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The crystal structure of jaskolskiite, $Cu_x Pb_{2+x} (Sb, Bi)_{2-x} S_5$ ($x \approx 0.2$), a member of the meneghinite homologous series

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Crystal structure / Jaskolskiite /* $Cu_x Pb_{2+x} (Sb, Bi)_{2-x} S_5$ ($x \approx 0.2$) / *Meneghinite homologous series

Abstract. The crystal structure of a new sulphosalt, jaskolskiite, $Cu_x Pb_{2+x} (Sb, Bi)_{2-x} S_5$ ($x \approx 0.2$), has been determined. The space group is *Pbnm*, with $a = 11.312(2)$, $b = 19.829(3)$, $c = 4.088(1)$ Å, $Z = 4$ for the composition $Cu_{0.19} Pb_{2.22} Sb_{1.17} Bi_{0.62} S_5$. The structure has been solved using its homologous relationship to meneghinite and refined from three-dimensional diffractometer data to an *R*-value of 0.072 for 472 observed reflections.

The structure consists of slices (010) of SnS-like arrangement mutually related by the *n*-glide planes and wavy interfaces. The metal positions M1 and M4 inside the slices represent Sb sites partly substituted by Bi and Pb. The M2 and M3 positions are on the surfaces of slices and represent Pb sites with some substitution by Bi in the case of M2. The tetrahedral sites in the slice interfaces are partially occupied by Cu. Jaskolskiite represents the 4th member of the meneghinite homologous series. The published chemical and structural data for the known homologues of meneghinite, with $N = 1, 2, (3), 4$ and 5, are systematized in the paper.

Introduction

Jaskolskiite was described in 1983 by Zakrzewski from the Vena ore deposit, Central Sweden, as a bismuth- and copper-containing analogue of the synthetic phase $Pb_2Sb_2S_5$ studied by Wang (1973). One of the authors

(E.M.) established the symmetry and lattice parameters of the new species using single crystals of the type material.

In 1973 Wang suggested that the modification of $Pb_2Sb_2S_5$ found in his study possessed an orthorhombic reciprocal lattice akin to that of meneghinite, $CuPb_{13}Sb_7S_{24}$ (Euler and Hellner, 1960). Our data confirmed this relationship and suggested that jaskolskiite ought to represent the nearest lower homologue of meneghinite, filling partly the gap between the presently known members of a potential homologous series. Confirmation of this situation and interest in the details of Sb/Bi/Pb substitution in some metal positions in the structure represent the rationale for the present structure determination.

Experimental

Single crystals of jaskolskiite were freed by Dr. Zakrzewski from the ore-bearing rock by dissolving the surrounding carbonate material in HCl. They represent short needles with irregular terminations.

A prismatic crystal with the dimensions $0.03 \times 0.05 \times 0.2$ mm was selected. Weissenberg X-ray photographs showed that jaskolskiite is orthorhombic with systematic absences in accordance with space group *Pbnm* (*cab* setting of space group *Pnma*) and its noncentrosymmetric equivalent *Pbn*2, (*bac* setting). The latter was excluded since the $hk0$ and $hk2$ layers have the same intensity distributions indicating that all atoms can be located in the special positions ($x,y,\frac{1}{4}$; $\bar{x},\bar{y},\frac{3}{4}$; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{4}$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{3}{4}$) of the space group *Pbnm*. The outcome of the investigation supports the choice of the space group.

Unit-cell parameters and orientation were determined from the setting angles of 10 reflections, $11.8 < \theta < 16.3°$, measured on a CAD4 single crystal diffractometer with Cu$K\alpha$ radiation monochromatized by a graphite crystal. The obtained data are listed in Table 1. The cell parameters are close to those derived earlier by Zakrzewski (1984) [a = 11.331(1), b = 19.871(2) and c = 4.100(1)]. Intensities were collected with the CAD4 diffractometer for all reflections with $\theta < 74.5°$, using the ω-2 θ scan technique. No decomposition of the crystal during the data collection could be detected from measurements of two standard reflections. Of the 830 reflections measured, 472 were considered as observed with $\sigma(I)/I < 0.2$, where $\sigma(I)$ was estimated from conventional counter statistics. The crystal habit was determined using a reflection goniometer arrangement connected to a Weissenberg camera. The crystal could be described by 11 crystal faces all belonging to the forms {110}, {010}, {120}, {100} and {210}, in the order of decreasing importance. Corrections for Lorentz and polarization effects as well as for absorption were performed. The transmission factors ranging from 0.02 to 0.17 were calculated with a grid of $12 \times 12 \times 12$ points used for the numerical Gaussian integration.

Table 1. Crystal data for jaskolskiite. E.s.d.'s in parentheses refer to the last significant digits

Formula $Pb_{2.22}Cu_{0.19}Sb_{1.17}Bi_{0.62}S_5$	
Mw = 904.4	$V = 917.0(3)$ Å^3
Space group *Pbnm*	$Z = 4$
$a = 11.312(2)$ Å	$D_x = 6.551(2)$ g · cm^{-3}
$b = 19.829(3)$ Å	$F(000) = 1515$
$c = 4.088(1)$ Å	$\lambda(CuK\alpha) = 1.54184$ Å
	$\mu = 138.8$ mm^{-1}

Structure determination and refinement

Initial atomic coordinates for jaskolskiite were obtained from those of meneghinite (Euler and Hellner, 1960) by the process of homologous contraction (Makovicky, 1981) of the parent structure by one metal polyhedron in the central parts of the SnS-like layers of meneghinite. Euler and Hellner's metal position No. 3 was deleted and the sulphur positions Nos. 7 and 11 coalesced in the process of this operation.

