Canadian Mineralogist
Vol. 15, pp. 339-348 (1977)

THE CRYSTAL STRUCTURE OF SYNTHETIC PAVONITE, $AgBi_3S_5$, AND THE DEFINITION OF THE PAVONITE HOMOLOGOUS SERIES

EMIL MAKOVICKY

Inst. of Mineralogy, Univ. of Copenhagen, Østervoldgade 7, DK-1350 Copenhagen, Denmark

W. G. MUMME AND J. A. WATTS

CSIRO, Division of Mineral Chemistrty, P.O. Box 124, Port Melbourne, Victoria 3207, Australia

ABSTRACT

The crystal structure of synthetic pavonite, $AgBi_3S_5$, was determined using intensity data from integrated Weissenberg photographs. Its space group is $C2/m$, $Z=4$, and from powder diffractometer data, a 13.305, b 4.042, c 16.417Å, β 94.02°. There are 3 independent Bi, 2(Ag/2) and 5S atoms in the asymmetric unit. Bi(1) and Bi(2) are both nearly octahedrally coordinated, Bi(3) is square-pyramidal, [$BiS_{3+2+(3)}$]. Ag(1) and Ag(2) are flattened octahedral. Two types of slabs parallel to (001) are present. In the thinner slabs, octahedra of Ag(2) alternate with paired square pyramids of Bi(3). The thicker, galena-like slabs are composed of parallel octahedra chains Bi(2)–Bi(1)–Ag(1)–Bi(1)–Bi(2) and are interconnected, via common sulfur atoms, with the thinner slabs.

The pavonite homologous series represents sulfosalt structures with thinner slabs of the above-defined type (octahedra and paired square pyramids) with galena-like slabs of variable thickness. Compounds with 2, 3, 4, 5 and 7 octahedra per diagonal chain of the galena-like layer are denoted as the pavonite homologues ^2P through ^7P. In general, ^NP has N octahedra in the diagonal chain and its chemical formula is $Me_{N+1}^{oct}Bi_2^{sq.pyr.}S_{N+5}$. Members of the series are, in the order of increasing N, $\sim PbBi_4S_7$, $\sim CuBi_5S_8$ (or $Cu_{1.6}Bi_{4.8}S_8$), $Ag_2Bi_6S_{10}$ (pavonite) and $\sim Ag_3Bi_7S_{12}$ (benjaminite).

SOMMAIRE

La structutre cristalline de la pavonite synthétique $AgBi_3S_5$ a été établie à l'aide d'intensités mesurées sur des photographies intégrées de Weissenberg. Le groupe spatial est $C2/m$, avec $Z=4$. Les paramètres cristallins tirés du diagramme de poudre sont: a 13.305, b 4.042, c 16.417Å, β 94.02°. L'élément asymétrique comprend 3 atomes indépendants de Bi, 2 d'(Ag/2) et 5 de S. Bi(1) et Bi(2) sont, tous les deux, en coordinence octaédrique, Bi(3) a pour polyèdre de coordinence une pyramide à base carrée [$BiS_{3+2+(3)}$]. Ag(1) et Ag(2) sont des octaèdres aplatis. On y trouve deux genres de couches parallèles à (001). Dans les couches les plus minces, les octaèdres de Ag(2) alternent avec les pyramides à base carrée appariées de Bi(3). Les couches les plus épaisses sont de type galène et sont composées de chaînes parallèles d'octaèdres Bi(2)–Bi(1)–Ag(1)–Bi(1)–Bi(2) et sont liées aux couches plus minces par des atomes de soufre.

On trouve parmi les homologues de la pavonite des structures de sulfosels avec des couches minces du type de celle décrite ci-dessus (octaèdres et pyramides à base carrée appariés) ainsi que des couches de différentes épaisseurs de type galène. Les composés à 2, 3, 4, 5, et 7 octaèdres par chaîne diagonale dans la couche de type galène sont définis comme les homologues ^2P à ^7P de la pavonite. De façon générale, ^NP présente N octaèdres dans la chaîne diagonale et sa formule chimique est $Me_{N+1}^{oct}Bi_2^{pyr.car.}S_{N+5}$. Les membres de la série sont, par ordre croissant de N, $\sim PbBi_4S_7$, $\sim CuBi_5S_8$ (ou $Cu_{1.6}Bi_{4.8}S_8$), $Ag_2Bi_6S_{10}$ (pavonite) et $\sim Ag_3Bi_7S_{12}$ (benjaminite).

(Traduit par la Rédaction)

INTRODUCTION

As part of an investigation to establish phase relationships in the copper- and silver-rich regions of the Ag_2S-Bi_2S_3 and Cu_2S-Bi_2S_3 systems, we prepared and examined crystals of synthetic Pb- and Cu-free pavonite. The present paper describes the crystal structure of pavonite and its relationship with the other members of an homologous series of which it is a type member.

Pavonite was identified by Nuffield (1954) when he studied "benjaminite" (previously "alaskaite") from Bolivia. He found that the Bolivian mineral was a new mineral, which he named pavonite, with a 13.35, b 4.03, c 16.34Å, β 94.5°, space group $C2/m$, and with an empirical chemical composition interpreted as (Ag,Cu) Bi_3S_5. Nuffield also described synthesis experiments in which charges of elements in the stoichiometric proportions Ag:Bi:S=1:3:5 were heated in evacuated, sealed silica tubes. After melting and slow cooling, the X-ray powder patterns of the crystals produced agreed "to the last detail" with the powder patterns of the mineral from Bolivia. Polished sections showed that a perfectly homogeneous product was formed in these experiments, and this observation together with density measurements led Nuffield to suggest $AgBi_3S_5$ to be the ideal structural formula of pavonite.

SUBSEQUENT STUDIES OF SYNTHETIC AND NATURAL PAVONITE

Van Hook (1960) apparently verified Nuffield's results (without reference) when he prepared single crystals from the composition Ag: Bi:S=1:3:5 by flux-growth methods, and obtained Weissenberg photographs which have unit-cell dimensions *a* 13.3, *b* 4.03, *c* 16.5Å, *β* 94°, space group alternatives *C*2/*m*, *Cm* or *C*2.

