

Refinement of the crystal structure of emplectite, CuBiS_2 *

By JAN C. PORTHEINE** and W. NOWACKI

Abteilung für Kristallographie und Strukturlehre, Universität Bern***

(Received 2 September 1974)

Auszug

Die Kristallstruktur des Emplektits, CuBiS_2 , wurde auf Grund von dreidimensionalen Röntgendaten verfeinert. Die Raumgruppe ist $Pnma$ und die Gitterkonstanten betragen: $a = 6,1426(3)$, $b = 3,9189(4)$ und $c = 14,5282(7)$ Å; $Z = 4$. Intensitäten wurden mit Hilfe eines Supper-Pace Autodiffraktometers unter Verwendung von $\text{CuK}\alpha$ -Strahlung gemessen. Für die 375 unabhängigen Reflexe ist der endgültige R -Wert gleich 0,063.

Die erhaltene Struktur stimmt mit derjenigen von HOFMANN (1933) und KUPČÍK (1965) überein. Die kürzesten (Bi—S)-Abstände [2,536(4) und 2 mal 2,653(2) Å] spannen eine trigonale Pyramide mit Bi als Spitze auf. Die BiS_3 -Pyramiden sind über gemeinsame Ecken zu endlosen Ketten verknüpft, welche die Zusammensetzung BiS_2 und die Periode b haben. Cu ist von vier S-Atomen [mit den Abständen 2,304(5), 2,317(5) und 2 mal 2,343(3) Å] in Form eines fast regulären Tetraeders koordiniert. Die BiS_2 -Ketten bilden zusammen mit den CuS_4 -Tetraederketten Schichten $\parallel (001)$. Wegen der endlosen BiS_2 -Ketten muß die Emplektitstruktur dem Typ IV.a₃ der Klassifikation von NOWACKI (1969) zugeordnet werden.

Die bekannten Strukturen der Cu,Bi-führenden Sulfosalze CuBi_5S_8 , $\text{Cu}_{2+x}\text{Bi}_{6-x}\text{S}_9$ ($x = 1,21$), Hodrushit, $\text{Cu}_4\text{Bi}_4\text{S}_9$ und Emplektit weisen gemeinsame strukturelle Einheiten, die als Doppelketten von viereckigen BiS_5 -Pyramiden beschrieben werden können, auf. Solch eine Pyramide wird von den fünf nächsten S-Nachbarn des Bi-Atoms gebildet, während das Bi-Atom selber dem Zentrum der Basisfläche naheliegt. Jede BiS_5 -Pyramide besitzt zwei gegenüberliegende Basiskanten, die mit angrenzenden Pyramiden gemeinsam sind, wodurch eine erste endlose Kette entsteht, und zwei Pyramidenkanten, die zu anderen angrenzenden Pyramiden gehören, welche eine zweite, mit der ersten parallele und äquivalente Kette bilden. Die Doppelkette hat eine Zusammensetzung von Bi_2S_4 und eine Periode von 4 Å, die mit der kleinsten Gitterkonstanten der genannten Strukturen übereinstimmt.

* Communication no. 263 b.—Part 78 on sulfides.

** Present address: Laboratoire de Cristallographie aux Rayons X de l'Université, 24 Quai Ernest Ansermet, 1211 Genève 4.

*** CH—3012 Bern, Sahlstrasse 6.

Abstract

The crystal structure of emplectite, CuBiS_2 , has been refined with the aid of three-dimensional x-ray intensity data. The space group is $Pnma$ and the lattice dimensions are: $a = 6.1426(3)$, $b = 3.9189(4)$ and $c = 14.5282(7)$ Å; $Z = 4$. The intensities were measured by means of a Supper-Pace autodiffractometer using $\text{CuK}\alpha$ radiation. The final R value for the 375 independent reflections is 0.063.

