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Cyclically twinned sulphosalt structures and their approximate analogues

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Abstract. Two homologous series of cyclically twinned sulphosalt structures are defined in the present paper, with different atomic configurations around the site of six- and threefold axes. The zinckenite homologous series, $M_{6+x+N(N+5)}\,A_{12+N(N+7)}$, contains zinckenite, a Pb–Sb sulphosalt, and sulphohalogenides of Bi and Pb. The Ba–Bi sulphide homologous series, $M_{12+x+N(N+5)}\,A_{18+N(N+7)}$, contains complex sulphides of Bi and alkaline earths. Degenerate (or approximate) cyclic twinning with only local threefold symmetry occurs in the structures of several Pb–Bi–Sb–(Cu,Fe) sulphosalts and $Eu_3Sb_4S_9$. The known and the missing members of these series are discussed and related hypothetical structures derived.

Introduction

Chemical twinning represents the most important of the large-scale structure building mechanisms recognized in recent chemical literature (Ito, 1950; Andersson and Hyde, 1974). In the majority of cases it is a polysynthetic twinning but several compounds or structural families based on cyclic twinning have also been recognized (Hyde et al., 1974). The concept of chemical twinning was applied to some of the complex sulphides of As, Sb and/or Bi (sulphosalts) by several authors, among others Otto and Strunz (1968), Hyde et al. (1974), Takéuchi and Takagi (1974), Takéuchi (1978), Wuensch (1979), Makovicky and Karup-Møller (1977), and Makovicky (1981). In several of these works entire families of homologues were defined, based on the same structural principles but with step-wise homologous expansion of slabs between the planes of chemical twinning.

In the present contribution two new homologous series derived by means of sixfold cyclic repetition (twinning) of (homologously expanding) basic elements are defined for which both known and hypothetical members are described. The description is based on building elements recognizable in the twinned structures; but at the same time an alternative description is given in terms of building elements from parent sulphosalt structures, to which cyclical twinning has to be applied in order to produce the two sulphosalt series studied here. The series are named after their typically developed (i.e. not the lowest) members, a mnemotechnic aid considered superior to the use of their complex general chemical formulae.

In the third part of this contribution several degenerate, i.e. approximately or partly cyclical structures are illustrated. No exhaustive classification is attempted because the spectrum of potential structures of this kind is very broad.

Several definitions will be used in the present work which were given (or summarized) by Makovicky (1981). According to this reference, in the majority of structures of the sulphosalts of bismuth, infinite or finitely broad slabs of archetypal, PbS-like arrangement can be discerned. Their surfaces represent either $(100)_{\mathrm{PbS}}$ or $(111)_{\mathrm{PbS}}$. More complicated slabs or rods are usually limited by combinations of these two types of planes. The slabs limited by $(100)_{\mathrm{PbS}}$ were called T slabs by Makovicky (1981). Their width is defined by a number of primitive, square subcells that can be counted on their surface and have axes parallel to the width and length of the slabs (Fig. 1). They represent coordination half-octahedra (square pyramids) of the metal atoms situated on the surfaces of the T slabs. The order number, N, of a homologue in a homologous series in which homologues differ by the width of T slabs (resp. width of T surfaces of more complicated rods) can conveniently be defined by the number of these "T subcells" across the width of T surfaces, T rods or T slabs. This is the N value used in all the formulae derived below.

The zinckenite homologous series

In the structures of the zinckenite homologues, sites of 6_3 axes are surrounded by ring walls composed of six columns of edge-sharing bicapped trigonal coordination prisms of Bi, Sb or Pb. The prisms are arranged "en echelon" and share two sulphur atoms with each neighbouring prism. For all homologues with $N > 0$ the capped flanks of each prism pair issue a slab $(100)_{\mathrm{PbS}}$ of a galena-like structure which is two atomic planes thick (i.e. a T slab as described by Makovicky, 1981). Altogether six T slabs interconnect each ring wall with adjacent ring walls. The number of half-octahedra (T subcells, Makovicky, 1981) which span two ring walls determines the order number N of the homologue (Fig. 1).

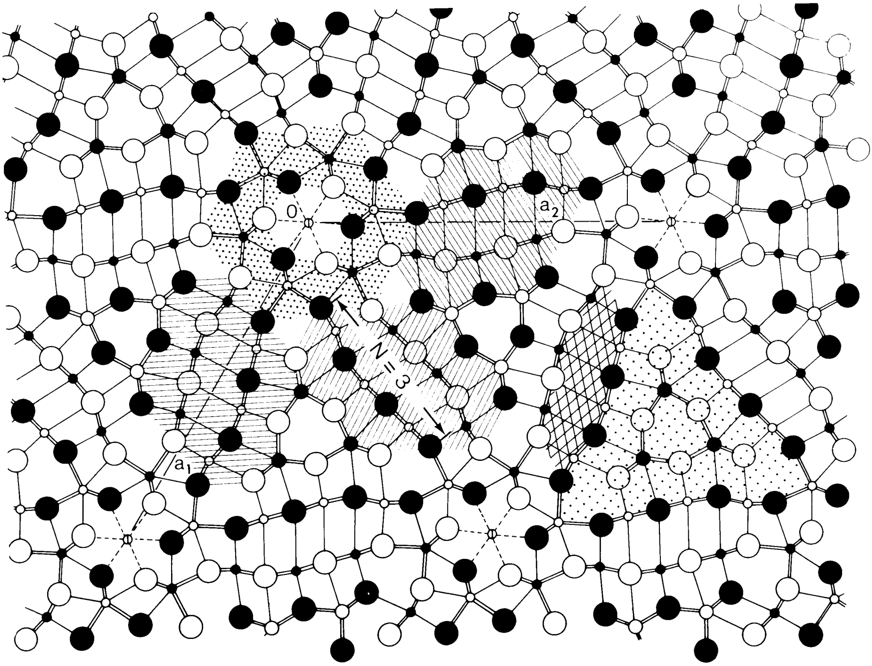

Fig. 1. The crystal structure of zinckenite, $\mathrm{Cu}_x\mathrm{Pb}_{9+x}\mathrm{Sb}_{22-x}\mathrm{S}_{42}$, the type structure of the zinckenite homologous series. The order number of the homologue, N, is equal to 3. The 4.3 Å substructure refined by Portheine and Nowacki (1975) is shown. Circles in order of decreasing size indicate S, Pb, and Sb or (Sb,Pb). Empty and filled circles indicate atoms around two z levels 2.1 Å apart, hatched circles the metal atoms in the 6_3 channels of the structure. The hexagonal ring walls and the triangular channels between the T slabs are stippled. The lozenge-like rods of PbS-like structure are hatched. An example of a T rod is cross-hatched

With increasing N the cross-section of triangular channels between three adjacent T walls rapidly increases and eventually the channels can accomodate additional anions and cations. There is a rather complex relationship between the number of ions inserted in these triangular spaces and the order number N of the homologue. The relationship $\mathrm{M}_{\mathrm{N}(\mathrm{N}-1)}$ $\mathrm{A}_{\mathrm{N}(\mathrm{N}+1)}$ is established, where M = cations, and A = anions, primarily sulphur atoms. The framework of ring walls and T slabs has the composition

$$\mathrm{M}_{6+x+6\mathrm{N}}\,\mathrm{A}_{12+6\mathrm{N}}\,,$$

where the coefficient x (the value of which lies between zero and 1 per formula unit) denotes the additional cation which may reside in the 6_3 channels. The complete formula is then

$$\mathrm{M}_{6+x+\mathrm{N}(\mathrm{N}+5)}\,\mathrm{A}_{12+\mathrm{N}(\mathrm{N}+7)}\,.$$

Tables 1 and 2 respectively give the known representatives and the theoretical data for the first six homologues of the series.