The derived structural model was refined by full-matrix least-squares techniques. In the first trials all atoms were restricted to vibrate isotropically, but the Sb(1) and Sb(4) (Table 2) positions were allowed to be partially substituted by Bi. The copper atoms, indicated by the chemical analysis (Zakrzewski, 1983) to have an occupancy below 0.2, were not included at this stage. The initial refinements yielded R-values of 0.25. Allowing the metal atoms to vibrate anisotropically, but keeping the substitution parameter at the M 1 position fixed at 0.4, lowered the R-value to 0.09. The highest peak, 6 e.A^{-3}, found in a subsequent difference electron density map occurred at the proposed Cu-position. The strongest reflection 002 seemed to suffer severely from extinction ($|F_o| = 649$ and $|F_c| = 905$) and was excluded from the further refinements. In the final refinement yielding an R of 0.072 the substitutional parameters of the M 1 and M 4 atoms were varied simultaneously with their anisotropic thermal parameters, and the occupational parameter of the Cu atom was varied with an isotropic thermal parameter. The only correlation coefficients with magnitudes above 0.5, *viz.* -0.53 and 0.76, occurred between the substitutional and occupational parameters of the M 4 and Cu atoms and their U_{22} and U_{11} values respectively. Thus, we migth look on the occupational parameter 0.16(3) of the Cu atom with some suspicion, while the Bi (resp. Bi + Pb) substitution parameters, 0.40(3) and 0.29(3), of the M1 and M 4 positions respectively are likely to be statistically relevant. The chemical formula obtained from the structural refinements is in good agreement with that found by chemical analysis (vide infra). The atomic coordinates and thermal parameters are listed in Tables 2 and 3.

Table 2. Fractional atomic coordinates ($\times 10^4$) for jaskolskiite and equivalent isotropic temperature parameters ($\text{Å}^2 \times 10^4$), estimated as one third of the trace of the orthogonalized U_{ij} tensor

Site	Occupancy	x	y	z	U
M(1)	0.71(3)Sb + 0.29(3)(Pb, Bi)	3014(4)	−237(2)	2500	333(15)
M(4)	0.60(3)Sb + 0.40(3)Bi	3753(4)	1281(2)	7500	293(15)
M(2)	Bi, Pb	4991(3)	4043(2)	7500	323(11)
M(3)	Pb	1688(3)	2923(2)	7500	341(11)
Cu	0.16(3)Cu	3915(48)	2587(25)	2500	255(99)
S(1)	S	6285(12)	4764(7)	2500	204(32)
S(2)	S	5632(13)	793(8)	2500	254(34)
S(3)	S	2467(15)	1711(8)	2500	309(35)
S(4)	S	4948(13)	2335(7)	7500	236(36)
S(5)	S	3184(13)	3680(7)	2500	184(33)

Table 3. Anisotropic thermal parameters ($\times 10^3$) for metal atoms in jaskolskiite. The temperature factor expression used is $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
M(1)	392(23)	271(18)	337(33)	0	0	−26(14)
M(4)	347(23)	157(17)	374(34)	0	0	11(12)
M(2)	341(16)	281(14)	346(24)	0	0	6(10)
M(3)	513(18)	163(12)	347(23)	0	0	−7(10)

The atomic scattering factors used were those of the International Tables of Crystallography (1974). The weights used for minimizing $\Sigma w(|F_o| - |F_c|)^2$ in the refinements were proportional to $1/(\sigma(F_o) + 0.001 F_o^2)$. In the last refinement iteration the ratios $|\Delta/\sigma|$ were less than 0.004.

Description of the structure

General features

The crystal structure of jaskolskiite consists of (010) slices composed of slabs of semioctahedral structure which are two atomic layers thick. The slabs follow approximately the (130) and ($1\bar{3}0$) planes of the crystal lattice of jaskolskiite. Adjacent (010) slices are related by n-glide reflection planes situated at $y = \frac{1}{4}$ and $\frac{3}{4}$ (Fig. 1). The composition planes between the adjacent slices are wavy and are bridged by long Pb−S bonds and by coordination tetrahedra partly occupied by Cu. In an individual (010) slice, adjacent (130) slabs do not add up to a galena-like structure – as it was often erroneously suggested for the closely related structure of meneghinite – but to an SnS-like arrangement. Therefore, all metal coordination polyhedra inside the slice represent monocapped trigonal coordina-

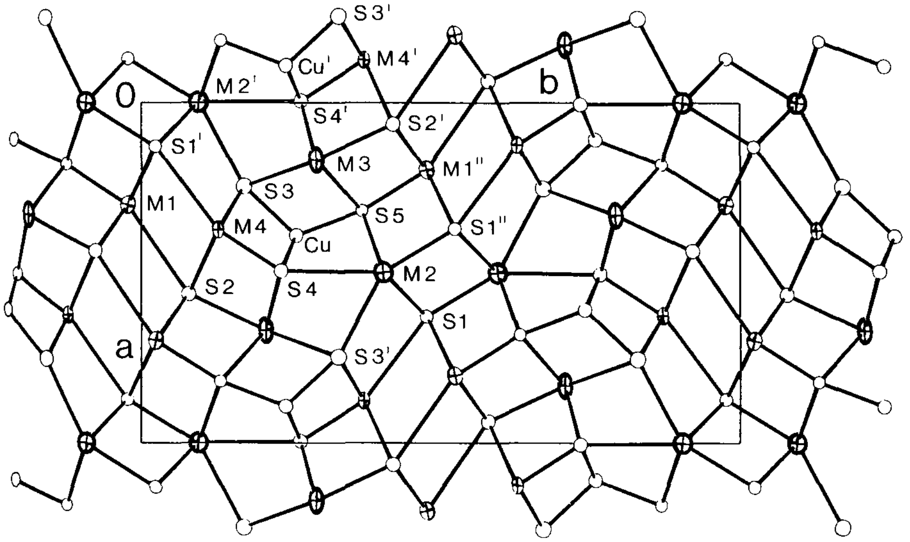

Fig. 1. The crystal structure of jaskolskiite projected along [001]. The thermal (and disorder) ellipsoids of anisotropically refined metal atoms are drawn at 50% probability levels. Cu and S were isotropically refined

tion prisms. At least two out of four distinct metal coordination polyhedra in the slice, those of M1 and M4, can be alternatively described as square coordination pyramids [MeS_{3+2}] with the metal atoms in the base of the pyramid and an additional, long Me – S distance to the sixth sulphur atom below the pyramidal base.