The resulting structure corresponds to the structures of HOFMANN (1933) and KUPČÍK (1965). The three smallest Bi—S distances [2.536(4) and two of 2.653(2) Å] span a trigonal pyramid with Bi at the vertex. The BiS_3 pyramids are coupled by corner sharing to endless chains with composition BiS_2 and b as period. Cu is coordinated by four S atoms [at distances 2.304(5), 2.317(5) and two of 2.343(3) Å] in a nearly regular tetrahedron. The BiS_2 chains join with chains of CuS_4 tetrahedra to form sheets parallel to (001). Because of the endless BiS_2 chains emplectite belongs to type IV.a₃ of NOWACKI's (1969) classification.

The known structures of the Cu,Bi-bearing sulfosalts CuBi_5S_8 , $\text{Cu}_{2+x}\text{Bi}_{4-x}\text{S}_9$ ($x = 1.21$), hodrushite, $\text{Cu}_4\text{Bi}_4\text{S}_9$ and emplectite have in common structural units which can be described as double chains of BiS_5 square pyramids. Such a pyramid is formed by the five nearest S neighbours of the Bi atom, while the Bi itself lies near the center of the basal plane. Each BiS_5 pyramid shares two opposite edges of the basal plane with adjacent pyramids in one endless chain; two side edges are shared with pyramids belonging to the second chain, which is parallel and equivalent to the first chain. The double chain has a composition of Bi_2S_4 and a period of 4 Å corresponding to the shortest lattice dimension of the structures mentioned.

Introduction

The crystal structures of the sulfosalt minerals wolfsbergite CuSbS_2 and emplectite CuBiS_2 , which are isotopic, were determined by HOFMANN in 1933. His atomic coordinates were obtained by trial and error methods on the basis of photographic intensity data. KUPČÍK (1965) refined the emplectite structure, using photographic data, and showed that HOFMANN's (1933) structure is correct. At present a refinement of emplectite is reported in which diffractometer data are used. The resulting geometry is essentially the same as the previous ones, but more accurate.

Experimental

For this investigation a crystal was selected from a sample originating from Schwarzenberg in Germany. The crystal had the shape of a short needle with one naturally rounded-off end. It had an anthracite-like appearance and dimensions $0.085 \times 0.094 \times 0.127$ mm. The longest dimension was along the needle axis [010].

Because of the systematic absences $hk0$ for h odd and $0kl$ for $k + l$ odd the diffraction symbol is $mmmPn-a$. $Pnma$ (D_{2h}^{16}) and $Pn2_1a$

(C_{2v}^9) are the possible space groups. The centric space group was adopted and this proved satisfactory.

The lattice parameters were determined with the aid of zero-level Weissenberg photographs of the specimen rotated about [001] and [010]; the camera radius was 57.29 mm. Superposed Si powder lines were used for the calibration. The parameter values were calculated (T. ITO, unpublished) from 78 θ values between 50 and 80°. In Table 1 some diffraction data are given.

For the collection of the intensities the crystal was mounted on a Supper-Pace autodiffractometer for rotation around [010]. 1406 dependent reflections, comprising all accessible ones with this mounting, were measured with the ω -scan technique using Ni-filtered Cu radiation.

An ellipsoidal absorption correction according to JOHNSON (1963) was applied and structure amplitudes, F , were derived as mentioned earlier (PORTHEINE and NOWACKI, 1975). 375 independent¹ amplitudes, F_o , were obtained by averaging $F_o = (1/n) \sum_{i=1}^n F_i$, where n is the number of equivalent ones. 11 reflections were not significant at the 1⁰/₀ level.

The discrepancy between equivalent reflections $\left\langle \sum_{i=1}^n |F_i - F_o| / \sum_{i=1}^n F_i \right\rangle$, averaged over all, amounted to 0.073. This discrepancy is a measure for the inaccuracy of the absorption correction which implies rotational symmetry about [010]. The error in the average F_o due to absorption is probably smaller than 7.3⁰/₀.

Table 1. *Diffraction data of emplectite*
Composition CuBiS₂, $M = 336.6 \text{ g} \cdot \text{mole}^{-1}$,
space group $Pnma$, $Z = 4$, $F(000) = 576$ electrons,
 $\lambda = 1.54178 \text{ \AA}$, $\mu = 1125 \text{ cm}^{-1}$.

