

THE CRYSTAL STRUCTURE OF BENJAMINITE



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ABSTRACT

The crystal structure of benjaminite, from Manhattan, Nevada, $\text{Cu}_{0.50}\text{Pb}_{0.40}\text{Ag}_{2.30}\text{Bi}_{6.80}\text{S}_{12}$, has been determined to $R = 10.7\%$ on 585 independent reflections recorded with a single-crystal diffractometer. Its space group is $C2/m$, $Z = 2$, and from single-crystal film data, a 13.299(8), b 4.070(8), c 20.209(10) Å, β 103.32(5)°. There are 4(*Me*/2), 2(*Me*/4), and 6 (*S*/2) atoms in the asymmetric unit; $\frac{1}{2}$ *Me*(1) and *Me*(4) are coordinated by S atoms in flattened octahedra and are occupied respectively by Ag(Cu) in configuration approaching a distorted tetrahedron and by Ag(Bi,Pb). *Me*(2) is square-pyramidally coordinated Bi. The coordination of *Me*(5) [Bi] and *Me*(6) [0.8 Bi + 0.2 Ag] is closer to deformed octahedral, whereas that of $\frac{1}{2}$ *Me*(3) [Bi,Pb] is regular octahedral. The structure consists of two types of slabs parallel to (001). In the thinner slabs, *Me*(1) octahedra alternate with paired *Me*(2) pyramids. The thicker, galena-like slabs are composed of parallel, 7-membered octahedral chains, *Me*(6-5-4-3-4-5-6), and are interconnected via common *S*(2) atoms with the thinner slabs. The site of the Ag-Cu substitution in benjaminite, *Me*(1), is characteristic of the skewed and much substituted octahedra of the thinner slabs in pavonite homologues. Within the thicker slabs, *Me*(4) octahedra are the sites of (Ag, Pb, Bi), (Bi, Ag) and (Bi, Pb) substitutions. In the process, the *Me*(1) and *Me*(4) octahedra of benjaminite become flattened and elongated, respectively, in comparison to their counterparts in the $\text{Ag}_2\text{Bi}_6\text{S}_{10}$ structure.

SOMMAIRE

On a déterminé, jusqu'à un résidu $R = 10.7\%$, la structure cristalline de la benjaminite, $\text{Cu}_{0.50}\text{Pb}_{0.40}\text{Ag}_{2.30}\text{Bi}_{6.80}\text{S}_{12}$, sur un cristal de Manhattan (Nevada, E.U.A.), au moyen de 585 réflexions indépendantes obtenues au diffractomètre. La maille, a 13.299(8), b 4.070(8), c 20.209(10) Å, β 103.32(5)°, et le group $C2/m$ avec $Z = 2$ ont été établis photographiquement. Le domaine asymétrique contient 4(*Me*/2), 2(*Me*/4) et 6(*S*/2).

Les atomes Ag(Cu) et Ag(Bi,Pb) occupent $\frac{1}{2}$ *Me*(1) et *Me*(4), entourés d'atomes S formant des octaèdres aplatis, le premier pouvant aussi être considéré comme tétraèdre difforme. Le Bi, en *Me*(2), occupe le sommet d'une pyramide à base carrée formée de quatre atomes S. La coordination de Bi en *Me*(5) et ($\text{Bi}_{0.8}\text{Ag}_{0.2}$) en *Me*(6) est octaédrique, l'octaèdre étant respectivement difforme et régulier. La structure consiste en plaquettes (001) de deux types fines et épaisses. Dans les plaquettes fines, les octaèdres *Me*(1) alternent avec des pyramides *Me*(2) accouplées. Les plaquettes épaisses, qui rappellent la structure de la galène, sont constituées de chaînes d'octaèdres à 7 maillons, *Me*(6-5-4-3-4-5-6), et sont reliées aux plaquettes fines par des atomes *S*(2) mis en commun. Le site *Me*(1) de la substitution (Ag,Cu) dans la benjaminite est caractéristique des octaèdres difformes, à forte substitution, des plaquettes fines des homologues de la pavonite. Dans les plaquettes épaisses, les octaèdres *Me*(4) sont des sites de substitutions (Ag,Pb,Bi), (Bi,Ag) et (Bi, Pb). Ces remplacements sont à l'origine de la difformité des octaèdres *Me*(1) et *Me*(4), qui sont, respectivement, aplatis ou allongés, en regard des octaèdres de la structure cristalline de $\text{Ag}_2\text{Bi}_6\text{S}_{10}$.

(Traduit par la Rédaction)

INTRODUCTION

The name benjaminite was used originally by Shannon (1925) to describe a silver-containing mineral in a specimen from the Outlaw mine, Nye County, Nevada. In a later study of the type material by Nuffield (1953), benjaminite was defined more exactly as a monoclinic sulfosalt of unknown composition, with a 13.34, b 8.12, c 20.25 Å, β 104°, space group $C2/m$. Shannon's physical data for "benjaminite" were found to be attributable to aikinite, a much less abundant mineral with the above crystallographic data that contributed the Ag content reported in the original chemical analyses and motivated Shannon to propose a new

mineral species. The name benjaminite was retained by Nuffield for this second mineral. Nuffield pointed out a pseudocell with $b' = b/2$, which turned out to be our structural cell.

In 1975 both Nuffield and Harris & Chen refined the lattice-parameter data for benjaminite and defined its chemical composition as $(\text{Ag,Cu})_3(\text{Bi,Pb})_7\text{S}_{12}$. They also gave the full history of the species. Together with Borodayev & Mozgova (1971) they pointed out the chemical and crystallographic similarities between benjaminite and pavonite, which often lead to doubts about the true identity of individual pavonite/benjaminite occurrences. Makovicky *et al.* (1977) defined the pavonite homologous series and presented a structural scheme for benjaminite as the seventh member of the homologous series ${}^N\text{P}$, $\text{Me}^{\text{oct}}_{\text{N}+1}\text{Bi}_2\text{S}_{\text{N}+5}$. [Following a reviewer's suggestion, all formulae of benjaminite and other pavonite homologues in this paper will be based on the general formula ($Z=2$)]. On the basis of this scheme, Karup-Møller & Makovicky (1979) defined the composition of idealized, averaged benjaminite as $\text{Cu}_a\text{Pb}_b\text{Ag}_{3-y}\text{Bi}_{7-y}\text{S}_{12}$ with $a + b \geq 2y$ and, in the known cases, $0.3 < y < 0.9$.