Karup-Møller (1972) determined optical and physical data for natural pavonite from several localities. His refined lattice parameters for pavonite from Silver Bell mine, Colorado, were *a* 13.333, *b* 4.039, *c* 16.346Å, *β* 94.21°. The specimens from Alaska mine, Colorado, contained visible lamellae formed by exsolution. X-ray patterns of these composite crystals were described as showing a single, distinctly triclinic lattice with a doubling of the *c* axis. The following cell dimensions were recorded: *a* 13.2, *b* 3.86, *c* 2× 16.2Å, *α* 92.0°, *β* 94.5°, *γ* – not determined. Microprobe analyses showed that, in addition to Ag, Bi, and S, pavonite may contain up to 13.1% Pb, 5.6% Cu (both in the exsolved lamellae of the sample from the Alaska mine) and 1.0% Sb. Karup-Møller suggested $[(Bi,Sb)_{1-x}Pb_x]_9Ag_2CuS_{15-4.5x}$ ($x_{max}=0.1$) as the structural formula* of pavonite. Harris & Chen (1975) studied the type material from Bolivia, confirmed Nuffield's data from 1954, and specified the composition of type pavonite as $Cu_{0.24}Ag_{0.93}Pb_{0.15}Bi_{2.80}S_{5.17}$.

Chen & Chang (1974), in an investigation of the Ag_2S-Cu_2S-Bi_2S_3 system, reported complete solid solution between $CuBi_3S_5$ (for which they used the old name eichbergite; see Dana p. 485) and $AgBi_3S_5$ (pavonite). At 454°C the series was reported to have a wedge shape in the ternary system because of the extensive solid solution in $CuBi_3S_5$ along the Cu_2S-Bi_2S_3 join, and almost negligible solid solution along the Ag_2S-Bi_2S_3 join. However, the phase $CuBi_3S_5$ reported by Sugaki & Shima (1965, 1971) has been studied by Ohmasa & Nowacki (1973), who concluded that it has the structural formula $CuBi_5S_8$. Ohmasa (1973) has also described another phase $Cu_{2+x}Bi_{6-x}S_9$ ($x=1.21$) closely related to $CuBi_5S_8$, in which Bi atoms are partly replaced by Cu atoms. Recent studies (Mumme & Watts, unpublished data) have demonstrated that at 450°C the "solid solution" region referred to by Chen & Chang (1974) as eichbergite *(ss)* is in fact a two-phase region between the $CuBi_5S_8$-type (Ohmasa & Nowacki 1973) and $Cu_{2+x}Bi_{6-x}S_9$-type (Ohmasa 1973) structures. However, the end member with the $CuBi_5S_8$-type structure has a composition close to, if not equal to, $CuBi_3S_5$. i.e. it should have the structural formula $Cu_{1.6}Bi_{4.8}S_8$. The other end member, with the $Cu_{2+x}Bi_{6-x}S_9$-type structure has the composition $Cu_3Bi_5S_9$ (or very close to this formula), suggesting that *x* in the complicated formula proposed by Ohmasa (1973) is equal to 1. Our experimental compositions are close to those obtained by Buhlmann (1971) and Sugaki & Shima (1971).

Hoda & Chang (1975) have described extensive solid solution between $AgBi_3S_5$ (synthetic pavonite) and 73 $PbS \cdot 27Bi_2S_3$ (synthetic lillianite) at 400°C and 500°C. A more limited solid-solution range of $AgBi_3S_5$ towards $PbBi_2S_4$ (galenobismutite) was also suggested. $AgBi_3S_5$ was repeatedly determined as a line phase in the Ag_2S-Bi_2S_3 system (cf Van Hook 1960; Chen & Chang 1974). A 1.6% increase in volume is reported with increasing Pb substitution from the end member containing 25% Ag_2S, 75% Bi_2S_3, to pavonite *(ss)* containing 20% PbS, 18% Ag_2S, 62% Bi_2S_3.

Karup-Møller & Makovicky (in prep.) have revised the chemistry and crystallography of the natural pavonites (and benjaminites) described by Karup-Møller (1972). Comparison of their data with the lillianite homologous series allowed them to derive a linkage pattern for this mineral, confirm the basic formula as $AgBi_3S_5$, and devise formulae for distinguishing pavonites from benjaminites, using chemical data. Natural pavonites were found to have a composition range $Ag_{0.90-0.70}Cu_{0.23-0.43}Pb_{0.06-0.33}Bi_{2.93-2.70}Sb_{0.07-0.00}S_5$. The exsolved lamellae, the only "pavonite" with a doubled *c* axis, have the composition $Ag_{0.48}Cu_{0.87}Pb_{0.59}Bi_{2.44}Sb_{0.01}S_5$.

EXPERIMENTAL

Synthetic pavonite was prepared by reacting Ag_2S and Bi_2S_3 in the stoichiometric proportions 1:3 in a sealed silica tube at 600°C followed by rapid cooling to room temperature in water. The Ag_2S-Bi_2S_3 system (*cf* Van Hook 1960; Chen & pure elements. High-purity Koch-Light sulfur (99.9999%) was used together with high-purity

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*It has been pointed out by Harris & Chen (1975) that the formula as given in Karup-Møller (1972) has a typographical error.

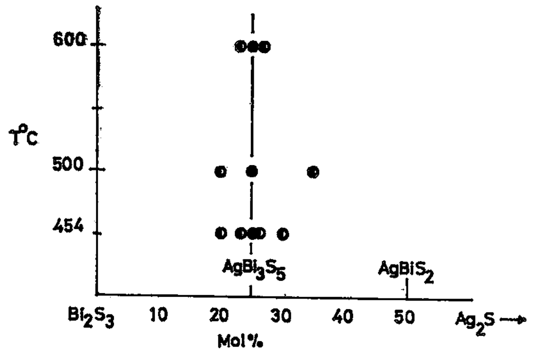

FIG. 1. *T-X* diagram showing synthetic runs (present work and published data) for determination of the chemical composition of synthetic pavonite. Solid circles: one-phase runs; half-filled circles: two-phase runs.