	HOFMANN (1933)	KUPČÍK ^I (1965)	present work ^{II}	DANA (1944)
a	6.14(1) Å (from kx)	6.15(1) Å	6.1426(3) Å	
b	3.90(1)	3.92(1)	3.9189(4)	
c	14.54(1)	14.55(2)	14.5282(7)	
ρ_c	6.43 g · cm ⁻³	6.37 g · cm ⁻³	6.393 g · cm ⁻³	6.38 g · cm ⁻³

^I KUPČÍK's unit cell has been transformed according to {100, 00 $\bar{1}$, 010} and the origin has been moved towards the equivalent centre at 0 $\frac{1}{2}$ 0.

^{II} Quoted errors are twice the calculated standard deviations.

¹ The number of possible independent reflections in the Cu sphere is 456.

The statistics of the normalized structure amplitudes, E , indicate the presence of a center of symmetry (see Table 2).

Refinement

The structure was refined by Fourier and least-squares methods using programs adapted for the IBM 370/155 by T. ITO². The quantity $\sum w(F_o) \cdot (F_o - |F_c|/k)^2$ was minimized, where $w(F_o)$ is the weight of F_o , $|F_c|$ the calculated structure amplitude and k the scale factor.

As a start atoms at HOFMANN's (1933) positions for wolfsbergite (Sb replaced by Bi) were refined isotropically in space group $Pnma$. Unit weights were used and all measured reflections were included. The scattering factors for neutral atoms of DOYLE and TURNER (1968) were employed and the anomalous dispersion terms were taken from CROMER and LIBERMAN (1970). In three cycles the conventional R value, $\sum |F_o - |F_c|/k| / \sum F_o$, dropped to 0.0793. A difference map at this stage indicated that the structure was correct. The only significant features were negative regions at the atomic sites (see below). There was also evidence for anisotropic vibration of the Bi atom with highest amplitude in the [100] direction.

The parameters varied in this refinement were: k and for each of the four atoms the isotropic temperature factor and the positional parameters x and z . One could have accepted the results of a subsequent refinement in $Pn2_1a$ at a 0.005 significance level if R had dropped below $0.0793/\mathfrak{R}_{4,358,0.005} = 0.0777^3$. On the basis of the resulting value of 0.0790 however, the centric space group was retained.

Analysis of $|F_o - |F_c|/k|$ as a function of F_o prompted us to consider the weighting scheme: $w(F_o \leq 49.52) = (3.94 \cdot 10^{-2} \times F_o + 2.198)^{-2}$ and $w(F_o > 49.52) = (9.65 \cdot 10^{-4} \times F_o^2 + 4.61 \cdot 10^{-2} \times F_o$

Table 2. *Distribution of normalized structure amplitudes observed for emplectite compared with the theoretical distribution for the centric case*

	theor.	obs.		theor.	obs.
$\langle E^2 \rangle$	1.000	1.002	$E > 1$	32.0%	28.9%
$\langle E^2 - 1 \rangle$	0.968	1.018	$E > 2$	5.0	6.0
$\langle E \rangle$	0.798	0.789	$E > 3$	0.3	0.0

² Now in Tokyo.

³ In this case: the indices of \mathfrak{R} are the number of additional parameters varied in $Pn2_1a$ (y 's of the four atoms), the number of degrees of freedom in the refinement and the significance level.

$-0.50)^{-2}$, which effected independence of $w(F_o)$. $(F_o - |F_c|/k)^2$ on F_o over most of the F_o range. After two cycles of refinement with this weighting scheme R and $R_w = [\sum w(F_o) \cdot (F_o - |F_c|/k)^2 / \sum w(F_o) \cdot F_o^2]^{1/2}$ both amounted to 0.095.

Introduction of anisotropic thermal parameters lowered the values of R and R_w to 0.067 and 0.071 respectively. Comparison of the R_w values of the isotropic and the anisotropic refinements shows that the results of the latter are significantly better ($\mathfrak{R}_{12, 350, 0.005} = 1.030$).