The present paper verifies the proposed structural model by means of a structure determination on natural material. Comparison of our results, obtained from a Cu-Pb-substituted phase, with the data obtained on unsubstituted synthetic pavonite $\text{Ag}_3\text{Bi}_6\text{S}_{10}$ by Makovicky *et al.* (1977) allows some conclusions to be drawn about the nature of the metal substitutions in these minerals.

EXPERIMENTAL

The benjaminite crystal we examined comes from material chemically and crystallographically studied by Karup-Møller & Makovicky (1979). The specimen is from the collections

TABLE 1. MINERAL ZONING IN THE PRINCIPAL TYPES OF MASSIVE SULFIDE DEPOSITS*

	TYPE 1: Cu-Zn	TYPE 2: Pb-Zn-Cu-Ag	TYPE 3: Cu
Examples	Archean greenstone belts (Noranda; Mattagami)	kuroko; Bathurst	Cyprus
hanging wall	pyritic tuffite	sediment with hem:py	hem-py mudstone
	py-spha1 py-spha1-cp po-py-cp-spha1 po-cp:mag:py	barite gal-spha1-py-barite py-cp	py-cp:spha1 py:cp
footwall	py:mag	py-cp	py mag(?)

*Data from Large (1977). Abbreviations: hem hematite, py pyrite, cp chalcopyrite, gal galena, po pyrrhotite, mag magnetite.

of the Royal Ontario Museum in Toronto (M13805). Provenance is Manhattan, Nevada, U.S.A.

It is associated with berryite, krupkaite matildite and chalcopyrite (Karup-Møller & Makovicky 1979, Karup-Møller 1972) in the sample. Benjaminite was described as pavonite in these reports.

According to the microprobe analysis (Table 1, from Karup-Møller & Makovicky 1979, anal. G), the composition of the examined benjaminite is $\text{Cu}_{0.52}\text{Pb}_{0.38}\text{Ag}_{2.29}\text{Bi}_{5.26}\text{S}_{11.14}$ (based on the metal ratios established by the ideal formula $\text{Cu}_a\text{Pb}_b\text{Ag}_{3-y}\text{Bi}_{7-y}\text{S}_{12}$; see Karup-Møller & Makovicky 1979); if based on six sulfur atoms per formula unit it becomes $\text{Cu}_{0.54}\text{Pb}_{0.40}\text{Ag}_{2.36}\text{Bi}_{5.56}\text{S}_{12}$. The accuracy of the analysis is affected by the presence of oriented exsolution lamellae of gustavite on a unit-cell scale; these were detected on the single-crystal X-ray photographs (Karup-Møller & Makovicky 1979; *cf.*, Nuffield 1975). The X-ray data also show a certain amount of structural disorder in the benjaminite itself, which indicates that the overall ${}^N\text{P}$ (Makovicky *et al.* 1977) could differ somewhat from 7.

The lattice parameters of the benjaminite crystal we studied are shown in Table 1. Because of the minimal amounts of available material, they were obtained from the Weissenberg and oscillation films. They are in good agreement with the data similarly obtained by Nuffield (1975) and Harris & Chen (1975). The systematic extinctions and intensity relationships suggest $C2/m$ and Cm as the possible space-groups. $C2/m$ was chosen from the structural scheme for ${}^7\text{P}$ (Makovicky *et al.* 1977) and was subsequently confirmed by the results of the structure determination.

The crystal (approximately $0.16 \times 0.02 \times 0.08$ mm) was drilled out of a polished section and represents the best crystal available to us from the very limited choice of natural benjaminite occurrences. Intensity data were collected with Cu $K\alpha$ using ω scans performed with a 2-circle Stoe single-crystal diffractometer. Background intensity was recorded for 50 seconds at $\pm 4^\circ$ from the diffraction maxima, and the total counts were accumulated as the crystal was rotated through 8° in ϕ at the scanning rate of $8^\circ/200$ s. Intensities were considered to be less than a detectable value when $\text{BG} + 0.67\sigma\text{BG} > \text{P} - 0.67\sigma\text{P}$ where BG is the integrated background count, P the total number of counts accumulated, and 0.67σ the probable error computed from counting

statistics (Arndt & Willis 1966). Corrections for absorption were performed with the program *ABSNTST* (Blount 1966) in which the crystal shape was approximated to a "coffin-lid"-like shape, which implies rotational symmetry about [010] by eight planar surfaces, and calculations were accomplished with a 8 x 16 x 8 grid. A total of 585 independent reflections were obtained by averaging all the equivalent ones measured; the discrepancy between equivalent reflections averaged overall is 4.73%, which gives an idea of the accuracy of the absorption correction. Intensities were corrected for Lorentz and polarization effects in the usual manner.

STRUCTURE DETERMINATION AND REFINEMENT

The idealized structural scheme for the seventh member (*P*) of the pavonite homologous series (Makovicky *et al.* 1977, Fig. 5) was used as the starting set of positional parameters (Table 2). (For the mathematical expressions describing the scheme see Makovicky & Karup-Møller 1977 and Makovicky 1977). One silver atom (Ag/2) was placed into the octahedral position *Me*(1) of the thinner structural slabs, a location similar to that in pavonite. For the second Ag atom, the *Me*(4) position, in many respects analogous to the Ag(2) position in pavonite, yielded the lowest initial *R*-value.

Neutral scattering-curves (Cromer & Waber 1965) were used for all atoms, and anomalous dispersion corrections (International Tables for X-ray Crystallography, 1962, Vol. III) were made for Bi. The structural parameters were

refined by a full-matrix least-squares version of ORFLS (Busing *et al.* 1962), and the weighting scheme of Cruickshank *et al.* (1961) was used.

Rapid refinement to *R* = 13.2%, with only small positional shifts and with reasonable values of individual isotropic temperature factors, justified the approach chosen. At this stage, both Ag positions displayed individual isotropic *U* values (0.167 and 0.032 Å², respectively) very different from the *U* values of the remaining metal positions. Their *Me*-S distances were appreciably different from the respective Ag-S distances in pavonite, which suggests that they were the sites of detectable Cu and Pb (± Bi) substitutions. The positions were refined with mixed occupancies to the minimum in the *R* value, equal to 12.5%. In the last stages of the refinement, the *U* value of Bi in the *Me*(6) site (equal to 0.104 Å²) and the lower value of the maximum for the atom in the Fourier synthesis suggested its partial occupancy by lighter metals. As there were no indications of additional maxima or variations in the *Me*(6)-S distances which would reveal the nature of any substitutions, this position was subsequently refined as 0.8Bi + 0.2Ag with a marginal improvement in the *R* value (12.4%). In all cases the only occupational constraint applied was that Σ*Me* = 1.0 for each position.