The first two homologues contain both sulphur and halogen atoms as anions. In the case with $N = 0$, the halogens partly substitute for S in the coordination polyhedra of Bi or Pb and the sulphur/halogen ratio adjusts to the average valency of cations (Table 1). For $N = 1$ the halogen atoms are weakly bonded and reside in the trigonal channels limited by the T slabs, together with lone electron pairs of Bi atoms (Figs. 2 and 3).

In the homologue with $N = 1$ the T slabs (and the adjacent coordination prisms from the ring walls) represent "inverted" lone electron pair micelles (Makovicky and Mumme, 1983) very closely related to those in Bi_2S_3 (as recognized by Miehe and Kupčík, 1971). From $N = 1$ to $N = 2$ (Fig. 4) inversion of the lone electron pair arrangement takes place and all homologues with $N \geq 2$ contain "normal" lone electron pair micelles which have the lone electron pairs of Sb or Bi accommodated inside the somewhat expanded T slabs. In these homologues, rods of galena-like arrangement are formed with lozenge-like cross-sections which besides the T slabs also comprise some of the metal and sulphur atoms residing in the now broad triangular channels. They are analogous to such rods observed in other, non-cyclically twinned Pb–Sb and Pb–Bi sulphosalts (Makovicky, 1981). Therefore, the homologues with $N \geq 2$ can be derived by cyclical twinning from structures like that of (2 Å-sheared) robinsonite (Petrova et al., 1978) or of a 4,5-lillianite (Makovicky and Mumme, 1983). On the contrary the homologues with $N < 2$ represent cyclically twinned structures derived from Bi_2S_3 and SbSI types (Fig. 5).

Compositional variations found in the members of the zinckenite homologous series are:

(1) Incomplete occupation of the hexagonal (6_3) channels in these structures by trigonally coordinated metals.

(2) Exchange of loosely bound halogen atoms in the triangular channels.

(3) Uptake of tetrahedrally coordinated Cu into positions in the corners of triangular channels for the homologues with $N > 1$, concurrent with the substitution of divalent metals (Pb) for trivalent metals (Sb) in adjacent framework positions.

Two of the processes just outlined affect the composition of zinckenite ($N = 3$) which has been a matter of long-standing controversy (Moëlo, 1982). From their structure determination, Portheine and Nowacki (1975) assumed the square-pyramidal metal positions in the lozenge-shaped rods to be occupied by Sb, the ring walls by (Sb, Pb) and the channels along the 6_3 axes by statistically occurring Pb atoms. Furthermore, sulphur vacancies were found in their refinement which was performed in the space group $P6_3$. In the somewhat different model of Lebas and Le Bihan (1976), two out of three square pyramidal metal positions present in the structure are

Table 1. The homologues of zinckenite

Compound/ mineral	Chemical formula	Homologue N	Lattice parameters (Å)		Space group	References
			a	c		
Synthetic	$Bi_4Cl_2S_5$[a]	0	19.80[b] (= 11.43 × 2 cos 30°)	12.36[b] (= 3 × 4.12)	$R\bar{3}$	Krämer, 1979
Synthetic	$Pb_7S_2Br_{10}$[c]	0	12.27	4.32	$P6_3/m$	Krebs, 1973
(Synthetic	Th_7S_{12}[d]	0	11.09	4.01	$P6_3/m$	Zachariasen, 1949)
Synthetic	$Bi(Bi_2S_3)_9I_3$[e]	1	15.63	4.02	$P6_3$[f]	Miehe and Kupčík, 1971
Synthetic	$Bi(Bi_2S_3)_9Br_3$[e]	1	15.55	4.02	$P6_3$	Mariolacos, 1976
Zinckenite	$Pb_9Sb_{22}S_{42}$	3	22.15	8.66 (= 2 × 4.33)	$P6_3$[h]	Portheine and Nowacki, 1975
	to $CuPb_{10}Sb_{21}S_{42}$[g]		22.15	8.64	$P6_3/m$[h]	Lebas and Le Bihan, 1976

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[a] Formula given by Krämer (1979), $Z = 15$. Structural formula reads $Bi_{0.67}Bi_6S_8Cl_4$ ($Z = 9$) if the full occupancy of all atom positions in the space group $R\bar{3}$ is maintained. Krämer's formula requires 3 anion vacancies in a cell

[b] The unit cell given represents a $(2\vec{a}_1 - \vec{a}_2;\ -\vec{a}_1 + \vec{a}_2;\ 3\vec{c})$ supercell of the basic periodicities of an ideal homologue $N = 0$. It is produced by ordering of Bi positions in the 6_3 channels and deformation of the framework

[c] Undeformed homologue $N = 0$. Unusually high temperature factors were observed for Pb

[d] Composition might be variable according to the number of positions occupied in the 6_3 channels (Hulliger, 1968)

[e] Formulae as given in original sources. Structural formulae read $Bi_{0.67}Bi_{12}S_{18}Hal_2$ with the positions of Bi in the channels statistically occupied by 2/3 Bi

[f] Also refined in $P6_3/m$

[g] Formulae given by Moëlo (1982); discussed in the text

[h] True symmetry is lowered to monoclinic in ordered cases. Discussion given in the text

Table 2. Theoretical data for the lower homologues of zinckenite

N	General formula		Theoretical formulae for sulphides and halogen-sulphides[a]											
	Cation	Anion	Hexagonal channels occupied						Hexagonal channels unoccupied					
			M^{4+}	M^{3+}	M^{2+}	M^{+}	S	X	M^{4+}	M^{3+}	M^{2+}	M^{+}	S	X
0	6→7	12	3	4			12		6				12	
				7−x	x		9−x	3+x		6−x	x		6−x	6+x
1	12→13	20	1	12			20		4	8			20	
				13−x	x		19−x	1+x		12−x	x		16−x	4+x
2	20→21	30		18−x	3+x		30−x	x		20−x	x		30−x	x
				18−y	3+y	y	30			20−y	y	y	30	
3	30→31	42		22−x	9+x		42−x	x		24−x	6+x		42−x	x
				22−y	9+y	y	42			24−y	6+y	y	42	
4[b]	42→43	56		26	17		56			28	14		56	
5	56→57	72		30	27		72			32	24		72	

[a] M^{+} reside in tetrahedral interstices; X represents Cl, Br, or I

[b] The above variations in composition, based either on the halogen/sulphur ratio or on the presence of M^{+} in tetrahedral interstices, apply also in this and the following cases. They can be combined in one compound. Cases with partly occupied hexagonal channels occur (see Table 1)

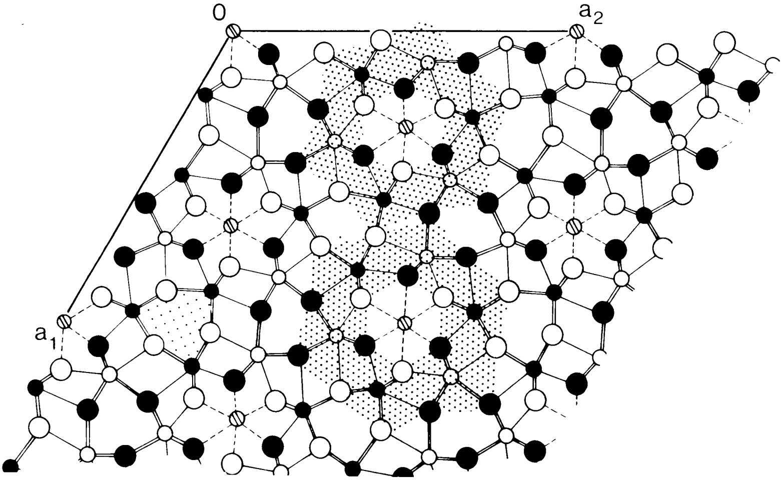


Fig. 2. The crystal structure of $Bi_4Cl_2S_5$ (Krämer, 1979), $N=0$ (zinckenite series). In order of decreasing size: (S, Cl), Bi. Colouring and shading as in Fig. 1