In the subsequent difference map the regions at the atomic sites proved to have virtually the same minima as before: -18 , -10 , -3.6 and $-3.2 \text{ e} \cdot \text{\AA}^{-3}$ for Bi, Cu, S(1) and S(2) respectively. In addition it was found that for the strong reflections $|F_c|$ was systematically larger than $k \cdot F_o$. From the ratios $\langle |F_c|/kF_o \rangle$, averaged for different groups of F_o , a value of $2.34 \cdot 10^{-6}$ was derived for the extinction parameter g in the relation of STOUT and JENSEN (1968): $|F_c| = kF_o \cdot (1 + gLp|F_c|^2)$, where L and p are the Lorentz and polarization factors, respectively. Corrected structure amplitudes were obtained from the above expression after replacing $|F_c|/k$ by $F_o(\text{corr})$.

Further refinement with the aid of the $F_o(\text{corr})$ values resulted in the final parameters of Tables 3 and 4. The parameter shifts were less

Table 3. *Positional coordinates for emplectite in fractions of the cell edges σ in terms of the last digit is added in parentheses*

	x		y	z	
	KUPČÍK	this work		KUPČÍK	this work
Bi	0.2299	0.23156(11)	$\frac{1}{4}$	0.0636	0.06304(4)
Cu	0.7495	0.7509(4)	$\frac{3}{4}$	0.1692	0.1719(2)
S(1)	0.6367	0.6362(6)	$\frac{1}{4}$	0.0970	0.0980(2)
S(2)	0.1235	0.1258(6)	$\frac{3}{4}$	0.1786	0.1777(2)

Table 4. *Thermal parameters and associated σ 's for emplectite*

The Debye-Waller factor is defined as:

$$\exp \{-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{13}hla^*c^*)\}$$

	U_{11}	U_{22}	U_{33}	U_{13}	B^1
Bi	0.0259(4) \AA^2	0.0223(5) \AA^2	0.0141(4) \AA^2	-0.0010(2) \AA^2	1.64 \AA^2
Cu	0.0329(14)	0.0331(18)	0.0209(14)	-0.0006(9)	2.29
S(1)	0.0255(18)	0.0226(18)	0.0132(16)	-0.0014(13)	1.61
S(2)	0.0277(19)	0.0222(18)	0.0134(15)	0.0010(14)	1.66

¹ The equivalent isotropic temperature factor, B .

Table 6. *Interatomic distances and associated σ 's in emplectite*

Bi—S(1)	2.536(4) Å	S(1)—Cu } —Cu'' }	2.343(3) Å
—S(2) } —S(2)'	2.653(2)	—Bi	2.536(4)
Average	2.614		
Bi—S(1)' } —S(1)'' }	3.158(3)	—Bi' } —Bi'' }	3.158(3)
—S(1)'''	3.692(4)	—Bi'''	3.692(4)
Bi—Cu'	3.415(3)	S(1)—S(2)''	3.772(5) 2 ×
—Cu'''	3.881(2)	—S(2)'''	3.804(4) 2 ×
—Cu ^{IV}	4.322(3) 2 ×		
Cu—S(2)''	2.304(5)	S(2)—Cu'''	2.304(5)
—S(2)'''	2.317(5)	—Cu ^{IV}	2.317(5)
—S(1) ^{IV} } —S(1) }	2.343(3)	—Bi } —Bi ^{IV} }	2.653(2)
Average	2.327		
Cu—Cu ^{IV}	3.819(4) 2 ×	S(2)—S(2)'''	3.721(5) 2 ×