Individual anisotropic temperature factors were then introduced and the structure was refined to the *R* value of 10.7%. Refinement was discontinued when parameter shifts were less than one-third of their estimated standard deviations. Interatomic distances and bond angles are presented in Table 3.

TABLE 2. ATOMIC PARAMETERS AND ANISOTROPIC TEMPERATURE FACTOR COEFFICIENTS FOR BENJAMINITE

Atom	Equi-point	Occup.	IDEAL STARTING COORDINATES				RESULTS OF ANISOTROPIC REFINEMENT*			
			x	z	x	z	β ₁₁	β ₂₂	β ₃₃	β ₁₃
Me1	2 a	½(Ag+Cu)	0	0	0	0	10(8)	1704(313)	21(5)	-1(4)
Me2	4 i	Bi	.74718	.08334	.7599(3)	.0913(2)	23(3)	694(68)	10(1)	-3(1)
Me3	2 c	½Bi	0	½	0	½	25(4)	649(98)	10(2)	-3(2)
Me4	4 i	.7Ag+.3Bi(Pb)	.69351	.41667	.6958(5)	.4092(3)	31(4)	756(100)	15(2)	3(2)
Me5	4 i	Bi	.38700	.33333	.3856(2)	.3193(2)	19(3)	789(71)	13(1)	0(1)
Me6	4 i	.8Bi+.2Ag	.08051	.25000	.0781(4)	.2283(3)	34(3)	899(78)	15(1)	4(2)
S1	4 i	S	.87359	.04167	.8594(17)	.0279(14)	3(13)	232(375)	19(8)	5(7)
S2	4 i	S	.62077	.12500	.6170(24)	.1080(13)	44(20)	639(494)	3(6)	8(8)
S3	4 i	S	.84675	.45833	.8461(24)	.4633(14)	45(20)	380(433)	9(8)	1(9)
S4	4 i	S	.54028	.37500	.5386(21)	.3688(14)	22(16)	324(397)	12(8)	-5(8)
S5	4 i	S	.23376	.29167	.2407(27)	.2832(15)	46(25)	1222(551)	15(8)	-7(9)
S6	4 i	S	.92726	.20833	.9302(18)	.1985(14)	4(14)	989(480)	12(8)	-6(7)

$y = 0$ for all metal atoms and $y = 1/2$ for all sulfur atoms.

*Anisotropic temperature factor expression: $\exp \{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$ with $\beta_{12} = 0$ and $\beta_{23} = 0$ for all atoms. All β_{ij} values are multiplied by 10^4 . Estimated standard deviations are given in parentheses in terms of the last digit.

TABLE 3. INTERATOMIC DISTANCES AND BOND ANGLES IN BENJAMINITE

Interatomic distances				Bond angles			
Me(1)-S(2)	2.37(3)x2	Me(4)-S(5)	2.74(3)x1	S(1)-Me(1)-S(1)	88.9	S(4)-Me(5)-S(4)	89.1
S(1)	2.91(2)x4	S(3)	2.76(3)x1	S(1)-Me(1)-S(2)	97.9	S(5)-Me(5)-S(5)	94.0
Me(2)-S(1)	2.56(3)x1	S(3)	2.89(2)x2	S(1)-Me(2)-S(1)	89.8	S(4)-Me(5)-S(5)	88.3
S(2)	2.86(2)x2	S(4)	2.89(2)x2	S(1)-Me(2)-S(1)	80.2	S(3)-Me(5)-S(4)	85.9
S(1)	2.88(2)x2	Me(5)-S(6)	2.64(3)x1	S(2)-Me(2)-S(1)	80.0	S(3)-Me(5)-S(5)	89.4
S(6)	3.42(2)x2	S(5)	2.78(2)x2	S(1)-Me(2)-S(2)	86.3	S(6)-Me(5)-S(5)	92.7
S(5)	3.95(3)x2	S(4)	2.90(2)x2	S(2)-Me(2)-S(2)	90.9	S(6)-Me(5)-S(4)	92.0
Me(3)-S(4)	2.80(3)x2	S(3)	3.07(3)x1	S(3)-Me(3)-S(3)	90.7	S(5)-Me(6)-S(5)	85.8
S(3)	2.86(2)x4	Me(6)-S(2)	2.60(3)x1	S(3)-Me(3)-S(4)	92.0	S(6)-Me(6)-S(6)	93.3
		S(6)	2.80(2)x2	S(3)-Me(4)-S(3)	89.7	S(5)-Me(6)-S(6)	89.9
		S(5)	2.99(3)x2	S(4)-Me(4)-S(4)	89.7	S(4)-Me(6)-S(5)	85.1
		S(4)	3.02(3)x1	S(3)-Me(4)-S(4)	89.9	S(4)-Me(6)-S(6)	86.5
				S(3)-Me(4)-S(3)	85.3	S(2)-Me(6)-S(6)	94.6
				S(3)-Me(4)-S(4)	88.3	S(2)-Me(6)-S(5)	93.7
				S(4)-Me(4)-S(5)	92.3		
				S(3)-Me(4)-S(5)	94.1		

Estimated standard deviation for bond angles is $.7^\circ$.

The relatively high *R*-value is due primarily to the high absorption-coefficient of benjaminite (for its ideal formula of $\text{Ag}_3\text{Bi}_7\text{S}_{12}$, this is 1429 cm^{-1}) and the very approximate description of the irregular crystal fragment used for the absorption corrections. Regrettably, benjaminite always occurs in intimate fine-grained intergrowths with other sulfosalts, so that chemical means of separation are excluded; it is possible to obtain only mechanically freed material such as we have used in the present study.