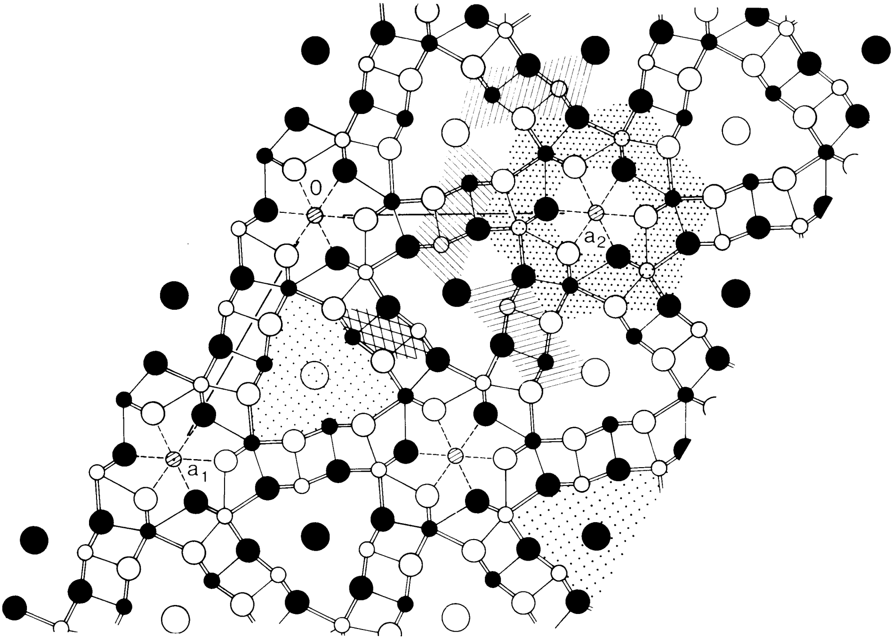


Fig. 3. The crystal structure of Bi $(Bi_2S_3)_9I_3$ (Miehe and Kupčík, 1971), the homologue of zinckenite with $N=1$. Circles in order of decreasing size: I, S, Bi. Colouring and shading as in Fig. 1

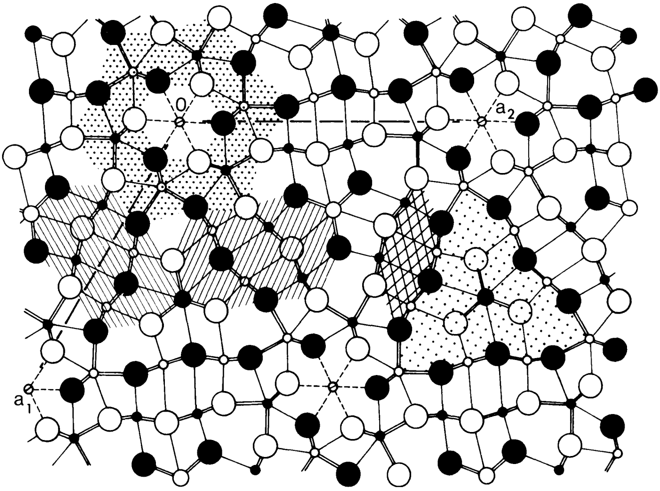


Fig. 4. The crystal structure of the hypothetical zinckenite homologue $N = 2$. Colouring and shading as in Fig. 1

occupied by (Sb, Pb), the third position and the ring walls by Sb, and the channels along the 6_3 axes are void. Similarly to Takeda and Horiuchi (1971), the French authors refined the structure in $P6_3/m$. None of the refinements included the usually disordered weak reciprocal lattice levels which indicate the true c parameter of zinckenite to be 8.7 Å. Lebas and Le Bihan (1976) explained the pseudohexagonal monoclinic 8.7 Å superstructure by compositional segregation in zinckenite and proposed a non-stoichiometric general formula $Pb_{1+n}\ Sb_{4-n}\ S_7$ ($0.502 < n < 0.67$). In 1983, Makovicky and Mumme explained the observed discrepancies between the two sets of structure determinations for the 4.3 Å substructure of zinckenite as stemming from configurational complexities of the (mostly disordered) pseudohexagonal 8.7 Å structure of the mineral and not from compositional segregation in the latter.

In 1982 Moëlo showed that the $Pb \rightleftarrows Sb$ substitution in zinckenite is connected with a variable Cu content and suggested that the substitution mechanism

$$Sb^{3+} + \text{vacancy} \rightleftarrows Pb^{2+} + Cu^{+}$$

resulted in the compositions of zinckenite observed in his microprobe analyses

$$Cu_x\ Pb_{9+x}\ Sb_{22-x},\ 0 < x < 1\ .$$

Moëlo suggested full occupancy by Sb for the trigonally coordinated metal positions on the 6_3 axes.

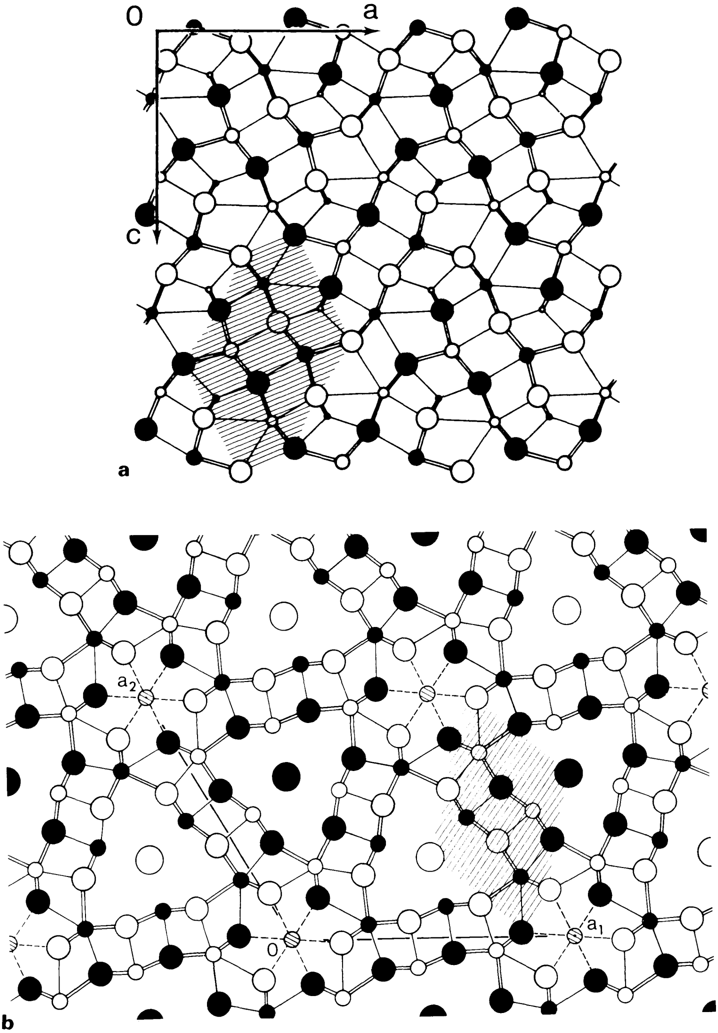


Fig. 5a, b. The common tiling element for the crystal structures of aikinite, $CuPbBiS_3$ (Ohmasa and Nowacki, 1970) (minus Cu, cf. the crystal structure of Bi_2S_3) and $Bi(Bi_2S_3)_9I_3$ (Miehe and Kupčík, 1971)