Coordination polyhedra of metals

Each tightly bonded (130) slab in the (010) slices contains two sets of four independent metal positions (Tables 4 and 5). The fifth position, partly occupied by copper, lies between the slices. The chemical formula obtained from the structure refinement using the different scattering power of (Bi, Pb) on one hand and of Sb on the other hand, as well as the occupancy factor of Cu, is $Cu_{0.16(3)}Pb_{2.16(3)}Sb_{1.31(4)}Bi_{0.51(5)}S_5$, in good agreement with the chemical formula of jaskolskiite derived as an average of several microprobe analyses (Zakrzewski, 1983).

The Bi $\rightleftarrows$ Sb and Pb $\rightleftarrows$ (Bi, Sb) substitutions take place in the M1 and M4 sites. The shorter bond lengths at the M4 site suggest that this site is occupied by Sb and Bi without a visible substitution by Pb. The larger, more isotropic disorder ellipsoid and longer Me – S distances indicate that excess Pb concentrates in the M1 site. Comparison with the similar coordination polyhedra of Sb, Bi and Pb in Sb_2S_3 (Bayliss and Nowacki, 1972),

Table 4. Interatomic distances in jaskolskiite [Å]

$M(1)_0-S(5)_8$	2.54	$M(3)_0-S(2)_{11}$	2.81	$Cu_0-S(5)_0$	2.32(5)
$-S(2)_{5,6}$	2.78	$-S(4)_{11,12}$	2.88	$-S(3)_0$	2.39(5)
$-S(1)_{11,12}$	2.98	$-S(5)_{0,1}$	3.05	$-S(4)_{0,2}$	2.41(3)
$-S(2)_0$	3.60	$-S(3)_{0,1}$	3.28		
$M(2)_0-S(1)_3$	2.77	$M(4)_0-S(4)_0$	2.49		
$-S(1)_{0,1}$	2.89	$-S(3)_{0,1}$	2.65		
$-S(5)_{0,1}$	2.98	$-S(2)_{0,1}$	3.10		
$-S(3)_9$	3.18(2)	$-S(1)_{11}$	3.48		
$-S(4)_0$	3.39				

Code: 0 x, y, z
1 $x, y, z+1$
2 $x, y, z-1$
3 $1-x, 1-y, 1-z$
4 $1-x, 1-y, -z$
5 $1-x, -y, -z$
6 $1-x, -y, 1-z$
7 $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
8 $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$
9 $x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$
10 $x+\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$
11 $x-\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$
12 $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$

Except when indicated otherwise, the standard deviations of interatomic distances all lie close to 0.01 Å. All M – S distances below 3.7 Å are listed

Table 5. Angles between M – S vectors in jaskolskiite [deg]

$S(2)_0$	$-M(1)_0-$	$S(2)_{5,6}$	76.8(3)	$S(3)_{0,1}$	$-M(3)_0-$	$S(5)_{0,1}$	78.1(3)
$S(2)_0$		$S(5)_8$	156.9(4)	$S(3)_0$		$S(3)_1$	77.2(2)
$S(2)_0$		$S(1)_{11,12}$	111.2(3)	$S(3)_{6/1}$		$S(5)_{1/0}$	129.1(4)
$S(2)_5$		$S(2)_6$	94.6(3)	$S(3)_{0,1}$		$S(2)_{11}$	141.1(2)
$S(2)_{5,6}$		$S(5)_8$	87.7(4)	$S(3)_{0/1}$		$S(4)_{11/12}$	119.7(4)
$S(2)_{5/6}$		$S(1)_{11/12}$	89.0(3)	$S(3)_{0/1}$		$S(4)_{12/11}$	67.1(3)
$S(2)_{5/6}$		$S(1)_{12/11}$	171.8(4)	$S(5)_0$		$S(5)_1$	84.2(2)
$S(5)_8$		$S(1)_{11}$	85.2(3)	$S(5)_{0,1}$		$S(2)_{11}$	77.9(3)
$S(1)_{11}$		$S(1)_{12}$	86.6(3)	$S(5)_{0/1}$		$S(4)_{11/12}$	160.3(4)
				$S(5)_{0/1}$		$S(4)_{12/11}$	89.5(3)
$S(1)_{0/1}$	$-M(2)_0-$	$S(4)_{0/0}$	120.1(3)	$S(2)_{11}$		$S(4)_{11,12}$	82.6(3)
$S(1)_{0/1}$		$S(5)_{0/1}$	89.0(3)	$S(4)_{11}$		$S(4)_{12}$	90.3(3)
$S(1)_0$		$S(1)_1$	89.9(3)				
$S(1)_{0/1}$		$S(5)_{1/0}$	162.1(4)	$S(2)_{0,1}$	$-M(4)_0-$	$S(3)_{0,1}$	88.2(3)
$S(1)_{0,1}$		$S(1)_3$	80.9(3)	$S(2)_{0,1}$		$S(4)_0$	83.7(4)
$S(1)_{0,1}$		$S(3)_9$	77.7(3)	$S(2)_0$		$S(2)_1$	82.4(3)
$S(4)_0$		$S(5)_{0,1}$	75.4(3)	$S(2)_{0/1}$		$S(3)_{1/0}$	169.9(3)
$S(4)_0$		$S(1)_3$	147.8(4)	$S(2)_{0,1}$		$S(1)_{11}$	111.3(3)
$S(4)_0$		$S(3)_9$	62.7(4)	$S(3)_{0,1}$		$S(4)_0$	91.6(4)
$S(5)_0$		$S(5)_1$	86.7(3)	$S(3)_0$		$S(3)_1$	100.9(4)
$S(5)_{0,1}$		$S(1)_3$	81.3(3)	$S(3)_{0,1}$		$S(1)_{11}$	75.6(4)
$S(5)_{0,1}$		$S(3)_9$	119.4(3)	$S(4)_0$		$S(1)_1$	159.5(4)
$S(1)_3$		$S(3)_9$	149.5(4)				
$S(3)_0$	$-Cu_0-$	$S(4)_{0,2}$	100.5(1.4)				
$S(3)_0$		$S(5)_0$	115.8(2.3)				
$S(4)_{0,2}$		$S(5)_0$	111.5(1.3)				
$S(4)_0$		$S(4)_2$	116.2(2.2)				

Bi_2S_3 (Kupčík and Veselá-Nováková, 1970) and $CuPbBiS_3$ (Ohmasa and Nowacki, 1970) enables to make a semiquantitative check of the above metal distribution. Instead of using occupancies of respective metals in M 1 and M 4 as weighting factors, the products of occupancies with respective atomic numbers will be employed in order to better simulate the situation seen in the crystal structure analysis by means of X-ray diffraction.