DESCRIPTION OF THE STRUCTURE

General features

The crystal structure of benjaminite (Fig. 1) is composed of two types of slabs parallel to (001). The thicker slabs represent continuous layers of little-deformed galena-like structure, parallel to (113) of the galena submotif. These thicker slabs have identical orientations, but their continuity across the gap occupied by the thin layers is broken by the shift of adjacent slabs

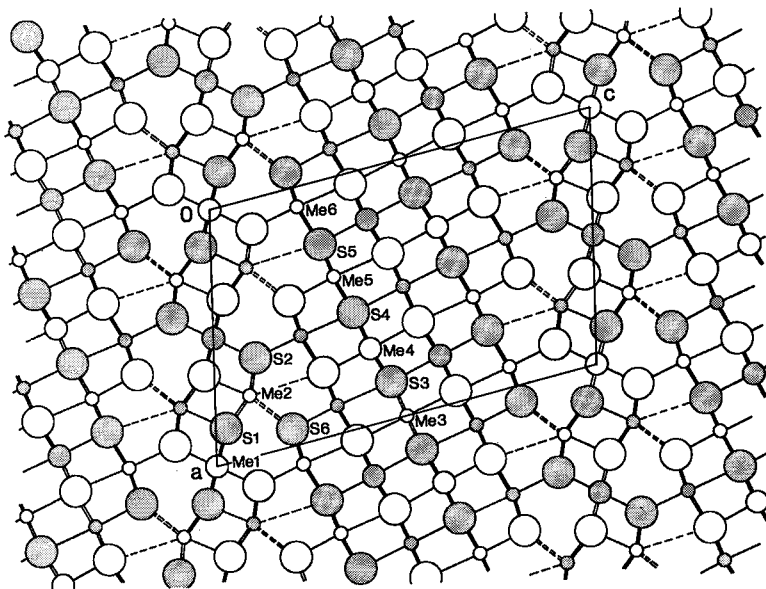


FIG. 1. The crystal structure of benjaminite. Projection on (010). Empty circles denote atoms at $y = 0$, solid circles those at $y = 0.5$. In the order of increasing size: Bi (primarily); Ag [& Cu for Me(1) & (Bi + Pb for Me(4))]; S.

by $\frac{1}{2}[001]_{\text{Pbs}}$. The number of octahedra in the diagonal chain of edge-sharing octahedra, running across an individual thicker slab and parallel to $[1\bar{1}0]_{\text{Pbs}}$, *i.e.*, to $[1, 0, 2/7]_{\text{benjaminite}}$, is equal to 7.

The thinner slabs contain only one octahedron, that of *Me*(1) [Ag + Cu], which alternates with paired square pyramids of *Me*(2) [Bi]. They resemble the thinner layer in unsubstituted pavonite, but the changes in the *Me*-S bond-lengths and angles arising from the extensive Cu-for-Ag substitution make them rather closer to the thinner layers in CuBi_6S_8 (Ohmasa & Nowacki 1973) and in $\text{Cu}_{2+z}\text{Bi}_{6-z}\text{S}_8$ (Ohmasa 1973).

The crystal structure of benjaminite follows closely the idealized pattern of $7P$ (Table 2). Only small positional deviations away from this pattern are necessary in order to satisfy the coordination requirements of atoms in the thicker layers. The most pronounced deformations are those in the thinner layers, owing to the substantial atomic replacement of Ag by Cu in the *Me*(1) position. No atoms interstitial to the basic $7P$ pattern were found.

Bismuth positions

The marginal parts of the thicker layers resemble in many details the corresponding por-

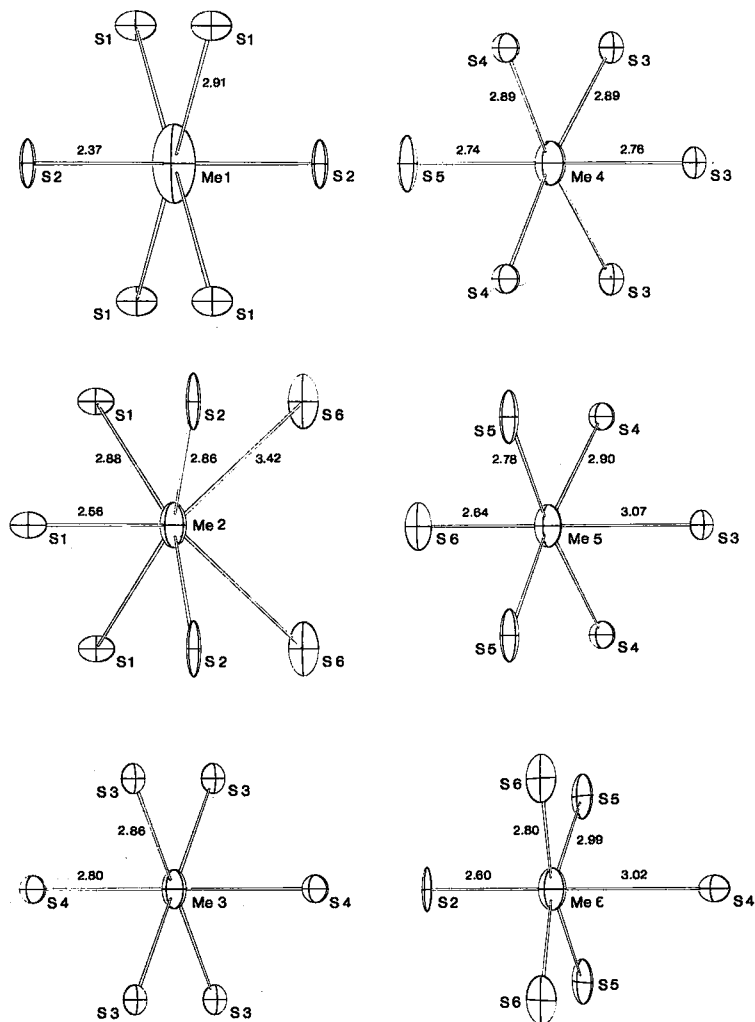


FIG. 2. Metal coordination-polyhedra in the crystal structure of benjaminite viewed along $[100]$. Thermal vibration (and disorder) ellipsoids are drawn at the 50% probability level. ORTEP drawing (Johnson 1965).

tions of the thicker layers in pavonite. The "apical" *Me*(6) which interconnects, *via* its shortest bond, the thicker and thinner slabs (Fig. 1) has the [1+2] shortest bonds, 2.60 (x1) and 2.80 Å (x2), clearly set apart from the remaining longer bonds, 2.99 (x2) and 3.02 Å (x1). The configuration is similar to that of the "apical" Bi(2) in pavonite, "apical" Bi(3) in CuBi_5S_8 (Ohmasa & Nowacki 1973) and of the similar Bi(2) in $\text{Cu}_{2+x}\text{Bi}_{6-x}\text{S}_9$ (Table 4A) (Ohmasa 1973).

Me(5) is situated below the coordination pyramid of *Me*(6), deeper in the layer; it has the coordination [2.64 (again towards the layer margin), 2.78 (x2), 2.90 (x2) and 3.07 Å] (Fig. 2). Once more it strongly resembles the corresponding atom of Bi(1) in pavonite as well as the similarly situated Bi(1) in $\text{Cu}_{2+x}\text{Bi}_{6-x}\text{S}_9$ (Table 4B).