Merck bismuth (<50 ppm total metallic) and Koch-Light Ag-wire (99.98%).

Synthetic pavonite has been described as a line phase by Van Hook (1960), Craig (1967), Chen & Chang (1974) and Hoda & Chang (1975). Evidence for even a limited solid-solution range along the Ag_2S-Bi_2S_3 join has never been given. Our X-ray powder-pattern peaks were extremely sharp, indicating that the bulk crystalline material which we prepared was a single phase. However, in view of the results of the structure refinement, it seemed possible that there could be some replacement of Bi by Ag in some of the octahedral sites. Therefore, we thought it necessary to re-investigate the possibility of a range of solid solution in pavonite. Our results and those of others (summarized in Fig. 1) confirm that synthetic pavonite has, at most, a very limited solid-solution range. However, the following point should be mentioned.

In preparing synthetic pavonite we have found it somewhat difficult to get all of the Ag_2S to react. Thus, regrinding and further reheating were necessary. We also observed that, in the sealed tubes, a small amount of crystalline material formed away from the main charge. This was found, when investigated by single-crystal techniques, to be Bi_2S_3. The amounts were small, less than 5 mg in a charge of 400 mg. This effect could be a compensation for a loss of Ag_2S (to walls) which was undetected, or could indicate only a 1% departure from stoichiometry towards a silver-rich phase. Polished sections of our synthetic material confirmed

TABLE 1. CRYSTALLOGRAPHIC DATA FOR $AgBi_3S_5$

Symmetry	Monoclinic
Unit-cell dimensions	a = 13.305(2)Å b = 4.042(1) c = 16.417(2) β = 94.02(1)°
Systematically absent reflections	hkl: $h+k \neq 2n$ $h0l$: $h \neq 2n$
Space-group alternatives	$C2/m$, Cm, $C2$
D(calc.)	6.79 g/cm^3
D(meas.)	6.74±(.05)*
Z	4
Radiation	Cu$K\alpha$
Total number of reflections	510
Linear absorption coefficient (cm^{-1})	1428

*Measured in $CHBr_3$ at 25°C. Nuffield (1953) obtained a value of 6.46 for natural material of non-ideal composition.

TABLE 2. X-RAY POWDER DATA FOR SYNTHETIC $AgBi_3S_3$*

h	k	l	d_{obs}	d_{calc}	I_{obs}
0	0	2	8.176	8.190	< 1
2	0	0	6.630	6.637	3
2	0	$\bar{1}$	6.297	6.309	1
0	0	3	5.458	5.459	12
2	0	$\bar{2}$	5.325	5.340	15
0	0	4	4.086	4.094)	20
2	0	3		4.079)	
1	1	0	3.865	3.868	6
2	0	$\bar{4}$	3.598	3.599	68
1	1	$\bar{2}$	3.521	3.525	< 1
1	1	2	3.464	3.470	51
2	0	4	3.383	3.380	53
4	0	0	3.317	3.318	34
4	0	1	3.204	3.209)	12
1	1	$\bar{3}$	3.188	3.187)	
1	1	3	3.122	3.126	5
3	1	0	2.981	2.985	15
3	1	$\bar{1}$	2.960	2.961	27
4	0	$\bar{3}$	2.929	2.928)	7
3	1	1	2.911	2.912)	
3	1	$\bar{2}$	2.848	2.848	100
3	1	2	2.761	2.762)	13
4	0	3		2.754)	
0	0	6	2.731	2.730	3
3	1	$\bar{3}$	2.673	2.673	3
2	0	$\bar{6}$	2.588	2.589	10
3	1	3	2.567	2.568	7
4	0	4	2.494	2.494	3
2	0	6	2.464	2.464	8
3	1	4	2.358	2.359	2
0	0	7	2.338	2.340	1
1	1	$\bar{6}$	2.251	2.252	30
1	1	6	2.209	2.209)	13
6	0	0		2.212)	
6	0	$\bar{2}$	2.175	2.174	8
3	1	5	2.155	2.156	2
5	1	2	2.110	2.111	9
6	0	$\bar{3}$	2.101	2.102	11
0	0	8	2.047	2.048	25
0	2	0	2.022	2.021)	42
1	1	$\bar{7}$		2.020)	
5	1	3	2.016	2.014	29
6	0	$\bar{4}$	2.006	2.006	16
6	0	3	2.002	2.002	3
3	1	6	1.969	1.969	10
2	0	8	1.919	1.919	2
5	1	$\bar{5}$	1.890	1.889)	
6	0	4		1.892)	11
2	2	$\bar{2}$		1.891)	
4	0	7	1.852	1.852	3
1	1	$\bar{8}$	1.825	1.825	8
3	1	7	1.800	1.800)	8
4	0	$\bar{8}$		1.799)	
1	1	8	1.795	1.794	1
5	1	$\bar{6}$	1.773	1.773	5
2	2	$\bar{4}$	1.763	1.763	15
2	2	4	1.735	1.735	7
4	2	0	1.726	1.726)	15
2	0	9		1.725)	
7	1	$\bar{1}$	1.719	1.719	13
4	0	8	1.690	1.690	2
8	0	0	1.660	1.659)	
6	0	6		1.662)	7
7	1	2		1.659)	
5	1	6	1.674	1.674	3
2	2	5	1.650	1.650	5
8	0	1	1.639	1.639)	13
0	0	10		1.638)	
2	2	$\bar{6}$	1.593	1.593	2
2	2	6	1.562	1.563	3
4	2	$\bar{6}$	1.483	1.484)	4
7	1	5		1.482)	
3	1	$\overline{10}$	1.465	1.465)	2
8	0	$\bar{6}$		1.464)	
6	0	8	1.453	1.453	4
5	1	$\bar{9}$	1.449	1.449	2
0	2	8	1.439	1.438	3
4	0	10	1.430	1.429	5
6	2	$\bar{4}$	1,424	1.424)	9
6	2	3		1.423)	
8	0	$\bar{7}$	1.399	1.399)	2
1	1	$\overline{11}$		1.400)	
6	2	4	1.380	1.380)	4
1	1	11		1.381)	
5	1	9	1.369	1.368	1
3	1	$\overline{11}$	1.358	1.358)	5
7	1	$\bar{8}$		1.359)	
7	1	7	1.344	1.344)	2
4	2	$\bar{8}$		1.344)	
9	1	3	1.322	1.322)	8
1	3	2		1.322)	
8	0	7	1.311	1.311)	2
10	0	$\bar{3}$		1.311)	
8	2	$\bar{1}$	1.284	1.284)	5
6	2	6		1.284)	
4	0	12	1.232	1.232)	3
6	2	7		1.232)	