The outer metal coordination polyhedra of the M_4S_6 ribbons in the above mentioned reference structure correspond closely to the M 4 sites of jaskolskiite. If the latter site contains $Sb_{0.6}Bi_{0.4}$, the predicted weighted average of three shortest M – S distances will be 2.61 Å and that of five M – S distances 2.80 Å. The actually observed values are 2.60 Å and 2.80 Å, respectively, in good agreement with the predicted values.

The inner metal coordination pyramids of the M_4S_6 ribbons in the reference compounds can be compared with the M 1 site of jaskolskiite. For the occupation of the M 1 site obtained from the refinement, $Sb_{0.71}Pb_{0.16}Bi_{0.13}$, the predicted averages of the three and five shortest bond lengths will be 2.70 Å and 2.78 Å, respectively. The observed averages, 2.76 Å and 2.81 Å, represent considerably longer Me – S distances. They suggest that the site ought to contain more Pb than the value of 16% that was derived from the observed amounts of Cu according to the coupled substitution (Sb, Bi) + vacancy $\rightleftarrows$ Pb + Cu. With the Sb occupancy at the site equal to 71%, the heavy component alone should display the average of 5 shortest bond lengths equal to 2.98 Å, i.e. it should represent pure lead.

The seven-coordinated Pb 3 site has the average bond length in the complete polyhedron equal to 3.03 Å (that of five shortest bonds is 2.94 Å). The values indicate a pure lead site. The corresponding average of all seven Me – S distances in the adjacent Pb 2 site is only 2.99 Å, lower than the average value of 3.04 Å for seven coordinated lead derived by Edenharter (1976). Using the same reference coordination polyhedra as for the M 1 site, a combination of 45% occupancy by Pb with 55% occupancy by Bi is obtained, by about 25% in variance with the overall chemical formula. Although introduction of some Sb could reduce the difference, it seems realistic to conclude that the M 1 site is enriched in Pb in excess of the expected concentration of 16% and that the M 2 site accommodates corresponding amounts of Bi, but their exact amounts cannot be assessed from the current structure determination.

The tetrahedrally coordinated copper site is only statistically occupied by copper at a relatively low rate of approximately 16%. This value can be compared with the 25% occupation of this site in meneghinite (Euler and Hellner, 1960) and its full occupancy in aikinite (Ohmasa and Nowacki, 1970; Kohatsu and Wuensch, 1971). The average bond length is 2.38 Å, higher than in other cases of tetrahedrally coordinated Cu in sulphosalts (Edenharter, 1976). The coordination tetrahedron of Cu is rather irregular.

The obvious reason for these irregularities is that in 84% of the cases the coordination tetrahedra are unoccupied, i.e. larger than the coordination tetrahedra of copper.

Meneghinite homologous series

The homologous series of complex sulphides (sulphosalts) to which jaskolskiite belongs will be called the meneghinite homologous series after its longest known characteristic member, the mineral meneghinite. This name was also used by Mozgova et al. (1983) although these authors included only meneghinite and $Pb_2Sb_2S_5$. The crystal structures of this series can be visualized as composed of slices (501) or $(\bar{5}01)$ of SnS-like (B 16) structure. The somewhat oscillating surfaces of these slices form wavy composition planes on which the two adjacent slices face each other and are mutually related by an *n*-glide plane parallel to (010) of meneghinite. Two coordination polyhedra on the margins of each tightly bonded slab $(100)_{SnS}$ include the sulphur atoms of the opposite slab. They represent mono- or bicapped trigonal prisms, respectively parallel and perpendicular to the 4 Å axis. Tetrahedral coordination sites located in the wavy interfaces can be occupied by Cu atoms according to the coupled substitution Cu + Pb $\rightleftarrows$ vacancy + Sb (or Bi).

Individual homologues differ in the number of cation polyhedra strung diagonally across the ($\pm$ 5.0.1) slice of the SnS-like structure, along the surfaces of the tightly bonded slabs $(100)_{SnS}$. Homologous contraction (or expansion) is taking place in the SnS-like portions of the slices.

In the homologue $N = 2$ only the two marginal polyhedra remain and, finally, for $N = 1$ only the apical polyhedra are preserved. At $N = 1$ the configuration of the interface changes as well, setting this structure against the higher homologues. It is between the 2nd and 3rd homologues that the elongated, closed lone electron pair micelles of the higher homologues turn into inverted lone electron pair micelles of the lowest homologues. The lone electron pair micelles represent means of structural accommodation of stereochemically active lone electron pairs in the structures of sulphosalts. They were defined by Makovicky and Mumme (1983) as groupings of coordination polyhedra of (primarily) As, Sb or Bi which enclose extended structural spaces that contain their lone electron pairs. Other metal atoms adhere to the micelles on their outer surfaces and thus propagate the structure motif. The inverted lone electron pair micelles are groupings of coordination polyhedra with lone electron pairs oriented outwards, i.e. positioned on their surfaces. The inverted lone electron pair micelles are interconnected only by weak residual bonds.