To check Moëlo's derivations against those of the previous authors, we should refer back to the linkage pattern established by all three structure determinations on zinckenite. It predicts the composition $Me_{30}S_{42}$ for the structure with the 6_3 sites empty, in contrast to $Me_{31}S_{42}$ for the case with these sites completely filled. There are 6 tetrahedral sites per unit cell. Therefore, the resulting composition ought to lie between the theoretical

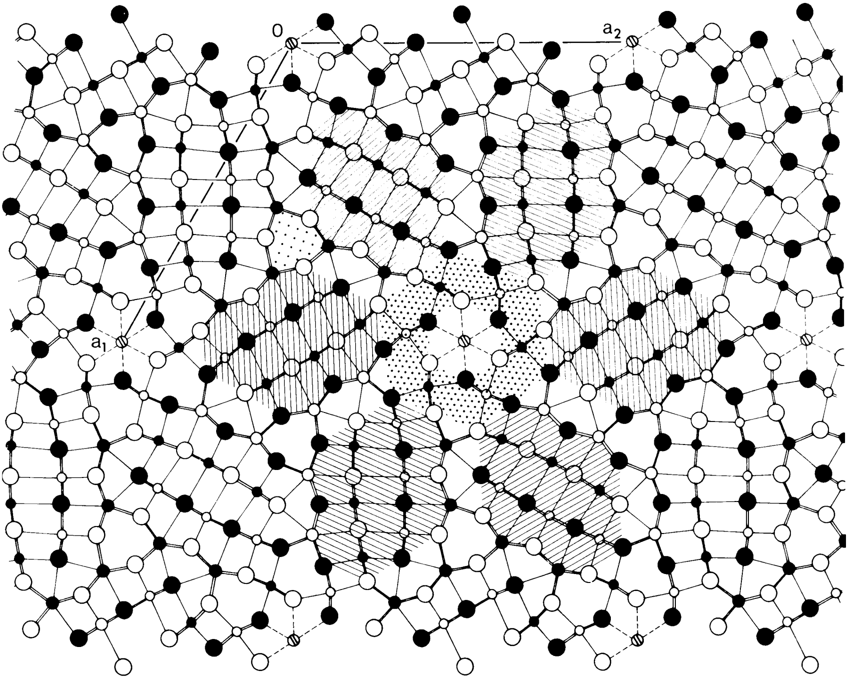


Fig. 6. The crystal structure of $Ba_{\sim 12}Bi_{\sim 24}S_{48}$ (Aurivilius, 1983), the type structure of the Ba – Bi sulphide homologous series. The order number, *N*, of this homologue is defined as the number of T subcells across the shaded lozenge-shaped rods of PbS-like arrangement and is equal to 3. Circles in the order of decreasing size: S, Ba, Bi. Empty and filled circles denote atoms at two levels *z*, 2 Å apart; the hatched circles represent atoms in the 6_3 channels of the structure. Shading as in Fig. 1

extremes of $Pb_6Sb_{24}S_{42}$ (Pb/Sb = 0.250) and $Cu_6Pb_{12}Sb_{18}S_{42}$ (Pb/Sb = $0.\overline{66}$) in the first case, and $Pb_9Sb_{22}S_{42}$ (Pb/Sb = 0.409) and $Cu_6Pb_{15}Sb_{16}S_{42}$ (Pb/Sb = 0.938) in the second case.

Moëlo (1982) found the Pb/Sb ratio to be equal to 0.41 for natural, Cu-free zinckenite samples and to change linearly towards 0.46 in Cu-containing zinckenite with 1% Cu. The latter composition corresponds to the formula $CuPb_{10}Sb_{21}S_{42}$. All the compositions observed thus correspond to the variant with the 6_3 metal positions *fully occupied.* The initial Pb/Sb ratio of 0.41 would imply as much as 2.72 Cu atoms per formula unit if the second alternative, with the 6_3 positions unoccupied, was true. At present, 1% Cu represents the highest copper content observed in zinckenite, implying the average occupancy of 1/6 for each tetrahedral site in the unit cell (1 copper atom per cell). This limitation may be due to the problems arising from the considerable difference between the sizes of the Pb and Sb coordination polyhedra involved in this coupled substitution.

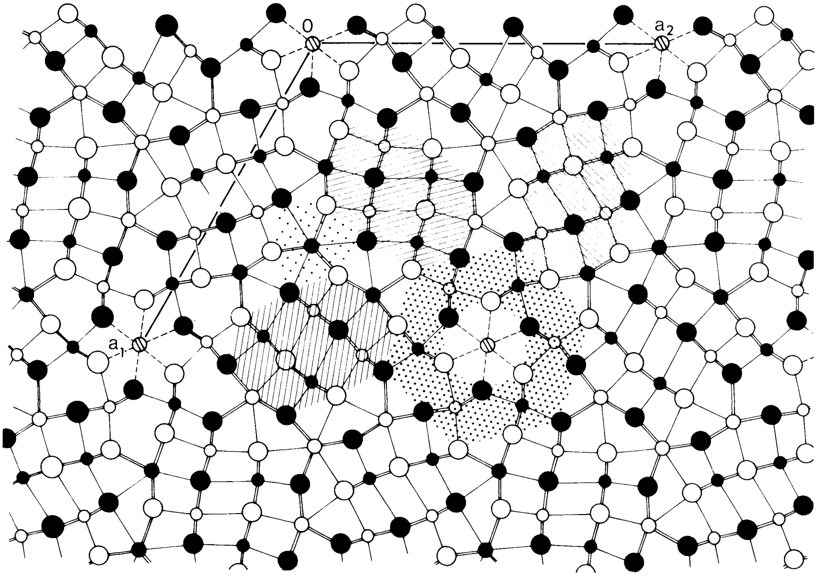


Fig. 7. The crystal structure of $Ba_9Bi_{18}S_{36}$, $N = 2$ (Aurivilus, 1983). Colouring and shading as in Fig. 6

The Ba—Bi sulphide homologous series

In this series, the ring walls which surrounded the sites of 6_3 axes are composed of columns of slightly distorted coordination octahedra, linked together via single columns of shared S atoms (Figs. 6 and 7). In the known homologues, $N = 2$ and 3 (Table 3), a rod of "galena-like" arrangement with lozenge-shaped cross-section issues from each octahedral column. It is directed towards a column of octahedra in the ring wall around adjacent 6_3 axis. The number of T subcells in the rod determines its largest diameter and with it the order number of the homologue. The rods are 4 atomic rows thick, with a distorted octahedral coordination [$Bi\ S_{3+2+1}$] and a lone electron pair micelle in their central parts. Using the stated principles, it was possible to derive the crystal structures of the yet unknown members with $N = 1$ and $N = 4$ (Figs. 8 and 9, Table 4).