The central atom in the diagonal chain of octahedra, *Me*(3), has the site symmetry $2/m$

TABLE 4. SELECTED TYPES OF THE COORDINATION POLYHEDRA OF BISMUTH IN SULFOSALTS

Compound	Site	Occu- pancy	Me-S distance, Å				Ref.
			(x1)	(x2)	(x2)	(x1)	
A							
Benjaminite	Me(6)	Bi, (Ag)	2.60	2.80	2.99	3.02	1
$\text{Ag}_2\text{Bi}_6\text{S}_{10}$	Bi(2)	Bi	2.65	2.82	2.90	2.93	2
$\sim\text{CuBi}_5\text{S}_8$	Bi(2)	Bi	2.68	2.71	2.94	3.08	3
$\sim\text{Cu}_{3.21}\text{Bi}_{4.78}\text{S}_9$	Bi(2)	Bi, Cu	2.66	2.74	2.89	3.01	4
B							
Benjaminite	Me(5)	Bi	2.64	2.78	2.90	3.07	1
$\text{Ag}_2\text{Bi}_6\text{S}_{10}$	Bi(1)	Bi	2.73	2.83	2.88	2.96	2
$\sim\text{Cu}_{3.21}\text{Bi}_{4.78}\text{S}_9$	Bi(1)	Bi, Cu	2.66	2.77	2.87	3.12	4
C							
			(x1)	(x2)	(x2)		
Benjaminite	Me(2)	Bi	2.56	2.86	2.88		1
$\sim\text{CuBi}_5\text{S}_8$	Bi(2)	Bi	2.59	2.83	2.86		3
$\sim\text{Cu}_{3.21}\text{Bi}_{4.78}\text{S}_9$	Bi(3)	Bi	2.60	2.84	2.89		4
$\text{Ag}_2\text{Bi}_6\text{S}_{10}$	Bi(3)	Bi	2.57	2.78	2.86		2
D							
Cuprobismutite	Bi(4)	Bi	2.58	2.69	3.09		6
Emplactite	Bi(1)	Bi	2.55	2.66	3.16		8
$\text{Cu}_4\text{Bi}_5\text{S}_{10}$	Bi(2)	Bi	2.63	2.74	3.04		7
E							
			(x2)	(x4)			
Benjaminite	Me(3)	Bi, (Pb)	2.80	2.86			1
Hodrushite	Me(1)	Bi ⁺	2.79	2.84			5
Hodrushite	Me(2)	Bi ⁺	2.82	2.80			5
$\sim\text{CuBi}_5\text{S}_8$	Bi(1)	Bi	2.79	2.81			3
Cuprobismutite	Bi(1)	Bi, Cu	2.84	2.77			6
$\text{Cu}_4\text{Bi}_5\text{S}_{10}$	Bi(1)	Bi, (?Pb)	2.82	2.85			7

*Minor amounts of unspecified lighter metals (primarily Cu?), especially in Me(2).

1. This work. 2. Makovicky *et al.* (1977) (synthetic pavonite). 3. Ohmasa & Nowacki (1973). 4. Ohmasa (1973). For comments on 3 & 4 see 2. 5. Kupčik & Makovicky (1968). For composition see Makovicky & MacLean (1972). 6. Ozawa & Nowacki (1975). 7. Mariolacos *et al.* (1975). 8. Kupčik (1965).

A & B: 'deformed octahedral' Bi coordinations (A) on the surfaces of, and (B) deeper in the thicker structural slabs of pavonite homologues. C & D: square pyramidal Bi coordinations forming paired columns of pyramids (C) in the pavonite homologues and (D) elsewhere. E: octahedral Bi coordinations.

and displays a relatively undeformed octahedral coordination with bond lengths 2.80 (x2) and 2.86 Å (x4) (Fig. 2). According to the refinement results, this position is occupied by Bi with possible but undetectable amounts of Pb replacing bismuth. It is similar to the highly regular octahedral positions of bismuth (primarily), described by Kupčik & Makovicky (1968) in hodrushite $\text{Cu}_4\text{Bi}_6\text{S}_{11}$, by Ohmasa & Nowacki (1973) in CuBi_5S_8 , by Ozawa & Nowacki (1975) in cuprobismutite, $\sim\text{Cu}_{2.58}\text{Bi}_{3.14}\text{S}_6$, and by Mariolacos *et al.* (1975) in $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ (Table 4E). Thus, the known bond-length information neither proves nor disproves a small partial contribution to *Me*(3) by Pb.

The only bismuth position in the thinner layer, *Me*(2), typically forms paired columns of square coordination pyramids [BiS₅], with additional long Bi-S distances towards the sulfur atoms of the thicker layer, *i.e.*, with the lone electron-pair accommodated in the interlayer space (Fig. 2). The interesting distribution of the Bi-S distances [2.56, 2.86 (x2), 2.88 Å (x2)] in the square pyramid differs from that in the unsubstituted pavonite and comes closer to the configuration observed in CuBi_5S_8 . In contrast, $\text{Cu}_{2+x}\text{Bi}_{6-x}\text{S}_9$ has a more ambiguous distribution of bond distances (Table 4C). The apparent reason for this peculiar distribution, different from other typical Cu-Bi cases with paired columns of pyramids (Table 4D), is that the S(2) atoms are drawn into the layer in order to accommodate the short average (Ag, Cu)-S distances (2.37 Å) in the *Me*(1) octahedron. The latter phenomenon does not occur in unsubstituted pavonite, where the relevant Ag-S bond is 2.58 Å.

Silver positions and the metal substitutions

The *Me*(4) position in the thicker structural slab is primarily occupied by silver. The *Me*-S distances [which differ from those of Ag(2) in unsubstituted pavonite], the higher average scattering power of the metal atom in the site, its larger individual isotropic mean-square displacement (at the minimum of the *R* value), as well as the higher *U*s of the sulfur atoms S(3) and S(5) [which make up 2/3 of the vertices of the *Me*(4) coordination octahedron] all suggest appreciable replacement of Ag in this site by a heavier metal. Whereas the approximately corresponding Ag(2) position in pavonite has the Ag-S bonds equal to 2.58 (x2) and 2.92 Å (x4), *i.e.*, a linear (average) S-Ag-S coordination in a flat-octahedral environment,