The structural definition of the meneghinite homologous series was given independently by Makovicky (1983a, b) and, under the name of the $Sb_2S_3 \cdot n$ PbS series, by Smith and Hyde (1983). The latter authors give a

Table 6. Selected data on meneghinite homologues

Mineral	Formula	N	Unit cell parameters (Å)			Space group	Reference
Meneghinite	$CuPb_{13}Sb_7S_{24}$	5	*a* 11.36	*b* 24.06	*c* 99.08	$Pn2_1m$	Euler and Hellner (1960)
	Subcell:		*a′* 11.36	*b′* 24.06	*c′* 4.13	($Pbnm$)	
Synthetic	$Pb_{12}Sb_8S_{24}$[1]	5	*a* 11.36	*b* 23.98	*c* 4.10	$Pbnm$	Wang (1977)
Synthetic	$Pb_2Sb_2S_5$	4	*b* 11.40	*a* 19.80	*c* 4.04	$Pnma$	Wang (1973)
Synthetic	$Sn_2Sb_2S_5$	4	*c* 11.42	*a* 19.60	*b* 3.94	$Pnma$ or $Pn2_1a$	Wang and Eppelsheimer (1976), Eppelsheimer (1981)
Jaskolskiite	$Cu_{0.2}Pb_{2.2}(Sb,Bi)_{1.8}S_5$	4	*a* 11.43	*b* 19.81	*c* 4.08	$Pbnm$	Zakrzewski (1984)
Synthetic	$Bi_xSb_{2-x}Sn_2S_5$	4	*b* 11.26	*c* 19.49	*a* 3.95	$Pmcn$	Kupčík-Wendschuh (1982)
Stibnite	Sb_2S_3	2	*c* 11.23	*a* 11.31	*b* 3.84	$Pnma$	Bayliss and Nowacki (1972)
Bismuthinite	Bi_2S_3	2	*a* 11.12	*b* 11.25	*c* 3.97	$Pbnm$	Kupčík and Veselá-Nováková (1970)
Pekoite	$CuPbBi_{11}S_{18}$	2	*a* 3×11.17	*b* 11.32	*c* 3.99	$Pb2_1m$	Mumme and Watts (1976)
Gladite	$CuPbBi_5S_9$	2	*a* 3×11.18	*b* 11.49	*c* 4.00	$Pbnm$	Kohatsu and Wuensch (1976)
Krupkaite	$CuPbBi_3S_6$	2	*a* 11.20	*b* 11.56	*c* 4.00	$Pb2_1m$	Mumme (1975)
Lindströmite	$Cu_3Pb_3Bi_7S_{15}$	2	*a* 5×11.22	*b* 11.57	*c* 4.00	$Pbnm$	Horiuchi and Wuensch (1977)
Hammarite	$Cu_2Pb_2Bi_4S_9$	2	*a* 3×11.26	*b* 11.59	*c* 4.01	$Pbnm$	Horiuchi and Wuensch (1976)
Friedrichite	$Cu_5Pb_5Bi_7S_{18}$	2	*a* 3×11.28	*b* 11.65	*c* 4.01	$Pb2_1m$	Schioler and Wuensch (1979)
Aikinite	$CuPbBiS_3$	2	*a* 11.32	*b* 11.64	*c* 4.04	$Pbnm$	Ohmasa and Nowacki (1970)
Synthetic	SbSBr	(1)	*b* 9.79	*a* 8.26	*c* 3.97	$Pnam$	Christofferson and McCullough (1959)
Synthetic	BiSJ	(1)	*b* 10.18	*a* 8.52	*c* 4.17	$Pnam$	Haase-Wessel (1973)
Synthetic	SbSJ	(1)	*b* 10.14	*a* 8.53	*c* 4.10	$Pnam$	Haase-Wessel (1973)

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[1] A different formula is given in the original sources

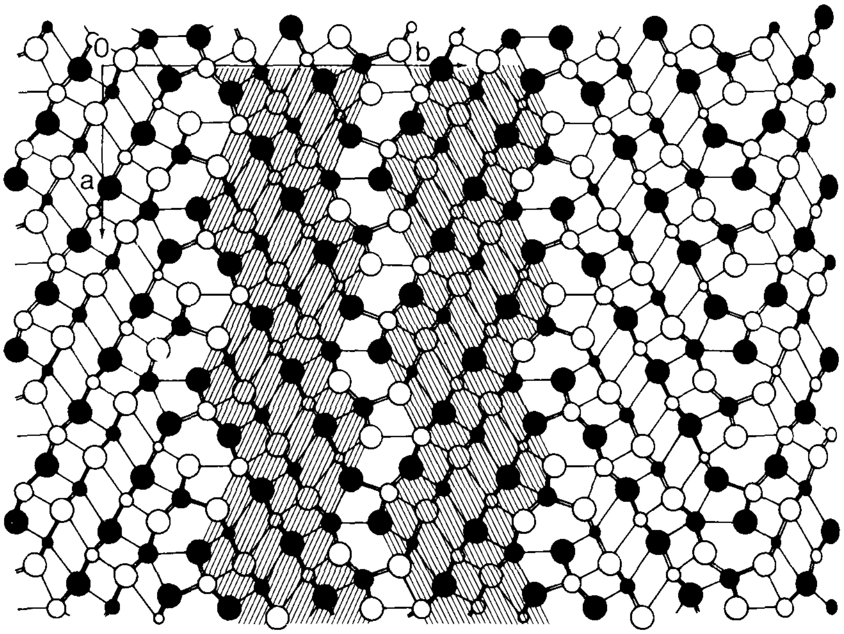

Fig. 2. The crystal structure of meneghinite (Euler and Hellner, 1960) projected along [001]. In order of decreasing size the cricles represent S, Pb, ($\frac{1}{2}$Pb + $\frac{1}{2}$Sb) and ($\frac{1}{4}$Pb + $\frac{3}{4}$Sb). Two distinct levels at $z = \frac{1}{4}$ and $z = \frac{3}{4}$ are respectively denoted by empty and full circles. Hatched areas represent slabs (501) and ($\bar{5}$01) of SnS-like structure. The unrefined Cu positions are not illustrated

different definition of the series, as intergrowths of slabs of the Sb_2S_3-like and TlI-like structures on unit cell scale. Varying width of TlI-like slabs leads to distinct homologues of this series.