* Cu$K\alpha$

Caption: $AgBi_3S_3$ should be $AgBi_3S_5$

Nuffield's (1954) earlier result that only a homogeneous single phase can be recognized.

The powder diffractometer pattern from the compound thus formed corresponded closely with those of previously reported synthetic pavonite (Van Hook 1960) and natural pavonite (Nuffield 1954; Karup-Møller 1972). The unit-cell dimensions and space-group alternatives (Table 1) obtained from Weissenberg films from small single crystals were also close to those reported previously. Powder data (Table 2) were collected with a Philips diffractometer from specimens internally calibrated with KCl(a= 6.2929Å) using Cu$K\alpha$ radiation and slow scans (½°/min). The data were refined by a least-squares procedure to a 13.305(2), b 4.042(1), c 16.417(2)Å, β 94.02(1)°. The systematic absences of the $h0l$, $h1l$ and $h2l$ Weissenberg films recorded about the short 4Å axis, namely hkl, $h+k\neq 2n$; $h0l$($h\neq 2n$, defined the space group alternatives as $C2/m$, Cm or $C2$.

Intensity data were collected using an integrating Weissenberg camera, multiple film packs and Cu$K\alpha$ radiation, and were corrected for Lorentz and polarization effects. Corrections for absorption were performed with the program ABSNTST (Blount 1966) in which the crystal shape was approximated by seven planar surfaces, and calculations were accomplished with a 4×16×16 grid.

The departure of the crystal from a flat plate bounded by the "pinacoids" {100}, {010}, {001} only took into account a small chip off one of the edges normal to [010]. Good agreement between equivalent reflections on the Weissenberg films was observed. The discrepancy between ninety equivalent reflections, thirty from each level, when averaged overall was found to be less than 5% after the absorption corrections were applied. However the high linear absorption coefficient (1428 cm^{-1}) and the only approximate description of the crystal shape due to its small size (.03×0.3×.007 mm) were obviously the main factors which limited both the accuracy of the final set of structure factors and the subsequent level of refinement of the structure.

TABLE 3. ATOMIC COORDINATES IN SYNTHETIC PAVONITE, $AgBi_3S_5$

Atom	x	y	z	B(Å^2)
Bi(1)	.2369(6)	½	.1110(4)	1.85(15)
Bi(2)	.4722(6)	0	.2169(4)	2.07(17)
Bi(3)	.2192(5)	0	.3891(5)	2.17(17)
Ag(1)	0	0	0	2.51(44)
Ag(2)	0	½	½	2.43(43)
S(1)	.3688(32)	0	.0534(26)	1.20(75)
S(2)	.0979(38)	0	.1479(30)	2.20(100)
S(3)	.3386(30)	½	.2612(24)	.99(75)
S(4)	.0772(33)	½	.3603(26)	1.38(82)
S(5)	.3439(33)	½	.4664(27)	1.50(85)

STRUCTURE DETERMINATION, REFINEMENT AND DESCRIPTION

Structure determination and refinement

Because of the short b-repeat distance, the structure solution was attempted using the $h0l$ data to construct a Patterson function ρ (u,0,w). Reflections with $k = 0$, 2 showed the same intensity distribution, a reciprocal-space feature which is characteristic of many Bi-sulfosalt structures, and which indicated that all of the atoms in this structure were in planes normal to the b axis, separated by ½ the repeat distance of 4Å. Therefore, only the two-fold and four-fold sites at y=0 and ½ of the most probable space group $C2/m$ were considered in the model derived from the Patterson projection. Using the $h0l$ data, three Bi, two Ag and five S atomic sites were located by structure-factor and Fourier calculations. Neutral scattering curves were used (Cromer & Waber 1965) and anomalous dispersion corrections were made for Bi. The atomic positions, their temperature factors and occupances refined by a least-squares version of ORFLS (Busing *et al.* 1961) are given in Table 3. The weighting scheme of Cruickshank *et al.* (1961) was used.

In order to ensure that the displacements of the nearly octahedral atoms of Bi from the ideal octahedral position were correct, several attempts were made to move them in various directions off the refined positions. In all the subsequent refinement cycles these atoms returned to the same (above) positions which suggests their correctness.

Refinement proceeded to give an R-value of 0.11 when the shifts of all parameters were less than ⅓ of their *esd's*. This is a relatively high value, but without doubt due to the high absorption coefficient. The observed and calculated structure factors are presented in Table 4*. Interatomic distances and angles are tabulated in Table 5.

Description of the structure

The structure contains three independent Bi atoms (Fig. 2). Bi(1) is nearly octahedrally coordinated with bond distances (2.73(x1), 2.83 (x2), 2.88(x2), 2.96(x1)Å. Bi(2) is also in an octahedral site, with bond distances 2.65(x1), 2.82(x2), 2.90(x2), and 2.93(x1)Å. Bi(3) is coordinated by five close and three additional,

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*Table 4 is available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada, K1A 0S2.