TABLE 5. THERMAL AND DISORDER ELLIPSOIDS IN BENJAMINITE

Atom	r.m.s. displacement	Angle to			Atom	r.m.s. displacement	Angle to		
		<u>a</u>	<u>b</u>	<u>c</u>			<u>a</u>	<u>b</u>	<u>c</u>
Me1	.0894(42)	161(10)	90	95(10)	S1	.0328(166)	178(15)	90	79(15)
	.2110(24)	109(10)	90	5(10)		.1389(112)	90	0	90
	.3764(35)	90	0	90		.1907(41)	88(15)	90	169(15)
Me2	.1126(9)	128(6)	90	128(6)	S2	.0546(148)	74(15)	90	177(15)
	.1720(7)	142(6)	90	38(6)		.1935(42)	16(15)	90	87(15)
	.2403(12)	90	0	90		.2303(69)	90	0	90
Me3	.1164(12)	126(8)	90	131(8)	S3	.1378(51)	98(30)	90	158(30)
	.1795(9)	144(8)	90	41(8)		.1778(99)	90	0	90
	.2323(18)	90	0	90		.2041(44)	172(30)	90	68(30)
Me4	.1578(10)	145(20)	90	112(20)	S4	.1085(56)	135(31)	90	122(31)
	.1798(9)	125(20)	90	22(20)		.1640(115)	90	0	90
	.2506(16)	90	0	90		.1903(43)	45(31)	90	148(31)
Me5	.1234(8)	151(7)	90	106(7)	S5	.1404(74)	121(19)	90	136(19)
	.1707(7)	118(7)	90	16(7)		.2400(468)	149(19)	90	46(19)
	.2561(12)	90	0	90		.3187(72)	90	0	90
Me6	.1689(7)	132(55)	90	124(55)	S6	.0264(220)	150(25)	90	107(25)
	.1746(7)	138(55)	90	34(55)		.1809(48)	121(25)	90	17(25)
	.2733(12)	90	0	90		.2867(70)	90	0	90

the (mean) *Me*(4) position in benjaminite displays bonds as follows: 2.76 and 2.89 Å (x2) to the disordered S(3), 2.74 Å to the disordered S(5), and 2.89 Å (x2) to S(4). Refinement indicates an occupancy of 0.7 Ag and 0.3 (Pb, Bi). The experimental errors, which result in flat *R*-value minima and in strong occupancy-

temperature-factor interactions, did not allow a more accurate determination of the occupancy.

The comparison of the observed *Me*(4) distances with Pb-S distances and with sets of octahedral or averaged non-octahedral Bi-S distances does not show any linear relationships between their lengths and the partial-occupancy

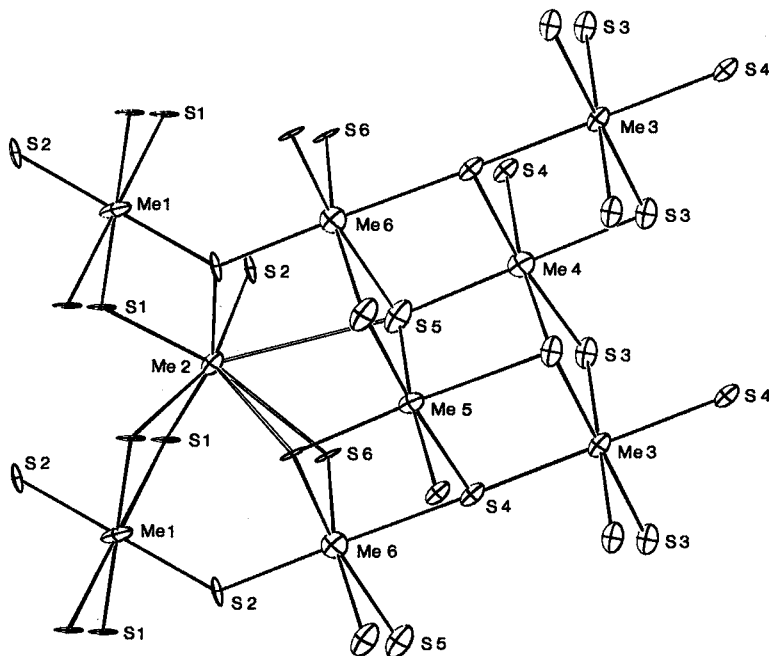


FIG. 3. A representative fragment of the crystal structure of benjaminite drawn with 50% probability ellipsoids. Projection along a direction close to $[0\bar{1}0]$, with \vec{a} pointing down. ORTEP drawing (Johnson 1965).

factors. However, the contraction of the four diagonal bonds from 2.92 Å in pavonite to 2.89 Å does suggest Bi as the principal substituting element. The increase in the "linear" S–Me–S distance against Ag(2) in pavonite remains non-indicative.

The Me(1) position is occupied by (approximately) equal atomic amounts of Ag and Cu. The linear average S–Me–S bond, parallel to (010), is considerably shortened (2.37 Å, x_2) over that in substitution-free pavonite (Ag(2): 2.58 Å, x_2). The diagonal bonds, completing the coordination of (Ag,Cu) into a much flattened, slightly skewed octahedron (with site symmetry $2/m$), are only insignificantly shorter (2.91 Å, x_4) than the corresponding bonds in the Ag(2) octahedron of pavonite (2.92 Å, x_4).

The isotropic individual temperature-factor of Me(1) is considerably larger than those of the other metals in the structure, indicating that the adjustments of the Me(1)–S bond-lengths in this site, statistically occupied by Ag and Cu, proceed primarily by positional disorder of the metal atoms. The results of the anisotropic refinement suggest the way that this adjustment is achieved.

The disorder and thermal-motion ellipsoid of Me(1) is strongly oblate, with the main axis parallel to b , and the medium axis approximately parallel to c (Figs. 2 and 3, Table 5). Both S(1) and S(2) display oblate ellipsoids, the former approximately perpendicular to the a direction, the latter parallel to the largest face of the [Me(1)S₆] coordination octahedron, with the principal axis parallel to b and the medium axis along the octahedron face.