Table 7. *Interatomic angles and associated σ 's in emplectite*

S(1)—Bi—S(2)	96.57(10)° 2 ×	Bi'''—S(1)—Cu	76.41(11)° 2 ×
—S(1)'	84.03(9) 2 ×	Bi'''—S(1)—Bi'	69.10(7) 2 ×
—S(1)'''	160.57(9)	—Bi	160.57(13)
S(1)'—Bi—S(2)	94.00(7) 2 ×	Bi'—S(1)—Cu	75.12(8) 2 ×
—S(1)''	76.71(6)	Bi'—S(1)—Bi''	76.71(8)
—S(1)'''	110.90(8) 2 ×	—Bi	95.97(9) 2 ×
S(2)—Bi—S(1)'''	70.80(9) 2 ×	Cu—S(1)—Bi	112.73(11) 2 ×
—S(2)'	95.24(8)	Cu—S(1)—Cu''	113.50(17)
S(2)''—Cu—S(1)	108.50(12) 2 ×	Cu ^{IV} —S(2)—Bi	120.74(10) 2 ×
—S(2)'''	107.28(17)	Cu ^{IV} —S(2)—Cu ^{III}	111.47(18)
S(1) ^{IV} —Cu—S(1)	113.50(16)	Bi—S(2)—Bi ^{IV}	95.24(11)
—S(2)'''	109.43(12) 2 ×	Bi—S(2)—Cu'''	102.82(12) 2 ×

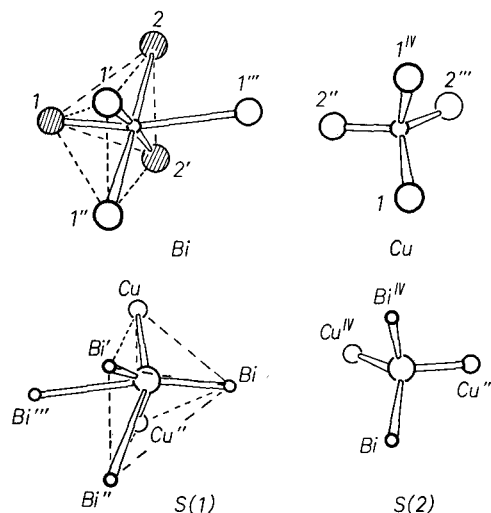


Fig. 1. Atomic coordinations in emplectite. For Bi and S(1) the square pyramids are indicated with broken lines. The three nearest S neighbours of Bi are marked by hatching

structures are 0.013, 0.036, 0.015 and 0.022 Å for Bi, Cu, S(1) and S(2) respectively.

The interatomic distances (Table 6) and angles (Table 7) are calculated with the aid of the program BDS (P. ENGEL, unpublished). Numerals of equivalent atoms are illustrated in Fig. 1 in which the coordinations of the atoms are drawn. In Fig. 2a the (010) projection of the structure is given.

Usually the Bi atom in sulfosalts has three S neighbours at approximately orthogonal distances smaller than 2.85 Å, spanning a trigonal pyramid⁴. This is also the case in emplectite and the average Bi—S distance of 2.614 Å lies near the lower limit of the range of averages 2.59–2.79 Å, observed in other sulfosalts. Each BiS₃ group shares corners with two adjacent groups in such a way that endless chains are formed running along *b*, having *b* as period and BiS₂ · $\frac{1}{2}$ + 1 = BiS₂ as composition.

The Cu atom is surrounded by four S atoms in a nearly regular tetrahedron. The average Cu—S distance of 2.327 Å lies well in the

⁴ Exceptions to this rule are the atoms Bi(1) in cosalite (Pb₂Bi₂S₅, WEITZ and HELLNER, 1960 and SRIKRISHNAN and NOWACKI, 1974) and in CuBi₅S₈ (OHMASA and NOWACKI, 1973). In cosalite Bi(1) has five S atoms nearer than 2.86 Å forming a square pyramid and in CuBi₅S₈ Bi(1) is coordinated octahedrally by six S atoms within this distance.