TABLE 5. INTERATOMIC DISTANCES AND BOND ANGLES IN SYNTHETIC PAVONITE

Interatomic distance	
Bi(1)-S(3)	2.73(3)x1
S(2)	2.83(4)x2
$S(1)^{i}$	2.88(3)x2
S(1)	2.96(4)x1
Bi(2)-S(4)	2.65(4)x1
S(3)	2.82(3)x2
S(2)	2.90(4)x2
S(1)	2.93(4)x1
Bi(3)-$S(5)^{i}$	2.57(3)x1
S(4)	2.78(3)x2
S(5)	2.86(3)x2
S(3)	3.39(4)x2
S(2)	4.17(5)x1
Ag(1)-S(2)	2.67(5)x2
$S(1)^{i}$	2.85(3)x4
Ag(2)-S(4)	2.58(3)x2
S(5)	2.92(3)x4

Bond angles	
$S(1)^{i}$-Bi(1)-S(1)	87.8
S(1)-Bi(1)-S(1)	89.1
S(3)-Bi(1)-S(1)	91.2
S(2)-Bi(1)-S(2)	90.9
$S(1)^{i}$-Bi(1)-S(2)	85.4
S(3)-Bi(1)-S(2)	95.6
S(1)-Bi(1)-S(2)	89.6
S(1)-Bi(2)-$S(2)^{i}$	83.6
S(2)-Bi(2)-$S(2)^{i}$	88.2
S(4)-Bi(2)-$S(2)^{i}$	93.7
S(1)-Bi(2)-S(3)	88.4
S(3)-Bi(2)-S(3)	91.5
$S(4)^{i}$-Bi(2)-S(3)	94.2
$S(2)^{i}$-Bi(2)-S(3)	89.6
$S(5)^{i}$-Bi(3)-S(4)	84.0
S(4)-Bi(3)-S(4)	93.0
$S(5)^{i}$-Bi(3)-S(5)	78.9
S(5)-Bi(3)-S(5)	90.1
S(4)-Bi(3)-S(5)	85.9
S(2)-Ag(1)-$S(1)^{i}$	89.5
S(2)-Ag(1)-$S(1)^{i}$	90.5
$S(1)^{i}$-Ag(1)-$S(1)^{i}$	90.3
$S(1)^{i}$-Ag(1)-$S(1)^{ii}$	89.7
S(4)-Ag(2)-$S(5)^{i}$	98.9
S(4)-Ag(2)-$S(5)^{ii}$	81.2
S(5)-Ag(2)-$S(5)^{i}$	87.4
S(5)-Ag(2)-$S(5)^{ii}$	92.6

much more distant, sulfur atoms at bond distances of 2.57(x1), 2.78(x2), and 2.86(x2), 3.39(x2) and 4.17(x1)Å.

The coordination polyhedron of Bi(3) is a square pyramid $[BiS_{3+2}]$ (the $p^3d^2s^2$ configuration). The deformed octahedra of Bi(1) and Bi(2), however, approach the $[BiS_{1+5}]$ type of Kupcik (1972). The latter case suggests considerable *p-d* hybridization of the bonds in the planes perpendicular to the remaining short *p* bond.

Ag(1) has octahedral coordination with bonds 2.67(x2) and 2.85(x4)Å. The Ag(2) site is also flattened octahedral with bonds of 2.58(x2) and 2.92(x4)Å. Both silver sites, especially Ag(2), tend towards a 2-fold linear coordination.

The crystal structure of pavonite (Fig. 2) is composed of two types of slabs, parallel to (001). The thicker slabs represent continuous layers of little-deformed galena-like structure with only small departures from the cubic close packing of sulfur atoms. The slabs are parallel to $(\bar{1}13)$ of the galena submotive, and $[110]_{PbS}$ corresponds to twice the *b* parameter of pavonite. $[001]_{PbS}$ is parallel to $[\frac{2}{3}01]_{pavonite}$. The slabs have zig-zag boundaries, with the coordination octahedra of Bi(2) protruding. All thick slabs have the same orientation and, with good approximation, adjacent slabs are out of phase by $\frac{1}{2}[001]_{PbS}$. It is convenient to describe the thickness of the slab by the number of octahedra in a chain of octahedra (sharing common edges) that stretch across the slab in the direction $[1\bar{1}0]_{PbS}$, i.e. $[10\bar{\frac{2}{5}}]_{Pavonite}$. In the pavonite structure this number, *N*, is equal to 5.

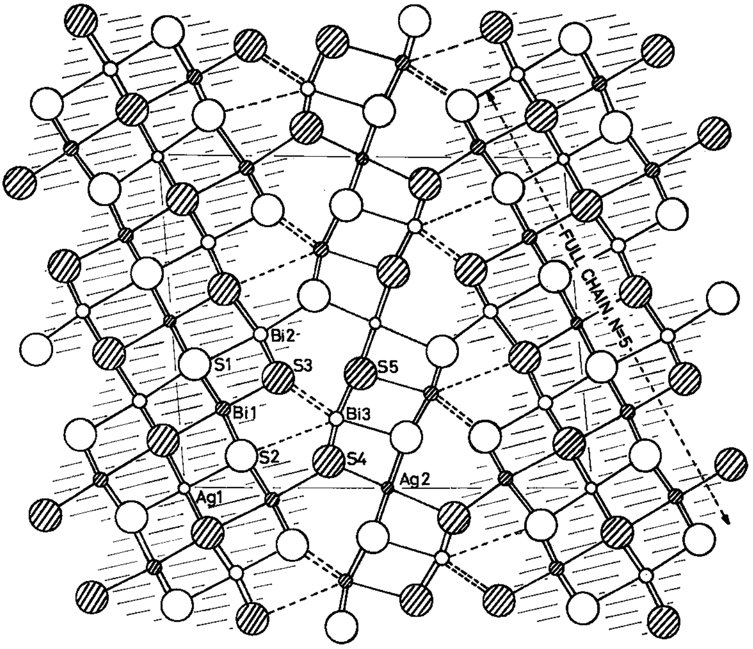

FIG. 2. Crystal structure of synthetic pavonite, $AgBi_3S_5$, viewed along the *b* axis. Empty circles denote atoms with $y=0$, shaded-circle atoms with $y=\frac{1}{2}$. Thick galena-like slabs with five octahedra per chain are hatched. Very long Bi-S distances are indicated by broken lines.