The structural scheme leads to the general formula $Me_{2N}\,S_{2N+2}$ per one tightly bonded slab $(100)_{SnS}$, varying between $Me^{2+}_{2N-4}Me^{+3}_{4}S_{2N+2}$ for the structures with tetrahedral holes unoccupied, and $Cu^{1+}_{2}Me^{2+}_{2N-2}Me^{3+}_{2}$ S_{2N+2} for those with the tetrahedral holes fully occupied. All members of the series have two lattice parameters nearly identical (Table 6) whereas the third dimension increases by regular increments of ~ 4.26 Å between two adjacent homologues.

The highest known homologue, $N = 5$, is meneghinite, $CuPb_{13}Sb_7S_{24}$, in which 25% of Cu positions are occupied, and all Sb positions are partly occupied by Pb (Berry and Moddle, 1941; Euler and Hellner, 1960) (Fig. 2). It was described as having a 24-tuple supercell along the 4.1 Å direction. However, only 2 weak reciprocal lattice levels describing this periodicity were found (l.c.) and therefore the structure could represent a long-range composition-modulated structure with variations taking place over the

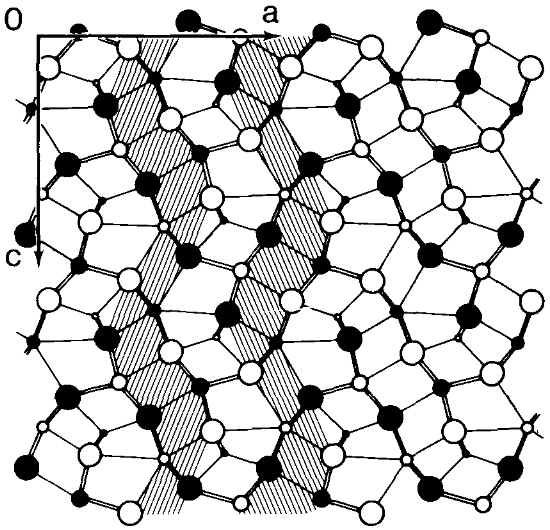

Fig. 3. The crystal structure of aikinite (Ohmasa and Nowacki, 1970; Kohatsu and Wuensch, 1971) projected along [010]. In order of decreasing size the circles represent S, Pb, Bi and Cu. Other symbols are analogous to those in Fig. 2

positions. A synthetic high-temperature analogue of meneghinite without Cu was described (Jambor, 1975; Wang, 1977), the structural formula of which presumably is $Pb_{12}Sb_8S_{24}$.

Besides jaskolskiite, several synthetic homologues of meneghinite with $N = 4$ were described. In 1973 Wang described a high temperature phase $Pb_2Sb_2S_5$ and in 1975 Wang and Eppelsheimer synthetized an isostructural phase, $Sn_2Sb_2Sb_5$; kinship to meneghinite was recognized in both cases. In 1982 Kupčík and Wendschuh described the crystal structure of synthetic $Bi_xSb_{2-x}Sn_2S_5$ $(0.4 > x > 0.2)$ which represents an undeformed homologue $N = 4$ of meneghinite. In 1983 Smith and Hyde offered an unrefined model of the crystal structures of $Pb_2Sb_2S_5$ and $Sn_2Sb_2S_5$ as homologues of meneghinite. Finally, Chang et al. (1980) synthetized so called Y-phases, Pb_2SbBiS_5, $Pb_2Sb_{\leq 1.5}Bi_{\geq 0.5}S_5$ and $Pb_{1.875}Fe_{0.313}Sb_{1.25}Bi_{0.625}S_5$, the powder diffraction data of which indicate their close kinship to $Pb_2Sb_2S_5$ reported by Wang (1973). The closeness of corresponding polyhedra in the crystal structures of jaskolskiite, meneghinite and $Bi_xSb_{2-x}Sn_2S_5$ is evident from Table 7.

No $N = 3$ homologue of meneghinite is known to us at present. However, berthierite, $FeSb_2S_4$, (Buerger and Hahn, 1955) is a closely related structure in which SnS-like slabs, completely analogous to those in meneghinite homologues, are related by *a*-glide planes instead of the *n*-glide planes of the former. This results in altered coordination polyhedra for the

Table 7. Metal coordination in meneghinite homologues

Compound	N	Coordination polyhedra					inter-stitial	R
References		apical		central		marginal		
$CuPb_{13}Sb_7S_{24}$	5	M4	M2	M1	M3	M5	Cu	$R = 0.237$
Euler and		Pb	Pb	0.5 Pb + 0.5 Sb	0.5 Pb + 0.5 Sb	0.25 Pb + 0.75	Occup. 0.25	
Hellner (1960)		2.83, 3.31(2×)	2.89, 3.12	2.57, 3.53	2.53, 3.52	Sb	not refined	
		2.94(2×)	2.96(2×), 3.30	2.80(2×)	2.76(2×)	2.45, 3.50		
		3.06(2×)	2.98(2×)	3.01(2×)	3.08(2×)	2.66(2×)		
						3.12(2×)		
$Cu_{0.16}Pb_{2.16}$	4	M3	M2		M1	M4	Cu	$R = 0.074$
$Sb_{1.31}Bi_{0.51}S_5$		Pb	Pb(Bi)		0.7 Sb + 0.3	0.6 Sb + 0.4 Bi	Occup. 0.16	
present study					(Pb, Bi)			$R_w = 0.072$
		2.81, 3.28(2×)	2.89, 3.18		2.54	2.49, 3.48	2.32	
		2.88(2×)	2.77(2×), 3.39		2.78(2×)	2.65(2×)	2.39	
		3.05(2×)	2.98(2×)		2.98(2×), 3.60	3.10(2×)	2.41(2×)	
$Bi_xSb_{2-x}Sn_2S_5$	4	M4	M2		M1	M3		
Kupčík and		Bi conc.	Bi conc.		(lightest)			
Wendschuh (1982)		2.71, 3.23(2×)	2.68, 3.43		2.52, 3.42	2.47, 3.30		$R = 0.101$
		2.74(2×)	2.91(2×)		2.66(2×)	2.59(2×)		
		2.99(2×)	2.96(2×)		2.86(2×)	2.13(2×)		$R_w = 0.082$