The coordination of Cu and Ag can be interpreted from these results in a number of ways that cannot be distinguished by structure determination. On one hand, the shortest linear Me(1)–S(2) distance will be approximately equal to 2.23 Å (x_2) [i.e., 2.37 Å less the net effect of the r.m.s. displacement (U_{22}) of S(2) towards Me(1)]. This value is close to the lower limit for the known Cu–S bonds (Makovicky & Skinner, 1979). If, however, the effect of the r.m.s. displacement of S(2) is added to the average bond-length of 2.37 Å, the linear Me(1)–S(2) coordination will have a bond-length of about 2.51 Å (x_2), less than that observed in Ag₂Bi₆S₁₀ (2.58 Å), but above the average Ag–S bond length 2.46 Å given for the S–Ag–S configuration by Edenharter (1976). On the other hand, the metal atoms at the r.m.s. distance (0.38 Å) along the b axis from the mean position Me(1) will have Me–S(2) bonds equal to 2.40 (x_2) and Me–S(1) bonds equal to 2.66 Å (x_2), both

measured to the mean sulfur positions. For the same model the bond angle S(2)–Me–S(2) is 162°, the S(1)–Me–S(1) angle is 103°, and the remaining angles 86° and 87°. If the effects of the r.m.s. displacement U_{22} (or U_{33}) of S(2) (Table 5) away from the deviated metal position are added, the Me–S(2) bond-length will increase to 2.45 Å (or to 2.55 Å) and the S(2)–Me–S(2) angle will lie in the vicinity of 152° (or 153°). Thus, the averages for the four-fold coordination lie below or at the value of 2.62 Å and 109°. The estimates compare favorably with the average values given for the 2- and 4-coordinated silver by Edenharter (1976), 2.46 Å and 155.4°, and 2.66 Å and 107.6°, respectively. The oblate shape of the Me(1) ellipsoid suggests that the actual Me position may be off the b axis so that the bonds will vary in length still more than in the above average model. This would again be in accordance with the observations on Ag in other sulfosalts (Edenharter 1976).

The distorted tetrahedral coordination of Me(1) at the r.m.s. distance from the mean position is closest to the coordination of 4-coordinated Ag in smithite (Hellner & Burzlaff 1964). It is similar to the deformed-tetrahedral coordination of the statistically occupied copper position in CuBi₅S₈ (Ohmasa & Nowacki 1973), although for (Ag,Cu) the deviation from the linear S–Me–S configuration is only one-half that observed for Cu. The Me–Me contact along the b axis between the two statistically occupied positions will then be 3.32 Å, far above the value of 2.56 Å found in CuBi₅S₈ (*ibid.*) and 2.88 Å in metallic silver.

Both Ag atoms in Ag₂Bi₆S₁₀ display somewhat larger U s than the Bi atoms. With only the isotropic refinement performed, no statements concerning the possible statistical disorder around the mean positions and the kinking of the S–Ag–S bond can be made. In this connection it is interesting to note that the "linear" S(3)–Me(4)–S(5) coordination in benjaminite can also be interpreted as a slightly kinked one, primarily owing to the strong positional disorder of S(5) along the b axis (Fig. 2). The straightest S–Ag–S group found in sulfosalts is that in miargyrite (Knowles 1964) with an angle of 175.3°.

The Me(6) position, with a typical "bis-muth-like" coordination, yields an occupancy of only 0.9 Bi. However, its higher B value and that of Me(5) seem caused instead by their attachment to the statistically replaced Me(4) and Me(1) octahedra, which have variable di-

TABLE 6. METRIC CHARACTERISTICS OF THE COORDINATION OCTAHEDRA IN THE STRUCTURES OF PAVONITE HOMOLOGUES

Compound	N_p	l	w	t	Skewness	Metal	Metal Coordination	Reference
Thinner structural slabs:								
$\sim\text{PbBi}_4\text{S}_7$	2	5.58Å	3.97Å	4.03Å	4.4°	Pb, Bi	Octahedral	Takéuchi <i>et al.</i> (1974)
$\sim\text{CuBi}_5\text{S}_8$	3	4.47	4.15	4.03	9.0°	Statistical Cu	deformed tetrahedral	Ohmura & Nowacki (1973)
$\text{Ag}_2\text{Bi}_6\text{S}_{10}$	5	5.15	4.22	4.04	12.3°	Ag	\pm linear	Makovicky <i>et al.</i> (1977)
Benjaminite	7	4.74	4.15	4.07	13.0°	Statistical Ag, Cu	deformed tetrahedral to linear	Present work
Thicker structural slabs:								
$\text{Ag}_2\text{Bi}_6\text{S}_{10}$	5	5.34	4.02	4.04	0.9°	Ag	\pm linear	Makovicky <i>et al.</i> (1977)
Benjaminite	7	5.50	4.08	4.07	3.3°	Ag, Bi, Pb	linear to octahedral	Present work

mensions and shapes (Fig. 2). No peaks of the type corresponding to the marginal copper atoms partly substituting for Bi, postulated by Ohmura (1973) in his structure determination of $\text{Cu}_{2+x}\text{Bi}_{6-x}\text{S}_9$ ($x = 1.21$), were found in the Fourier and difference-Fourier maps of benjaminite. Thus, with some reservations (especially concerning the effects of the small possible disorder in the slab thickness), the *Me*(6) position will be regarded as having a mixed occupancy 0.8 Bi + 0.2 Ag. To satisfy the local valence-balance not maintained by the above unequal atomic substitutions, an equivalent amount of Pb must replace one of the adjacent bismuth positions. The most likely site for this replacement is the *Me*(3) position. Unfortunately, substitution here cannot be verified for the reasons discussed above.

Generalization for the pavonite homologues

The octahedral positions in the two types of layer in the structure of benjaminite and the other pavonite homologues are occupied by linearly, tetrahedrally and octahedrally coordinated metal atoms (Table 6). For the study of substitutional possibilities, the structures can best be compared using the dimensions and shapes of octahedra (*sensu lato*) formed by sulfur atoms surrounding these metals. For this purpose, and in a manner similar to Makovicky & Karup-Møller (1977), we shall define their "width" w (e.g., the S(1)–S(1) distance parallel to (010) in benjaminite), "length" l (e.g., the S(2)–octahedron centre–S(2) distance in benjaminite) and "height" t (e.g., the S(1)–S(1) distance parallel to b in benjaminite). Furthermore, for the highly regular structures of the pavonite homologues, with the repeat period along b equal to one octahedron height, we can define skewness of an octahedron (*sensu lato*) as the difference between the angle comprised

by the l direction and the plane wt , and the ideal value of 90°. These values are given for selected pavonite homologues in Table 6.