The thinner slabs contain only one octahedron, that of Ag(2), which alternates with paired squared pyramids of Bi(3). The two layers are mutually connected by the short Bi(2) – S(4) bonds. S(4), shared by Bi(2) and Ag(2), is common to both types of slabs.

STRUCTURE AFFINITIES OF PAVONITE

Pavonite represents a type member of a homologous series which will hereafter be called the *pavonite homologous series*. Phases of this series, in their idealized form, are composed of two alternative types of slabs (Fig. 2):

(1) Thinner slabs composed of single $[MeS_6]$ coordination octahedra alternating with paired square pyramids $[BiS_5]$. Thus, the slabs have the composition $[Me^{\text{oct}}Bi_2S_4]$ where *Bi* stands for Bi, and partly also for Sb and (Bi,Pb).

(2) Thicker "galena-like" slabs with a variable number *N* of complete, little-deformed coordination octahedra. Their composition is $[Me_N{}^{\text{oct}}S_{N+3}]$

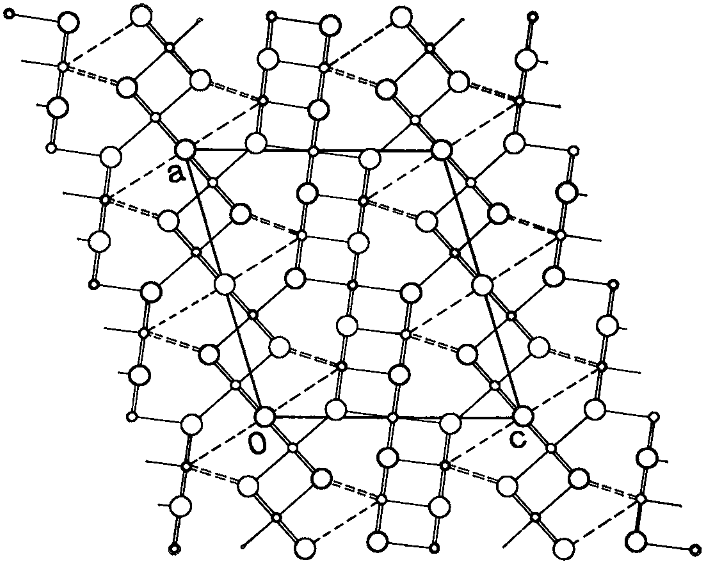

FIG. 3. Idealized structure of the pavonite homologue ^2P (phase V of Takeuchi *et al.* ~$PbBi_4S_7$). Large circles denote sulfur atoms, small circles metal atoms. Thick circles indicate atoms with $y=0$, thin circles atoms with $y=\frac{1}{2}$. Long Bi-S distances are indicated by broken lines.

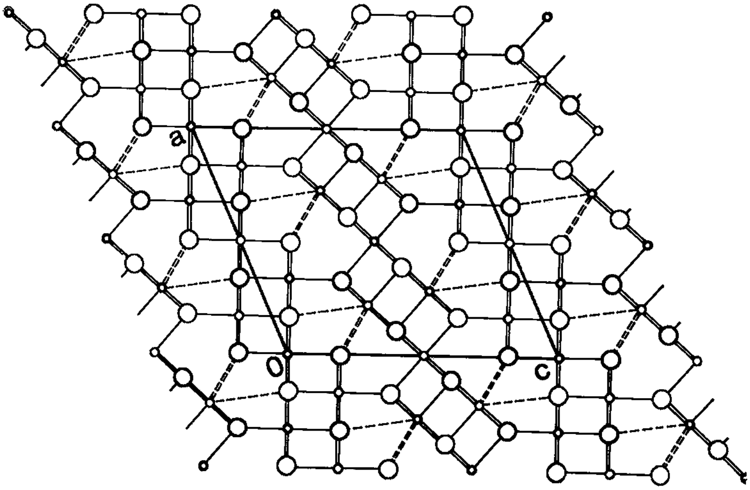

FIG. 4. Idealized structure of the pavonite homologue ^3P (~$CuBi_5S_8$). All explanations are given in Fig. 2.

with two out of $(N+3)$ sulfur atoms in common with the thinner slabs.

The two types of slabs are mutually oriented in such a way that the complete structure approximates the zig-zag pattern of lillianite homologues (Makovicky & Karup-Møller 1977). The slabs are interconnected via common sulfur atoms shared by the most protruding octahedron of the thicker slabs and the single octahedron of the thinner slabs. This arrangement ensures that the *Bi* atoms of the square pyramids only have (three) very long distances to the sulfur atoms of the thicker slabs.

Different members of the pavonite homologous series may be denoted by the symbol ^{N}P, where N is the number of octahedra per one diagonal octahedral chain of their thicker slabs (see above). The general chemical formula of the pavonite homologues is then:

$$Me^{oct}_{N+1}\,Bi_2\,S_{N+5}$$

Different pavonite homologues may contain different metals, as well as Bi, in the octahedral *Me* positions. In the known homologues these metals are Pb, Ag and Cu, sometimes partly substituting for each other. Thus, the pavonite homologous series can be thought of as "heteroelemental"*, contrary to the related lillianite homologous series (Makovicky & Karup-Møller 1977) which is composed of only Pb, Bi and Ag in variable proportions, and is thus "isoelemental".