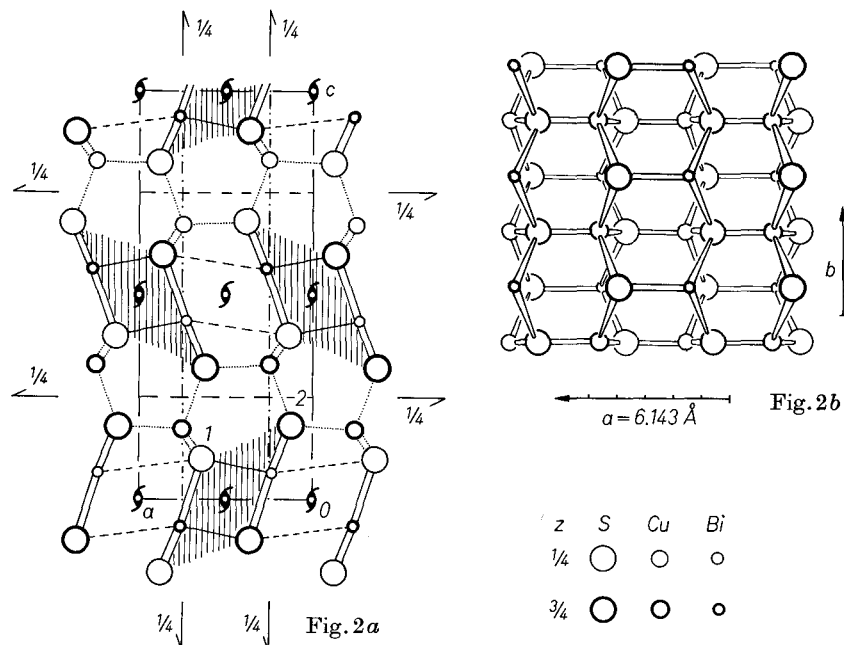


Fig. 2a. (010) projection of the emplectite structure. Bi—S distances inside the BiS_5 pyramids are fully drawn while those outside are broken. Cu—S distances are dotted. Double distances represent different distance vectors which are projected above each other. Hatched areas indicate the Bi_2S_4 double chains

Fig. 2b. Sheet of composition CuBiS_2 in emplectite perpendicular to c

range of 2.304–2.365 Å for Cu in tetrahedral coordinations not strongly distorted⁵. In the same way as the BiS_3 pyramids the CuS_4 tetrahedra are joint together into endless chains along b ; they have the composition $\text{CuS}_2 \cdot \frac{1}{2} + 2 = \text{CuS}_3$.

By means of corner sharing between the elementary tetrahedra and pyramids the two kinds of chains are joint in sheets perpendicular to c with a thickness of $\frac{1}{2}c$. The composition of these sheets as seen in Fig. 2b is CuBiS_2 . The sheet representation of the emplectite structure is in accordance with the principal cleavage along (001).

Within a distance of 3.2 Å the coordination of S(1) consists of three Bi and two Cu atoms in the form of a square pyramid. The farther Bi''' atom (see Fig. 1) completes a distorted octahedral coordination similar to that of Bi. The thermal parameters of Bi and S(1)

⁵ Coordinations with S—Cu—S angles of more than 115° are excluded.

are virtually equal which is consistent with this similarity. The thermal parameters of Cu and S(2) show the same trend, specifically $U_{\beta}(\text{Cu}) \sim 1.4 U_{\beta}\{\text{S}(2)\}$, but in view of the high symmetry of the coordinations involved it is not clear why in each case $U_{33} < U_{11} \sim U_{22}$.

Emplectite belongs to class IV in NOWACKI's (1969) classification since the atomic S/Bi ratio is equal to 2. The complete specification is IV.a₃ because of the endless chains of BiS₃ pyramids (of composition BiS₂).

Comparison of the structures of Cu,Bi-bearing sulfosalts

The structures of emplectite and the other Cu,Bi-bearing sulfosalts: CuBi₅S₈ (OHMASA and NOWACKI, 1973), Cu_{2+x}Bi_{6-x}S₉ ($x = 1.21$, OHMASA, 1973), hodrushite (Cu₃Bi₁₂S₂₂⁶, KUPČÍK and MAKOVICKÝ, (1968 and KODĚRA, KUPČÍK and MAKOVICKÝ, 1970) and Cu₄Bi₄S₉ (OZAWA and TAKÉUCHI, 1972) have in common Bi-containing structural units which are easily visualized if one takes into account neighbours more distant from Bi than the three nearest S atoms.

The five nearest S neighbours of Bi in sulfosalts are arranged in a square pyramid⁷ with Bi near the centre of the basal plane⁸. Distances towards the fourth and fifth nearest S atoms range between 2.86 and 3.16 Å.

