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THE CRYSTAL STRUCTURE OF Ag–Bi-BEARING HEYROVSKYITE

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ABSTRACT

The crystal structure of Ag- and Bi-substituted heyrovskyite from La Roche Balue, west of Nantes, France, has been refined using 341 independent reflections to an *R* value of 0.06. An electron-microprobe analysis of heyrovskyite yields $Pb_{3.67}Cd_{0.05}Ag_{1.15}Bi_{3.13}S_{9.19}$ (Moëlo *et al.* 1987), and the structure determination gave $Pb_{3.36}Ag_{1.32}Bi_{3.32}S_9$ for the crystal studied. Cell parameters are *a* 4.110(1), *b* 13.600(3), *c* 30.485(12) Å, space group *Cmcm*. Trigonal prismatic sites *Me*1 on planes of unit-cell twinning are fully occupied by Pb, octahedral sites *Me*2 and *Me*3 in central slab portions by ~80% Pb, ~20% Bi. semi-marginal octahedral site *Me*5 by Bi; Ag substitution takes place in the marginal octahedral site *Me*4: 0.657 Ag + 0.343 Bi. Departures from the PbS-like archetype in slabs are small, with the largest departures occurring in marginal sites *Me*4 and *Me*5.

Keywords: heyrovskyite, Ag and Bi substitution, crystal structure.

SOMMAIRE

La structure cristalline d'un échantillon de heyrovskyite dans lequel Ag et Bi sont incorporés par substitution, provenant de La Roche Balue, situé à l'ouest de Nantes (France), a été affinée jusqu'à un résidu *R* de 0.06 en utilisant 341 réflexions indépendantes. Les analyses à la microsonde électronique mènent à la composition $Pb_{3.67}Cd_{0.05}Ag_{1.15}Bi_{3.13}S_{9.19}$ (Moëlo *et al.* 1987); l'affinement de la structure donne $Pb_{3.36}Ag_{1.32}Bi_{3.32}S_9$ pour l'échantillon que nous avons étudié. Ses paramètres réticulaires sont *a* 4.110(1), *b* 13.600(3), *c* 30.485(12) Å, et le groupe spatial, *Cmcm*. Le plomb occupe les sites trigonaux prismatiques *Me*1 dans les plans de macle des mailles élémentaires; les sites octaédriques *Me*2 et *Me*3 de la couche centrale de la structure contiennent Pb (environ 80%) et Bi (20%). Le site octaédrique semi-marginal *Me*5 contient le Bi. Le remplacement par l'Ag affecte le site octaédrique marginal *Me*4 (0.657 Ag + 0.343 Bi). Les écarts structuraux de l'archétype PbS sont mineurs au sein des couches; les plus importants impliquent les sites *Me*4 et *Me*5.

(Traduit par la Rédaction)

Mots-clés: heyrovskyite, remplacement par Ag et Bi, structure cristalline.

INTRODUCTION

Heyrovskyite, $Pb_{5.16}(Ag,Cu)_{0.24}Bi_{2.48}S_9$, was described by Klomínský *et al.* (1971) as a natural analogue of Phase II, $Pb_{6-x}Bi_{2+2x/3}S_9$, synthesized and characterized by Otto & Strunz (1968). This characterization included a proposal of the schematic structure, which was confirmed and refined by Takéuchi & Takagi (1974) in their determination of the crystal structure of natural heyrovskyite, $Pb_{5.40}Ag_{0.18}Bi_{2.42}S_9$.

Considerable evidence has accumulated that heyrovskyite can contain appreciable amounts of silver, in the form of a coupled substitution Ag + Bi = 2Pb (Czamanske & Hall 1975). In 1977, Makovicky & Karup-Møller (1977b) defined heyrovskyite as the seventh member of the lillianite homologous series, $Pb_{N-1-2x}Bi_{2+x}Ag_xS_{N+2}$, where *N* is the order of the homologue, and *x* is the coefficient of Ag and Bi substitution, with the maximum value $x_{max} = (N-2)/2$. For heyrovskyite, the range of substitution can be conveniently expressed as the percentage of the maximally substituted end-member, $PbBi_{4.5}Ag_{2.5}S_9$ (defined as $^{Ag,Bi}Hey_{100}$, but generally used in the simplified form Hey_{100}), and the complementary percentage of the unsubstituted end-member, $Pb_6Bi_2S_9$, denoted as ^{Pb}Hey in the original paper (and usually omitted in the symbols used today). Thus, the material of Czamanske & Hall (1975) from Darwin, California, represents a selenian Ag- and Bi-substituted heyrovskyite Hey_{58-66}, whereas the heyrovskyite from Castelgar, British Columbia is Hey_{71} (Karup-Møller & Makovicky 1981), and the present material from La Roche Balue is Hey_{43-54} (Moëlo *et al.* 1987). The original heyrovskyite from Hurky, Bohemia, corresponds to Hey_{8-19} (Klomínský *et al.* 1971), and that from the Yakuki mine, Fukushima, Japan, is Hey_{10} (Karup-Møller 1977).