The first known member of the series is $PbBi_4S_7$ with $N=2$ (phase V of Takeuchi *et al.* 1974a,b). The general formula applied to this N, $Me_3^{oct}Bi_2S_7$ requires one divalent and two trivalent atoms in the octahedral positions of the structure (Fig. 3). Takeuchi *et al.* (1974) believe that Pb and Bi are statistically distributed over the available metal sites, with the *Bi* site representing primarily a Bi site. Univalent metals cannot form the ^{2}P structure unless they are accompanied by at least quadrivalent metals.

^{3}P (Fig. 4) is represented by the structural arrangement ascribed to $CuBi_5S_8$ by Ohmasa & Nowacki (1973). Recent studies (Mumme & Watts unpublished) support Buhlmann's (1971) results which indicate that, in the pseudo-binary system Cu_2S-Bi_2S_3, the phase $CuBi_5S_8$ does not exist at the temperature at which it was purported to have formed. The composition $CuBi_5S_8$ forms a mixed-phase assemblage of Bi_2S_3 and a phase very close to, if not equal to, $CuBi_3S_5$ (see also Chen & Chang 1974), but which has the ^{3}P structure and apparently has the structural formula $Cu_{1.6}Bi_{4.8}S_8$. Due to this as yet unresolved compositional problem, we prefer to refer to the ^{3}P structure determined by Ohmasa & Nowacki (1973) as $\sim CuBi_5S_8$.

The configuration of the boundary area between the thinner and thicker slabs in the structure of $\sim CuBi_5S_8$ closely resembles that in pavonite. Copper 'occupies' the single coordination octahedron of the thinner slabs split into two statistical 'half atoms' situated in the 'upper' and 'lower' (along b) flat-tetrahedral halves of the coordination octahedron.

Ohmasa (1973) described the crystal structure of $Cu_{2+x}Bi_{6-x}S_9$ ($x=1.21$) that represents ^{4}P. The octahedral columns parallel to b, of the thinner slabs, are supposedly occupied by copper atoms split into four statistical positions and placed at the same height, y, as the S and Bi atoms. Also, the marginal Bi atoms of the thicker layers show partial occupancies and partial substitutions by Cu atoms. The latter are placed in the trigonal planar sites in those faces, parallel to b, of the Bi coordination octahedra which are oriented towards the interlayer space (Fig. 2 in Ohmasa 1973). The observed superstructure along the b axis is interpreted by Ohmasa (personal comm) as a periodical alternation of Cu-rich and Bi-rich portions of the columns of octahedra in this direction. Ohmasa's proposal features correctly the thinner structural slabs and the N value of his thicker slabs (equal to 4) agrees fully with the expectations based on the lattice geometry of ^{4}P (*cf* Makovicky & Karup-Møller 1977). Mumme & Watts (unpublished) have isolated crystals which contain large-scale oriented intergrowths of ^{3}P and ^{4}P; thus, it is possible that Ohmasa examined an integrowth of ^{3}P and ^{4}P and treated it as ^{4}P. Therefore, it is also possible that although the basic features of the structure proposed for $Cu_{2+x}Bi_{6-x}S_9$ ($x=1.21$) are probably correct, not all features described by Ohmasa (1973) might be real and the structure may need some revision.

^{5}P is known only as the structure of pavonite ($Ag_2Bi_6S_{10}$ in the above notation). ^{6}P remains undescribed. ^{7}P (Fig. 5) has not been found among solved structures but both the crystallography and the chemistry of benjaminite suggest that this mineral is the pavonite homologue with N equal to 7. In all known cases its composition is basically $Ag_3Bi_7S_{12}$, with Ag and Bi partly substituted by other metals, principally Cu and Pb (Karup-Møller & Makovicky, in prep.).

The thinner slab in its classical form $[HgSb_2S_4]$ is also present in livingstonite $HgSb_4S_8$ (Niizeki & Buerger 1957; Srikrishnan & Nowacki 1975). Hg is octahedrally coordinated but the octahedra

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*Such terms relate only to the principal components of the phases in the series. There are no *pure* "hetero" or "iso-elemental" types.

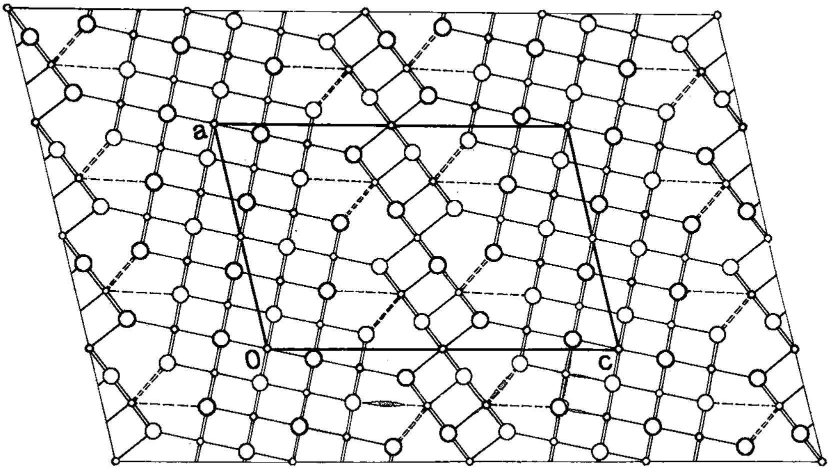

FIG. 5. Idealized structure of the pavonite homologue ^7P (benjaminite). All explanations as in Figure 2.

are very much flattened so that the Hg atoms actually have linear coordination with only two close sulfur neighbors. The size and shape of the Hg octahedra require arrangement of shorter and longer Sb-S bonds different from those in pavonite.

The matching [Sb_2S_4] slab only vaguely approximates an octahedral layer with N equal to 2. In comparison to the pavonite homologues it is shifted by $b/2$. Therefore, the octahedral bonds, which connect the two kinds of slabs in the pavonite homologues, disappear. The two kinds of layers are bound only by weak interactions. The occurrence of the S_2 group can be explained by the necessity to build a slab which is coherent with the [$HgSb_2S_4$] slab from only relatively small [SbS_5] pyramids. The structure of livingstonite suggests that purely Sb structures of pavonite type may not exist due to the reluctance of Sb to form nearly regular coordination octahedra, i.e. galena-like layers composed nearly of pure Sb.