Two types of Bi coordinations can be distinguished when further S neighbours are considered. Either there is one additional S at a distance between 2.99 and 3.45 Å completing an octahedron (type α) or there are two additional ones comprising a split vertex of an octa-

⁶ This is an idealized composition. The one resulting from microprobe analysis (KODĚRA *et al.*, 1970) is Cu_{8.12}Bi_{11.54}Fe_{0.29}S_{22.00}.

⁷ There are four examples where the square pyramid is not formed by the five nearest S atoms. The square pyramids of Bi(1) in bismuthinite (Bi₂S₃, KUPČÍK and VESELÁ-NOVÁKOVÁ, 1970), Bi(1) in Cu₄Bi₄S₉ and Bi(5) in hodrushite are formed by the three nearest S atoms together with the fifth and sixth nearest. For Bi(2) in galenobismuthite (IITAKA and NOWACKI, 1962) the square pyramid is realized within the six nearest S atoms if the third is omitted [see Fig. 3d].

⁸ The "square pyramid" for Bi in wittichenite Cu₃BiS₃ (KOCMAN and NUFFIELD, 1973) has an exceptional form. The three nearest S neighbours are arranged at virtually equal distances (2.57, 2.60 and 2.61 Å) and constitute a side face which is nearly perpendicular to the "basal plane". The fourth and fifth S atoms lie at unusual large distances 3.43 and 3.56 Å (normal value = 3.0 ± 0.15 Å). The BiS₃ pyramids occur as isolated units in the structure and consequently wittichenite, with its atomic S/Bi ratio of 3, belongs to type II.a₁ of NOWACKI's (1969) classification.

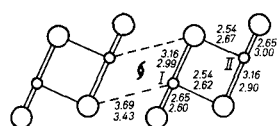


Fig. 3a

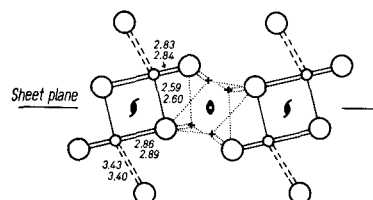


Fig. 3b

Fig. 3a. Schematic projection of two adjacent Bi_2S_4 chains in emplectite. In nuffieldite (KOHATSU and WUENSCH, 1973) a similar constellation of two chains is found. In the latter case M(4) (= Bi) corresponds to Bi(I) in the figure and M(1) (= Pb + Bi) to Bi(II). Distances are given in Å; upper values apply to emplectite

Fig. 3b. Fragment of the sheet which contains the type- β Bi atoms in CuBi_5S_8 and $\text{Cu}_{2+x}\text{Bi}_{6-y}\text{S}_9$. The square (on the twofold axis) and the crosses are the projections of the Cu atoms in the two structures respectively. Distances are given in Å

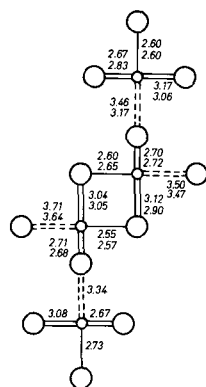


Fig. 3c

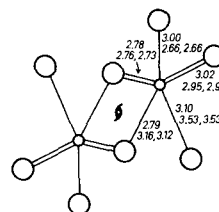


Fig. 3d

Fig. 3c. Schematic projection of the four-membered chain in hodrushite. Distances with two values indicate the three-membered subchain in $\text{Cu}_4\text{Bi}_4\text{S}_9$

Fig. 3d. Projections of the Bi_2S_8 chain in galenobismuthite (ITAKA and NOWACKI, 1962) and aikinite. The lower distance values correspond to aikinite (left: OHMASA and NOWACKI, 1970; right: KOHATSU and WUENSCH, 1971)

hedral coordination (type β). The octahedral coordination of Bi in emplectite will be characterized as type β , with one atom of the split vertex missing, because of the large deviation from regularity. The same coordination is found for M(4) (= Bi) in nuffieldite (KOHATSU and WUENSCH, 1973; see Fig. 3a).

