skinnerite has layers that have two types of *trans* configuration of Cu around octahedral voids alternating with layers with *cis* coordination. This is in contrast to the $P2_12_12_1$ distribution of Cu sites in wittichenite, where only octahedra with a *cis* configuration of Cu atoms occur. This difference is related to the smaller size of SbS_3 coordination pyramids, compared to BiS_3 pyramids. The pronounced splitting of the Cu4 position in skinnerite has the same origin.
(4) $P2_1/c$-skinnerite contains fragments of a branched network of short Cu–Cu distances as opposed to infinite chains of close Cu–Cu contacts in wittichenite. The Cu4 position in skinnerite and the Cu2 position in wittichenite gain short Cu–Cu contacts in the split.
(5) $P2_1/c$ skinnerite is a lower-temperature polymorph of ion-conducting Cu_3SbS_3; it has a "frozen" array of

TABLE 5. SHORT Cu-Cu CONTACTS IN SKINNERITE AND WITTICHENITE (Å)

	P2₁/c skinnerite					P2,2,2, wittichenite		
	Cu1	Cu2	Cu3	Cu4A	Cu4B		Cu1	Cu2
Cu6	2.64	2.60	2.97	-	-	Cu3	2.610	2.944
Cu5	2.65	-	-	-	2.77		2.743	
Cu4B	-	-	-	-	-	Cu2	2.991	-
Cu4A	2.66	-	-	-	-		(2.74)[1]	

[1] At *rms* displacement from average position

Cu atoms. Its unit-cell-twinned *hcp* skeleton bears a greater resemblance to Cu sulfide arrangements (especially chalcocite) than to an ideal *hcp* array.

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