FeSb$_2$S$_4$ Buerger and Hahn (1955)	(3)	Fe 2.45, 2.64(2 ×) 2.46 2.49(2 ×)	Sb1 2.48, 3.56(2 ×) 2.58(2 ×), 3.63 2.93(2 ×)	Sb2 2.43 2.48(2 ×), 3.47 3.24(2 ×)		R = 0.128
CuPbBiS$_3$ Ohmasa and Nowacki (1970)	2	Pb 2.89, 3.26(2 ×) 2.99(2 ×) 2.99(2 ×)	Bi 2.66, 3.16 2.76(2 ×), 3.53 2.95(2 ×)		Cu 2.31 2.35(2 ×) 2.40	R = 0.064
Bi$_2$S$_3$ Kupčík and Veselá-Nováková (1970)	2	Bi2 2.54, 3.28(2 ×) 2.76(2 ×) 2.97(2 ×)	Bi1 2.69, 3.05 2.67(2 ×), 3.33 3.07(2 ×)			R = 0.095
Sb$_2$S$_3$ Bayliss and Nowacki (1972)	2	Sb2 2.46, 3.37(2 ×) 2.68(2 ×) 2.85(2 ×)	Sb1 2.52, 3.17 2.54(2 ×) 3.11(2 ×)			R = 0.044
SbSJ (parael.) Haase-Wessel (1973)	(1)	Sb 2.47, 3.80 (J, 2 ×) 2.70(2 ×) 3.12 (J, 2 ×)				R = 0.060

cations facing adjacent slabs, e.g. the coordination octahedron of iron is created in this way. Berthierite is thus far the sole representative of a potential homologous series parallel to the meneghinite series.

Inspite of the thinness of the SnS-like slices and inversion of the lone electron pair micelles, the basic features of the crystal structures of the homologues $N = 2$ are the same as for the higher homologues (Table 7, Fig. 3). Notably, the configuration in the sinuous interlayer space is still preserved intact. Besides Sb_2S_3 (Bayliss and Nowacki, 1972) and Sb_2Se_3 (Dönges, 1950) these homologues comprise the extensively investigated aikinite-bismuthinite series of derivative structures $Cu_xPb_xBi_{2-x}S_3$ ($1 \geq x \geq 0$) based on ordered (at higher temperatures disordered) coupled substitution Cu + Pb $\rightleftarrows$ tetrahedral vacancy + Bi which takes place in the basic Bi_2S_3 structure (Kupčík and Veselá-Nováková, 1970). In the derivative structures of this series the unit-cell parameter a always represents a multiple ($x1, x3, x5$) of the fundamental parameter of 11.1 Å (changing to 11.3 Å with increasing substitution). Aikinite, $CuPbBiS_3$, has 100% occupancy of tetrahedral metal sites. More detailed discussion is given in Mumme et al. (1976), Wuensch (1979) and Makovicky and Makovicky (1978). Because of the misfit in the dimensions of the coordination polyhedra of Pb and Sb, the crystal structure of $CuPbSbS_3$ (bournonite) (Edenharter et al., 1970) is not derived from that of Sb_2S_3 but represents a different structure, a distorted 2 Å-shear derivative of Sb_2S_3 (Makovicky, 1981).

The last step in homologous contraction affects profoundly both the SnS-like layers and, for the first time, also the interface. Therefore, the resulting structure of the (tentative) homologue $N = 1$ collapses along the a direction in comparison to the higher homologues. This category (Dönges, 1951) comprises the crystal structures of halide-sulphides, e.g. SbSBr (Christofferson and McCullough, 1959), BiSI and SbSI (Haase-Wessel, 1973). They all contain inverted lone electron pair micelles and were extensively studied due to their electric properties.

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References

Bayliss, P., Nowacki, W.: Refinement of the crystal structure of stibnite, Sb_2S_3. Z. Kristallogr. **135**, 308–315 (1972)

Berry, L. G., Moddle, D. A.: Studies of mineral sulphosalts: V. Meneghinite from Ontario and Tuscany. Univ. Toronto Studies, Geol. Ser., **46**, 5–15 (1941)

Buerger, M. J., Hahn, Th.: The crystal structure of berthierite, $FeSb_2S_4$. Am. Mineral. **40**, 226–238 (1955)

Chang, L. L. Y., Walia, D. S., Knowles, C. R.: Phase relations in the systems $PbS-Sb_2S_3-Bi_2S_3$ and $PbS-FeS-Sb_2S_3-Bi_2S_3$. Econ. Geol. **75**, 317–328 (1980)

Christofferson, G. D., McCullough, J. D.: The crystal structure of antimony (III) sulfobromide, SbSBr. Acta Crystallogr. **12**, 14–16 (1959)

Dönges, E.: Chalcogenides of trivalent antimony and bismuth, and antimony III selenide. Z. Anorg. Allg. Chem. **263**, 280–291 (1950)

Dönges, E.: Chalcogenides of trivalent antimony and bismuth. III. The tellurohalides of trivalent antimony and bismuth; telluride of antimony and bismuth; selenide of bismuth. Z. Anorg. Allg. Chem. **265**, 56–61 (1951)

Edenharter, A.: Fortschritte auf dem Gebiete der Kristallchemie der Sulfosalze. Schweiz. Mineral. Petrogr. Mitt. **56**, 195–217 (1976)

Edenharter, A., Nowacki, W.: Verfeinerung der Kristallstruktur von Bournonit $[(SbS_3)_2|Cu_2^{IV}Pb^{VII}Pb^{VIII}]$ und von Seligmannit $[(AsS_3)_2|Cu_2^{IV}Pb^{VII}Pb^{VIII}]$. Z. Kristallogr. **131**, 397–417 (1970)