Changes in N influence substantially the configuration of channels between the rods, situated on the threefold axes at $(\frac{1}{3}, \frac{2}{3})$ and $(\frac{2}{3}, \frac{1}{3})$. Therefore, the general chemical formula is composed of the term for the "galena-like" rods including the octahedral ring walls, that is

$$M_{12N+x}A_{12(1+N)}$$

Table 3. The homologues of $BaBi_2S_4$

Compound	Formula	Homologue N	Lattice parameters (Å) a	c	Space group	Reference
(Fluoroborite	$Mg_3(F,OH)_3BO_3$	0	8.83	3.09	$P6_3/m$	Dal Negro and Tadini, 1974)
9-$BaBi_2S_4$[a]	~ $Ba_9Bi_{18}S_{36}$	2	21.71	4.16	$P6_3/m$	Aurivilius, 1983
12-$BaBi_2S_4$[a]	~ $Ba_{12}Bi_{24}S_{48}$	3	25.27	4.18	$P6_3/m$	Aurivilius, 1983
12-$SrBi_2S_4$[a]	$Sr_{12}Bi_{24}S_{48}$	3	24.93	4.10	$P6_3/m$	Aurivilius, 1983

[a] Following Aurivilius (1983) the formula of the homologue indicates the number of formula units in a unit cell. Both Ba-containing phases were defined as BaS. $(1 + \varepsilon)Bi_2S_3$ ($\varepsilon \gtrless 0$) in the original work

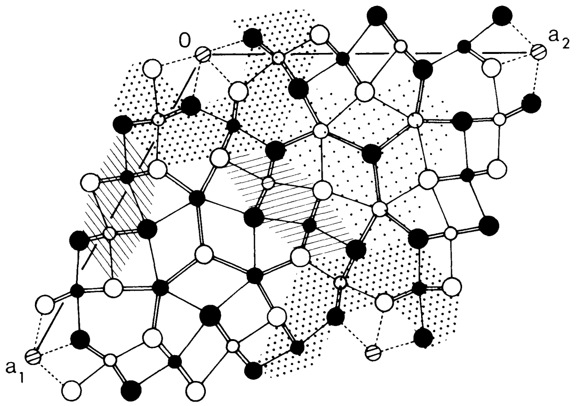


Fig. 8. The crystal structure of the hypothetical homologue $N = 1$ of the Ba – Bi sulphide homologous series. Colouring and shading as in Fig. 6

where $0 \leq x \leq 1$ represents the partly occupied metal positions on the 6_3 axis and the term which describes the interstitial atoms in the channels around threefold axes

$$M_{(N-3)(N-4)}A_{(N-2)(N-3)} \cdot$$

The resulting formula for the entire structure ($Z = 1$) is

$$M_{12+x+N(N+5)}A_{18+N(N+7)} \cdot$$

In the known structures anions A represent sulphur (Table 3).

The crystal structure of fluoroborite Mg_3 $(F,OH)_3(BO_3)$ (Fig. 10), can serve as a model for the $N = 0$ homologue of this series. The general formula

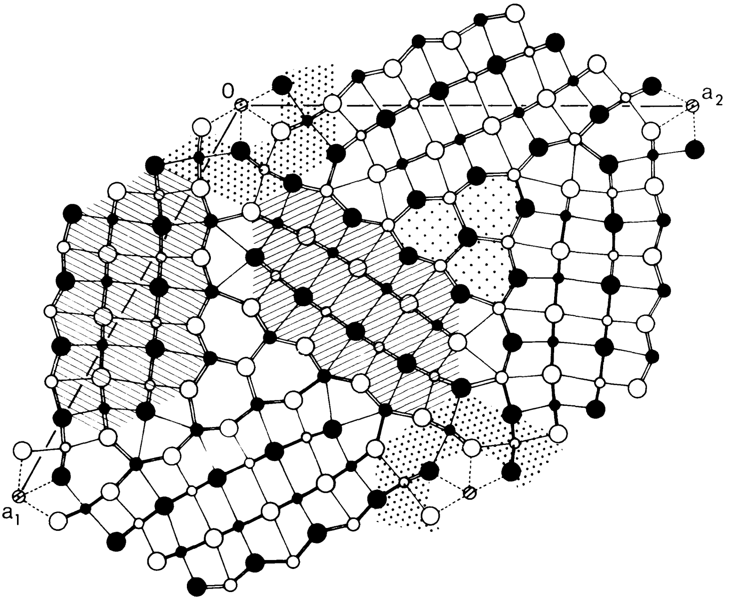


Fig. 9. The crystal structure of the hypothetical homologue $N = 4$ of the Ba – Bi sulphide homologous series. Colouring and shading as in Fig. 6

Table 4. Theoretical data for the lower homologues of $BaBi_2S_4$

N	General formula		Theoretical formulae for sulphides and halogen-sulphides[a]							
	Cation	Anion	M^{3+}	M^{2+}	S	X	M^{3+}	M^{2+}	S	X
0	12→13	18	10 – x	3 + x	18 – x	x	12 – x	x	18 – x	x
1	18→19	26	14 – x	5 + x	26 – x	x	16 – x	2 + x	26 – x	x
2	26→27	36	18 – x	9 + x	36 – x	x	20 – x	6 + x	36 – x	x
3	36→37	48	22	15	48		24	12	48	
4	48→49	62	26	23	62		28	20	62	
5	62→63	78	30	33	78		32	30	78	

[a] The outlined substitutions based on the changeable halogen/sulphur ratio apply to all homologues. X represents Cl, Br or I. Cases between the extremes with fully occupied (left) and unoccupied (right) hexagonal channels occur (see the text)

is still valid also for this phase (Table 4) in spite of the fact that it is without rod development between the octahedral ring walls.

The composition ranges of the homologues $N = 2$ and $N = 3$ have not been determined with certainty. Aurivilius (1983) describes both homologues as $BaS \cdot (1 + \varepsilon)Bi_2S_3$ where $\varepsilon \gtrless 0$. Without metal atoms in the channels situated on the 6_3 axes, the homologue with $N = 3$ would have