The pavonite structure type is closely related to the lillianite structure type (Makovicky & Karup-Møller 1977). If the idealized linkage patterns (illustrated in Figs. 2-5) of the two types are compared, the principal difference rests in the replacement of the square-pyramidal bismuth atom with the three additional long Bi-S distances (i.e. [$BiS_{3+2+(3)}$]) by a Pb atom in a trigonal prismatic coordination, capped on two prismatic faces (i.e. [PbS_{6+2}]). The geometrical configuration of the sulfur atoms remains nearly unchanged in this exchange. Pavonite homologues in this way parallel hypothetical lillianite homologues with only one octahedron in one (thinner) set of alternating slabs and with N octahedra in the other (thicker) set of slabs.

PAVONITE SOLID-SOLUTION RANGES

The continuous solid solution between $AgBi_3S_5$, $CuBi_3S_5$, and $Cu_3Bi_5S_9$ reported by Chen & Chang (1974) has been mentioned above. However, there are actually three compounds here which represent the three distinct pavonite homologues ^3P, ^4P and ^5P described above. Thus, the compounds are not isostructural and a true solid solution among them cannot exist within the stability range of the above three structures. The existence of oriented intergrowths with fully periodic or disordered slabs sequences is a likely alternative, and large-scale oriented intergrowths have been observed by us between the two Cu-Bi sulfosalts where the dimensional misfit is minimal. It should also be stressed that the powder patterns of various pavonite homologues will in general resemble each other (compare the powder data for pavonite and benjaminite which are given in Harris & Chen 1975), and the powder pattern of a mixture of two or more ^NP's might easily be interpreted as a solid solution of them.

The structural data (present work and Takagi & Takeuchi 1972) and the compositions of natural phases (Makovicky & Karup-Møller 1977) contradict Hoda & Chang's (1975) proposal of a solid solution between lillianite and pavonite. The crystal structure of pavonite can be paralleled to a hypothetical lillianite homologue $^{1,5}L$ (Makovicky & Karup-Møller 1977), which has a set of one-octahedron-wide galena-like slabs alternating with a set of five-octahedra-wide slabs (for the definition of the number of octahedra per slab, see above). In lillianite, both alternating sets of slabs are four octahedra wide, and are related by mirror planes (the "chemical twinning" of Andersson & Hyde 1974). Gustavite (ideal formula $PbAgBi_3S_6$) is a lillianite homologue with 4 octahedra per one galena-like layer and forms, at geological temperatures, an incomplete solid solution with lillianite. Exsolution phenomena in this series were described by Karup-Møller (1970) and are discussed at length by Makovicky & Karup-Møller (1977). The most likely structure of gustavite is that resembling the substructure of andorite VI (Kawada & Hellner 1971), with regularly alternating Ag and Bi atoms in the rows parallel to [001]. Chemical formulae of natural pavonites (Karup-Møller & Makovicky, in prep.) and lillianites-gustavites (Makovicky & Karup-Møller 1977) indicate a constant averaged number of octahedra per slab (~4 for lillianites, ~3 for pavonites) along their entire respective solid-solution ranges. In other words, on the Pb-Bi-Ag projection of the Pb-Bi-Ag-S system, the line describing the solid-solution series lillianite-gustavite ($Pb_3Bi_2S_6$-$PbAgBi_3S_6$) and the line describing the natural pavonite solid solution will be parallel.

Although there is no solid solution between lillianite and pavonite, oriented intergrowths of (gustavite$_{80}$ lillianite$_{20}$) with pavonite, of an unknown mode of formation, have been observed (Karup-Møller & Makovicky, in prep.). Similarly, exsolution lamellae of gustavite (or a gustavite-like mineral, Nuffield 1975), have been detected in benjaminite.

For the basic substitutional mechanism $2Pb \rightleftarrows Ag+Bi$, the refined structure offers at least two basic possibilities that involve either Ag(1) or Ag(2) and one of the adjacent Bi atoms. Replacement of either Bi(1) or Bi(2) by Pb would involve only a small expansion of the coordination octahedra in question. The sulfur configuration around Bi(3) also is slightly smaller than the corresponding trigonal coordination prism $[PbS_{6+2}]$ in lillianite (Takagi & Takeuchi 1972). Although substitution of Bi(3) by Pb might be feasible, it is difficult to speculate about the consequences of this expansion and of the changes in adjacent Ag octahedra, for the whole structure.

Chemical analyses (Karup-Møller & Makovicky, in prep.) show that up to one-half of the copper atoms in natural pavonite is in excess of the formula Me_4S_5 and should be interstitial (perhaps in tetrahedral voids). The other half should replace the basic metals of pavonite, either in the manner suggested by the structures of $\sim CuBi_5S_8$ (Ohmasa & Nowacki 1973) and of $Cu_{2+x}Bi_{6-x}S_9$ (Ohmasa 1973) (but see above for the discussion of these structures in relation to the compounds $CuBi_3S_5$ and $Cu_3Bi_5S_9$) or by the structure of cuprobismutite (Ozawa & Nowacki 1975). Consequently, we cannot assess the exact role of copper in the pavonite structure without a structure determination on a copper-rich natural crystal. We may conclude by noting that the two principal substitution metals in pavonite, Cu and Pb, change the lattice parameters of the mineral in opposite ways. Thus, their combined presence may be the main reason why the change of lattice dimensions with substitution is much lower in natural pavonite than in natural lillianite-gustavite.

ACKNOWLEDGMENTS

Valuable discussions with Dr. S. Karup-Møller (Univ. of Copenhagen) are gratefully acknowledged.

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Manuscript received September 1976, emended December 1976.