We can see that the dimensions and the shape of the skewed octahedra in the thinner layers are close for the Ag and Cu cases. This, together with the adjustability of the "apical" S position [S(2) in benjaminite] and the variability of the Cu and Ag coordinations (*cf.*, Edenarter 1976, appendix) explains the extensive (Cu, Ag) mutual substitution. The substitution limits are probably set by the limits in the positional variation for S(2) which interconnects the thicker and thinner layers, thus setting the lower

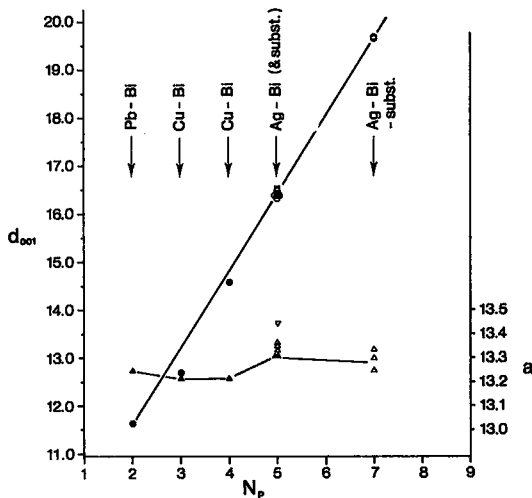


FIG. 4. Changes in a and $d(001)$ parameters for different members (N_p in the range 2 \rightarrow 7) of the pavonite homologous series. Notable are the negative deviations for pure Cu–Bi members. Open symbols refer to pavonites and benjaminites with partial Cu and Pb substitution for Ag and Bi (they are listed in Karup-Møller & Makovicky 1979). The highest values for $N_p = 5$ represent cupropavonites.

limit for the accommodation of Ag in the columns of $[Me(1)S_6]$ octahedra when their average size decreases.

The (predominantly) Ag-bearing octahedra in the thicker structural layers are much less flattened (*i.e.*, narrower and more elongated) and much less skewed (Table 6); they resemble closely the Pb (and Bi) octahedron in $PbBi_4S_7$. However, they remain appreciably smaller than the $[PbS_6]$ octahedra in galena. Their shape apparently precludes substitution by copper, whereas their size and occurrence in the predominantly Bi-bearing layers (dimensionally smaller than the corresponding Pb-bearing layers) suggest that replacement by Pb will be limited.

Substitutions ratio

The structure does not give a simple explanation for the regularly observed $Cu/Pb = 3/2$ ratio in benjaminites and pavonites. Replacement of Ag by Cu diminishes both the a and $d(001)$ parameters, whereas that by Pb (and Bi) increases them (Fig. 4). In the a direction these substitutions might bring about a misfit of the two layer types in the structure unless compensated by deformations, primarily of the thinner layers. In the $d(001)$ direction, the above two changes dimensionally compensate each other, resulting in the contraction of the thinner layer and expansion of the thicker layer, *i.e.*, in the change of the relative position of S(2) in the structure. Thus, during the combined Cu and Pb substitution the lattice parameters of benjaminite (and also of pavonite) remain nearly unchanged. Quantitative assessment of the dimensional changes on substitution (and possible structural explanation of the Cu/Pb ratio) is not possible on the basis of available structure refinements quoted in Table 6.

COMPOSITION AND STABILITY

The above substitution model results in the composition $Cu_{0.50}Pb_{0.40}Ag_{2.30}Bi_{6.80}S_{12}$. If we start from the hypothetical unsubstituted composition, Ag is more extensively substituted than Bi. This formula yields balanced valences for univalent copper. Its agreement with the empirical formula based on 12 sulfur atoms is good, in spite of the above described limitations in the refinement and interpretation. It should be stressed that, because of the finely exsolved gustavite, the contents of individual elements in the re-

finement were not constrained by the results of the microprobe analysis. Similar benjaminites, with more pronounced substitutions of Ag, have been described from Old Laut's mine, Colorado (Karup-Møller & Makovicky 1979) and from Nye County, Nevada (Nuffield 1975). Benjaminites from Nevada with more pronounced substitution of Bi than of Ag and enriched in Pb have been described by Harris & Chen (1975).

Benjaminites of the first substitutional type and, before exsolution, with the most pronounced substitution of Pb and Cu for Ag and Bi, exsolve (on cooling?) gustavites and an unidentified Cu-Bi mineral (Nuffield 1975, Karup-Møller & Makovicky 1979). A benjaminite-like phase analogous to cupropavonite formed by exsolution of Cu (and Pb)-rich pavonite (Kerup-Møller & Makovicky 1979) has not been identified.

Natural unsubstituted benjaminites have not been reported, nor has a synthetic unsubstituted (or substituted) benjaminite been prepared in the laboratory studies of any of the previous workers (van Hook 1960, Craig 1967, Chen & Chang 1974, Hoda & Chang 1975). This was also the outcome of our sealed-tube reactions of both $Ag_3Bi_7S_{12}$ and $Pb_{0.25}Ag_{2.875}Bi_{6.875}S_{12}$ at 550°C (Mumme & Watts, unpubl. data; α -matildite-galena solid solution (*ss*) and pavonite *ss* were confirmed in both cases. Overlapping of α -matilde and pavonite X-ray lines is prevalent on the powder diffractograms (Cu $K\alpha$ radiation), but the powder data indicate that for the mixed phase-assembly prepared from $Pb_{0.25}Ag_{2.875}Bi_{6.875}S_{12}$, the pavonite *ss* has, within the limits of estimated errors, an unchanged unit cell from that of pure end-member $Ag_3Bi_4S_{10}$. The α -matildite-galena *ss*, on the other hand, has a significantly expanded cell, ~ 5.69 Å, compared with 5.65 Å for α - $AgBiS_2$; this difference is estimated by using the shift of the position of its (111) line, from $d = 3.27$ Å for the $Ag_3Bi_7S_{12}$ starting composition to a position which is almost unresolved from the (400) line of pavonite, at $d = 3.32$ Å, for the $Pb_{0.25}Ag_{2.875}Bi_{6.875}S_{12}$ starting composition. The composition of α -matildite-galena *ss* with a unit-cell edge of 5.69 Å is close to $2PbS.4Ag_2S.4Bi_2S_3$, *i.e.*, galena_{11.1} matildite_{88.9} (Hoda & Chang 1975), so that for the mixture of pavonite and α -matildite-galena *ss* formed from the "benjaminite" starting composition at 550°C, lead must be preferentially incorporated into the α -matildite-galena *ss* structure. The relatively unchanged unit cell for the pavonite-type com-

ponent cannot be used to assess partitioning of lead owing to the smaller changes that accompany Pb substitution into its structure (Hoda & Chang 1975).

The reason benjaminite does not form in either of the two partial systems $PbS-Bi_2S_3-Ag_2S$ and $Cu_2S-Ag_2S-Bi_2S_3$ at and above $400^\circ C$ is probably that these temperatures exceed its upper stability limits; however, it is possible that benjaminite requires the presence of both Cu and Pb for its formation.

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