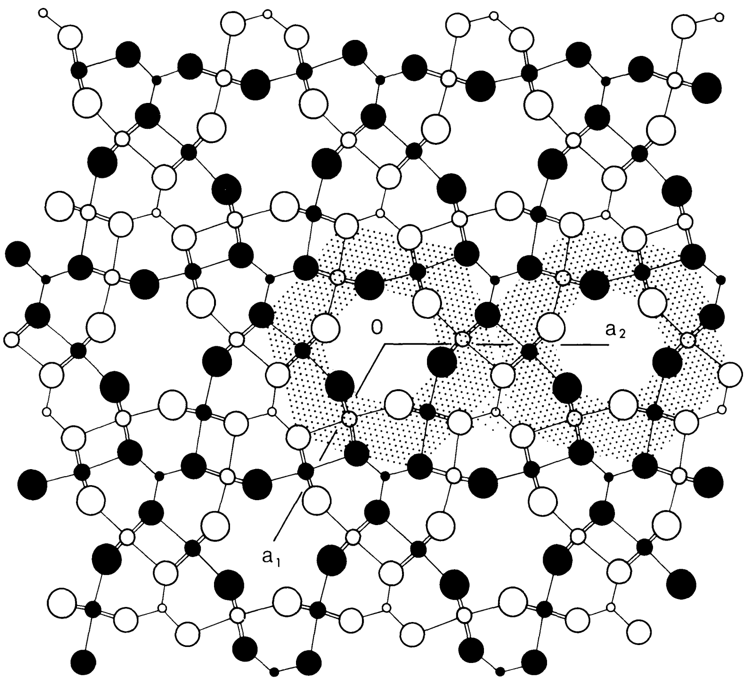
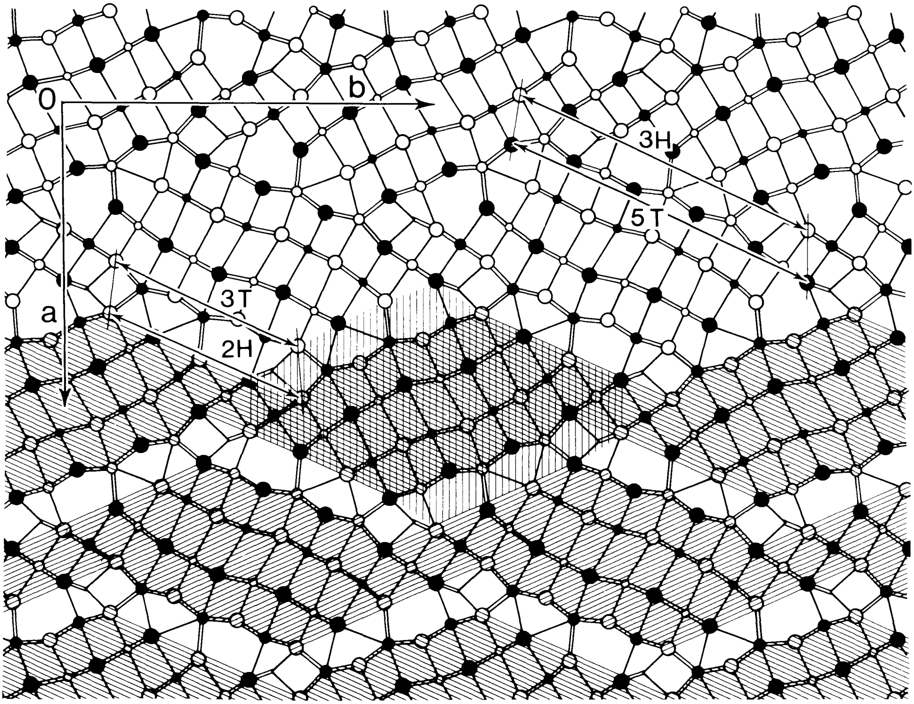


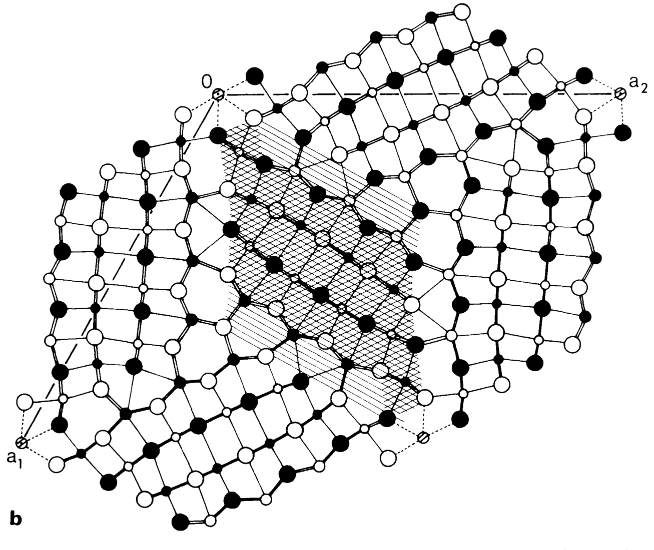
Fig. 10. The crystal structure of fluoroborite, $Mg_3(F,OH)_3BO_3$ (Dal Negro and Tadini, 1974), an oxysalt analogue of the 0th member of the Ba – Bi sulphide homologous series. Shading as in Fig. 6

the structural formula $Ba_{12}Bi_{24}S_{48}$ ($Sr_{12}Bi_{24}S_{48}$), equal to the ideal 1:2 formula $Me^{2+}_{12}Bi_{24}S_{48}$. Introduction of metals in the 6_3 channels must lead to an increased (Ba,Sr) : Bi ratio. Aurivilius has shown that for the strontium compound, and for the Ba compound at high temperatures, the Me^{2+}/Bi ratio is very close or equal to 1/2, i.e. $\varepsilon \approx 0$ and the channels on the 6_3 axes are nearly unoccupied. For the $N = 2$ homologue, the idealized structural formula without metal atoms in the 6_3 channels would be $Ba_8Bi_{18}S_{36}$ and would display unbalanced valencies. The composition can be stabilized by introduction of Ba into the channels, ideally $Ba_9Bi_{18}S_{36}$, i.e. again the 1:2 ratio of Me^{2+} to Bi. The accuracy of the structure determinations was not sufficient to describe the just mentioned compositional variations in detail (Aurivilius, 1983).

The homologue with $N = 4$ (Fig. 9) has not been found as yet. It is potentially interesting because it represents the cyclically twinned derivative of the crystal structure of cosalite (Fig. 11), thus underlining the structural affinities between the cyclically twinned series typified by the Ba – Bi sulphides and the cosalite homologues. While the lower homologues,



a



b

Fig. 11 a, b. The common tiling element for the crystal structure of cosalite, $Pb_2Bi_2S_5$ (Srikrishnan and Nowacki, 1974) and that of the hypothetical 4th member of the Ba–Bi sulphide homologous series

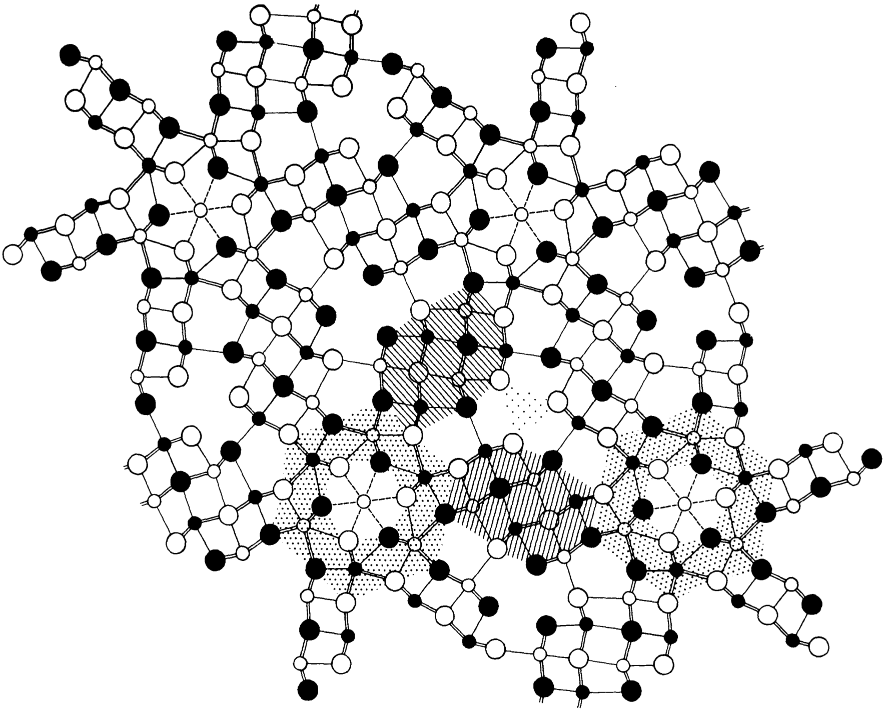


Fig. 12. A representative of the hypothetical homologous series parallel to the zinckenite and Ba – Bi sulphide series. Shading as in Fig. 6

$N = 1$ and 2 contain additional cations or entire groups of their coordination polyhedra in the channels on threefold axes, the homologue $N = 3$ has no additional ions in these spaces and for $N = 4$ additional anions reside in these positions.