Eppelsheimer, D.: Präparative und pulverröntgenographische Untersuchungen am System Sn–Sb–S. Z. Kristallogr. **156**, 36–37 (1981)

Euler, R., Hellner, E.: Über komplex zusammengesetzte sulfidische Erze VI. Zur Kristallstruktur des Meneghinits, $CuPb_{13}Sb_7S_{24}$. Z. Kristallogr. **113**, 345–372 (1960)

Haase-Wessel, W.: Röntgen-Strukturuntersuchungen zum paraferroelektrischen Phasenübergang des SbSJ und zur Struktur des BiSJ. Dissertation Universität Göttingen 1973

Horiuchi, H., Wuensch, B. J.: The ordering scheme for metal atoms in the crystal structure of hammarite, $Cu_2Pb_2Bi_4S_9$. Can. Mineral. **14**, 536–539 (1976)

Horiuchi, H., Wuensch, B. J.: Lindströmite, $Cu_3Pb_3Bi_7S_{15}$: Its space group and ordering scheme for metal atoms in the crystal structure. Can. Mineral. **15**, 527–535 (1977)

Jambor, J. L.: Synthetic copper-free meneghinite. Geol. Surv. Can. Paper. **75-1 B**, 71–72 (1975)

Kohatsu, T., Wuensch, B. J.: The crystal structure of aikinite, $PbBiCuS_3$. Acta Crystallogr. **B37**, 1245–1252 (1971)

Kohatsu, T., Wuensch, B. J.: The crystal structure of gladite, $PbCuBi_5S_9$, a superstructure intermediate in the series Bi_2S_3–$PbCuBiS_3$ (bismuthinite-aikinite). Acta Crystallogr. **B32**, 2401–2409 (1976)

Kupčik, V., Veselá-Nováková, L.: Zur Kristallstruktur des Bismuthinits, Bi_2S_3. Tschermaks Mineral. Petrogr. Mitt. **14**, 55–59 (1970)

Kupčik, V., Wendschuh, M.: The structure of antimony bismuth tin sulphide $Bi_xSb_{2-x}Sn_2S_5$. Acta Crystallogr. **B38**, 3070–3071 (1982)

Makovicky, E.: The building principles and classification of bismuth-lead sulphosalts and related compounds. Fortschr. Mineral. **59**, 137–190 (1981)

Makovicky, E.: Crystal structures of complex sulfides: from modulated to modular structures. NATO ASI Ser. E. **83**, 159–169 (1984)

Makovicky, E.: Archetypes, structure building principles and homologous series for sulphosalts of As, Sb and Bi. Abstr. 8th Europ. Crystallogr. Meeting, Liège, Belgium. **96** (1983)

Makovicky, E., Makovicky, M.: Representation of composition in the bismuthinite-aikinite series. Can. Mineral. **16**, 405–409 (1978)

Makovicky, E., Mumme, W. G.: The crystal structure of ramdohrite, $Pb_6Sb_{11}Ag_3S_{24}$, and its implications for the andorite group and zinckenite. Neues Jahrb. Mineral. Abh. **147**, 58–79 (1983)

Mozgova, N. N., Bortnikov, N. S., Tsepin, A. I., Borodayev, Yu. S., Vrublevskaya, S. V., Vyalsov, L. N., Kuzmina, O. V., Sivtsov, A. V.: Falkmanite, $Pb_{5.4}Sb_{3.6}S_{11}$, new data and relationship with sulphoantimonites of lead (re-examination of type material from Bayerland Mine, Bavaria). Neues Jahrb. Mineral. Abh. **147**, 80–98 (1983)

Mumme, W. G.: The crystal structure of krupkaite, $CuPbBi_3S_6$, from the Juno Mine at Tennant Creek, Northern Territory, Australia. Am. Mineral. **60**, 300–308 (1975)

Mumme, W. G., Watts, J. A.: Pekoite, $CuPbBi_{11}S_{18}$, a new member of the bismuthinite-aikinite mineral series: Its crystal structure and relationship with naturally and synthetically-formed members. Can. Mineral. **14**, 322–333 (1976)

Mumme, W. G., Welin, E., Wuensch, B. J.: Crystal chemistry and proposed nomenclature for sulfosalts intermediate in the system bismuthinite-aikinite (Bi_2S_3 – $CuPbBiS_3$). Am. Mineral **61**, 15–20 (1976)

Ohmasa, M., Nowacki, W.: A redetermination of the crystal structure of aikinite ($BiS_2|S|Cu^{IV}Pb^{VII}$). Z. Kristallogr. **132**, 71–86 (1970)

Schioler, L., Wuensch, B. J.: Crystal structure of friedrichite, $Cu_5Pb_5Bi_7S_{18}$, and pekoite, $CuPbBi_{11}S_{18}$, two superstructures intermediate in the system Bi_2S_3 – $CuPbBiS_3$. Am. Crystallogr. Assn. Abstr. 47 (1979)

Smith, P. P. K., Hyde, B. G.: The homologous series $Sb_2S_3 \cdot nPbS$: Structures of diantimony dilead pentasulphide, $Pb_2Sb_2S_5$, and the related phase diantimony ditin pentasulphide, $Sn_2Sb_2S_5$. Acta Crystallogr. **C39**, 1498–1502 (1983)

Wang, N.: A study of the phases on the pseudobinary join PbS – Sb_2S_3. Neues Jahrb. Mineral. Monatsh. **2**, 79–81 (1973)

Wang, N.: Synthesis and crystal data on a Cu-free "meneghinite". Can. Mineral. **15**, 115–116 (1977)

Wang, N., Eppelsheimer, D.: The ternary phases in the system Sn – Sb – S. Chem. Erde **35**, 179–184 (1976)

Wuensch, B. J.: Superstructures in sulfide minerals. Amer. Inst. Phys. Conf. Proc. **53**, 337–354 (1979)

Zakrzewski, M. A.: Jaskolskiite, a new Pb – Cu – Sb – Bi sulfosalt from Vena deposit, Sweden. Can. Mineral. **22**, 481–487 (1984)