Both the known and the hypothetical structures of this series require the presence of very large cations with trigonal prismatic coordination and are not known as naturally occurring compounds.

The alternative series

In the zinckenite homologous series, ring walls around adjacent 6_3 axes are interconnected by T layers which are two atomic layers thick. If the ring walls and the six attached T layers are rotated slightly around the sixfold axes, the interconnection is broken and the T layers issued from adjacent 6_3 centers become parallel-sided, forming a four atomic layers thick "galena-like" rod similar to that in the Ba – Bi-sulphide series. A hypothetical structure of this type, derived from the structure of $Bi(Bi_2S_3)_9I_3$ (Miehe and Kupčík, 1971) is shown in Fig. 12.

Table 5. Representatives of approximate cyclic twinning

Mineral	Formula[a]	Lattice parameters (Å)			Space group	Reference
Kobellite	$(Cu,Fe)_2Pb_{12}$-$(Bi,Sb)_{14}S_{35}$	*a* 22.58	*b* 34.10	*c* 4.04[b]	*P*2₁/*n*[c]	Miehe, 1971
Izoklakeite	$(Cu,Fe)_2Pb_{26}$-$(Sb,Bi)_{20}S_{57}$	*a* 37.69	*b* 33.93	*c* 4.06[d]	*Pnnm*	Makovicky and Mumme, in press
Eclarite	$(Cu,Fe)Pb_9$-$Bi_{12}S_{28}$	*c* 22.75	*a* 54.76	*c* 4.03	*Pnma*	Kupčík, 1983
Synth.	$Eu_3Sb_4S_9$	*b* 23.84	*a* 16.50	*c* 4.03	*Pnam*	Lemoine et al., 1981

[a] All complex formulae are idealized
[b] The monoclinic angle α is equal to 90.0° (Miehe, 1971)
[c] Very close to *Pnnm*
[d] The pronounced subcell of a very weak 8 Å cell

The zinckenite homologous series is parallel to the heterochemical homologous series of hexagonal structures $Fe_2P-Th_7S_{12}-Rh_{20}Si_{13}$ (Engström, 1965) in which capped trigonal coordination prisms organize themselves into trigonal columns of increasing complexity, equivalent to those observed in zinckenite and its next lower and higher homologues. The primary difference between the two series dwells in the different interfaces of adjacent trigonal columns. These columns face each other directly in the heterochemical series $Fe_2P-Rh_{20}Si_{13}$ whereas they are separated by two intervening layers of metal and sulphur atoms in the case of zinckenite homologues. As a result of this the hexagonal walls of anions around the 6_3 axes belong to different types of coordination polyhedra in the two series.

The two series intersect in a common member which has $N = 0$ in the zinckenite homologous series and $N = 2$ in the $Fe_2P-Rh_{20}Si_{13}$ series. For $N = 0$ the width of T walls in the zinckenite homologues is reduced to zero and the entire structure consists of intermeshed trigonal prisms.

Degenerate (approximate) cyclic twinning

Cyclically twinned structures are relatively rare due to the stringent requirements they impose on the geometric fit of individual motifs (elements) joined together in a structure with high symmetry. Conspicuous is the absence of tetragonally twinned 4 Å (8 Å)-sulphosalt structures, with the possible exception of the pseudotetragonal arrangement of certain motifs in

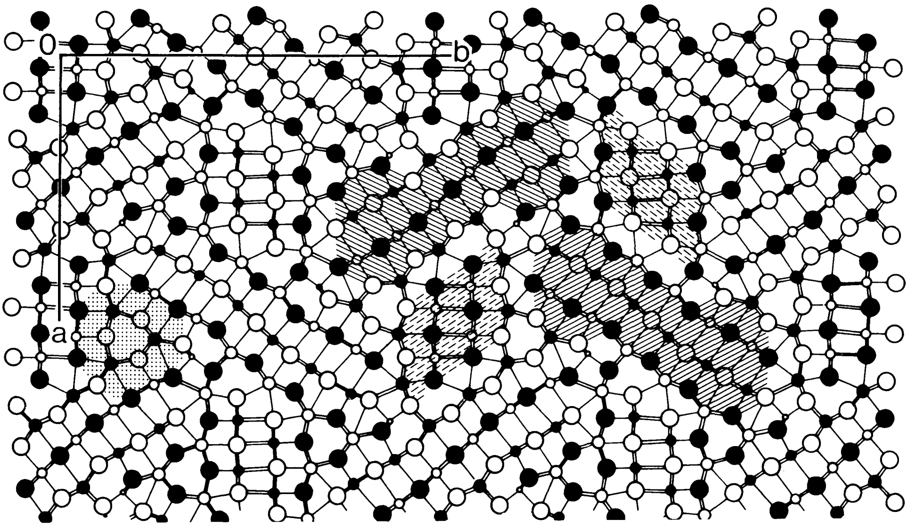


Fig. 13. The crystal structure of kobellite, $(Cu,Fe)_2Pb_{12}(Bi,Sb)_{14}S_{35}$ (Miehe, 1971). The threefold groups of coordination prisms of Pb as well as the rods based on PbS- and SnS-like arrangements of metal and sulphur atoms are indicated by stippling, hatching and dashing, respectively. Circles in order of decreasing size represent S, Pb, Bi or Sb or mixed positions, and Cu. Two atomic *z* levels, 2 Å apart

the crystal structure of bournonite, $CuPbSbS_3$ (Edenharter and Nowacki, 1970, see Fig. 29 in Makovicky, 1981), which is reflected by the fourfold twinning of the mineral (Godovikov et al., 1982). Similarly, chemically twinned structures of 4 Å (8 Å) sulphosalts with only threefold symmetry are not known to us, perhaps because the acute edges of lozenge-shaped rods, present in them, can only be fitted with sixfold repetition even if arrangement of such rods differs in the two sulphosalt structure families described above (Figs. 1 and 6).

Cyclically twinned structures with hexagonal or trigonal symmetry cannot be built from T rods which contain median planes of 2 Å shear, such as observed in jamesonite and related Pb – Sb sulphosalts (Makovicky, 1981). The presence of such rods will always result in a breakdown of crystallographic rotational symmetry as does also the non-equivalence (differing length, width, truncation or orientation) of “galena-like” rods around the original symmetry axis.

In the known sulphosalts of this family a very stable group of three bicapped trigonal coordination prisms of Pb (resp. RE) which share common vertical edges and are capable of attaching Pb, Sb or Bi coordination polyhedra along the perimeter of the group is often found. It survives the reduction of overall symmetry and builds cores of high local symmetry around which the pseudohexagonal(-trigonal) arrangement of these

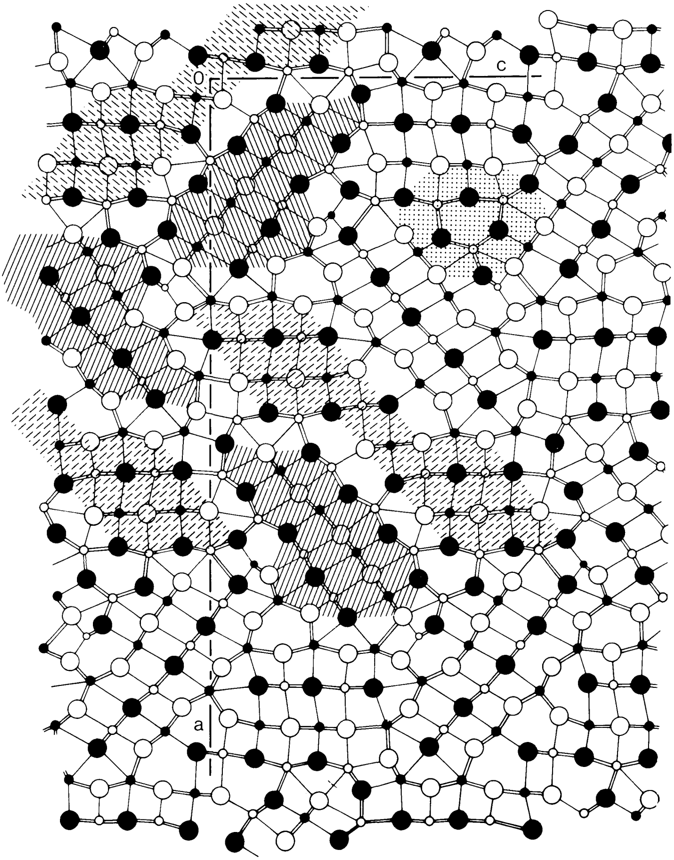


Fig. 14. The crystal structure of eclarite, $(Cu,Fe)Pb_9Bi_{12}S_{28}$ (Kupčík, 1983). The threefold groups of coordination prisms of Pb and the structural rods based on PbS-like arrangement are indicated in the manner analogous to the corresponding elements in the crystal structure of kobellite in Fig. 13

structures evolves. The vertical mirror planes of this group are not preserved even in the (sub)structure of zinckenite where its threefold axis becomes an element of space-group symmetry (Fig. 1). In the structures of kobellite (Miehe, 1971) (Fig. 13), eclarite (Kupčík, 1984) (Fig. 14) and izoklakeite (Makovicky and Mumme, in press), out of the three large rods around the local threefold axis, two are larger and with PbS-like arrangement. They are reflection-equivalent. The third rod differs from them both in length and shape. In the structures of kobellite and izoklakeite this rod even displays 2 Å-shear on its median plane (i.e., an SnS-like arrangement).

The arrangement of rods (domains) in the degenerate structures (Figs. 13 and 14) is strongly reminiscent of the domain arrangement in

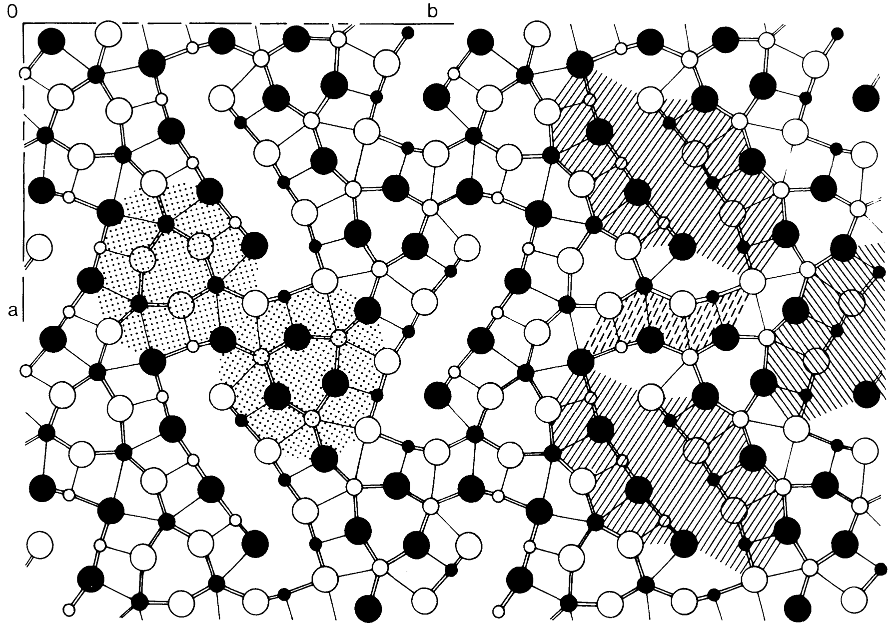


Fig. 15. The crystal structure of $Eu_3Sb_4S_9$ (Lemoine et al., 1981). The threefold groups of coordination prisms of Eu and the rods of SnS-like arrangement are indicated in a way analogous to the corresponding elements in kobellite (Fig. 13)

interpenetration twins of morphological crystallography whereas that in true cyclic structures resembles the domain mosaic in the contact twins. It should be stressed that, unlike to the case of the zinckenite homologues, domain boundaries are non-commensurate (Makovicky and Hyde, 1981) both in the structures of the Ba – Bi sulphide series and in the degenerate cyclic structures.

The crystal structure of $Eu_3Sb_4S_9$ (Lemoine et al., 1981) consists of interconnected threefold groups (columns) of bicapped trigonal coordination prisms of Eu. Sb coordination pyramids are attached to the re-entrant edges of this skeleton and arranged into elongated lone electron pair micelles (Fig. 15). Each threefold column of prisms conjugates directly with three other such columns. Two attachments obey fully the local three-fold axis of the central column (or the local reflection plane in the plane of the attachment). The third column is related to the central one only by a twofold screw axis that also entails the loss of the Sb coordination pyramid otherwise wedged between two threefold columns of prisms. If the latter "stacking errors" (apparently due to the valence balance) are eliminated, an openwork structure with trigonal symmetry will result in which the lone electron pair micelles expand into large triangular channels (Fig. 16). The

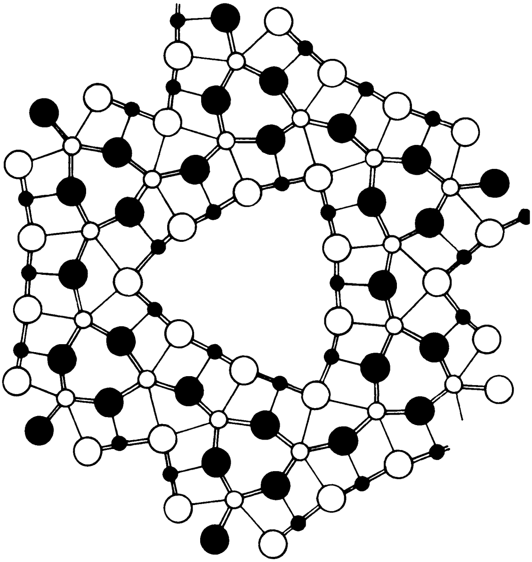


Fig. 16. The fundamental element of the hypothetical crystal structure of $(Eu_2Sb_3S_6)^+$ with large channels to accommodate additional ions; derived from the crystal structure of $Eu_3Sb_4S_9$ (Fig. 15)

resulting formula $(Eu_2^{2+}Sb_3S_6)^+$ has to be compensated by additional ions in the channels. It remains to be seen whether the small discrepancies between the sizes of coordination polyhedra that are observed in the original structure can be compensated for to build the new one.

Certain kinship can be traced between the crystal structure of $Eu_3Sb_4S_9$, in which Sb coordination pyramids fill the re-entrant portions of threefold columns of bicapped trigonal coordination prisms of Eu, and the (idealized) crystal structure of $Bi_4Cl_2S_5$ (Krämer, 1979) (resp. that of Th_7S_{12}) in which the re-entrant portions are occupied by caps of coordination prisms from adjacent threefold columns. These columns are packed much tighter in the latter case. On the other hand, as also indicated in Fig. 15, the crystal structure of $Eu_3Sb_4S_9$ can be interpreted in the same terms as those of kobellite and izoklakeite. However, the two larger, reflection-related rods, out of the three rods around the local threefold axis represent rods [001] of SnS archetype and not of the types encountered in the Pb—Bi—Sb sulphosalts.

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