The full extent of heyrovskyite solid-solution toward Hey_{100} is not known. Synthetic studies do not seem to contribute unambiguously to this problem. Hoda & Chang (1975) found no solubility of Ag in heyrovskyite at 400°C and 500°C, whereas Chang *et al.* (1988), in their study of the system Ag_2S–Cu_2S–PbS–Bi_2S_3 at 500°C, reported a field of solid solution between Ag- and Cu-free heyrovskyite and a substituted heyrovskyite with a composition that shows Cu contents higher than Ag contents. However, the end-member composition they gave, $Ag_{0.76}Cu_{1.31}Pb_{3.18}Bi_{3.18}S_9$, represents a lillianite homologue with $N = 14.2$ and 61% substitution. The order N is too high even if we assume the presence of Cu-for-Bi substitution, which could cause excessively high apparent values of N; obviously, more analytical work is needed on these synthetic products.

Possible compositional gaps in the heyrovskyite solid-solution at geologically interesting temperatures are not known, and all crystallographically studied cases display the same X-ray symmetry. The electron-microprobe data of Pattrick (1984) from Corrie Buie, Scotland (Hey_{30}), and unpublished data of W.H. Paar and collaborators on material from the Alps (oral comm.), have narrowed considerably the previously existing compositional gap between Hey_{50} and the original material (and that of Paar *et al.* 1980), which show a limited extent of Ag and Bi substitution. No compositional pairs or exsolution phenomena, which would suggest a compositional gap, have been found as yet. On the other hand, the above maximal extent of substitution, slightly above 70%, has not been exceeded to date.

Unsubstituted synthetic heyrovskyite ("Phase II"), $Pb_{6-x}Bi_{2+2x/3}S_9$, displays a compositional field toward values richer in Bi (Salanci & Moh 1969). The presence of cation vacancies has been postulated for Phase II by Otto & Strunz (1968), but this claim still awaits crystallographic confirmation (see Makovicky 1977). The distribution of Ag atoms and of the associated "additional" Bi atoms in the structure has not been studied either. The distribution of Pb and Bi in the only heyrovskyite structure published, that of $Pb_{5.40}Ag_{0.18}Bi_{2.42}S_9$ ($Hey_{7.8}$) from Yakuki mine, Japan by Takéuchi & Takagi (1974), is assumed to be largely statistical. Pb occupies the central zones of slabs (311) PbS, and mixed occupancies occur in the marginal zones of these slabs, closer to the planes of unit-cell twinning; an assumption was made that Ag atoms occur in the marginal areas as well. It is quite possible that the crystal structure of heyrovskyite, with its large PbS-like areas, is stable only if Pb and Bi are statistically distributed in quasi-octahedral coordination. Heyrovskyite is presumed to be a high-temperature phase that is unstable at lower temperature (Klomínský *et al.* 1971), combined with higher sulfur fugacities (Salanci & Moh 1969). Therefore, the discovery of aschamalmite, $Pb_{5.9}Bi_{2.1}S_9$ (Mumme *et al.* 1983), which shows evidence of cation ordering and ensuing distortion of the heyrovskyite-like anion framework, to a monoclinic symmetry, opens a new, as yet unexplored possibility of Pb–Bi cation ordering in lillianite homologues in the absence of Ag and Bi substitution as a possible means of stabilization at lower temperatures.

For at least a narrow range of heyrovskyite compositions, $\sim Pb_{2.5}Ag_{1.8}Bi_{3.8}S_9(\sim Hey_{71})$ (Karup-Møller & Makovicky 1981), a monoclinic dimorph, eskimoite, exists ($N_1;N_2 = 5;9$ instead of $N_1;N_2 = 7;7$ where N_1 and N_2 are the order parameters for a pair of adjacent, alternating PbS-like slabs) with the compositions $\sim Cu_{0.1}Pb_{2.4-2.6}Ag_{1.8-1.7}Bi_{3.8-3.7}S_9$ (Esk_{71-68}) (Makovicky & Karup-Møller 1977b). Differences in pressure–temperature conditions, kinetics of crystallization, or minor-element concentrations may lie behind this dimorphism; nothing is known about these factors at present. Eskimoite (unanalyzed) overgrows in trace amounts heyrovskyite(50) from La Roche Balue; disordered material with both heyrovskyite and eskimoite domains present, besides disordered portions, was found by one of the authors (W.G.M.) in NMNH specimen 127023 ("neyite" from Alice Arm, British Columbia, kindly provided for study by Dr J.S. White, Smithsonian Institute, Washington). For many occurrences, *e.g.*, Corrie Buie (Pattrick 1984), only microprobe data exist, so that material can only be assumed to be heyrovskyite and not eskimoite.

In the current program of study of the heyrovskyite solid-solution, we intend to perform crystal-structure refinements on several members: synthetic Phase II, natural low-Ag heyrovskyite, aschamalmite and selected samples of Ag- and Bi-substituted heyrovskyite. These studies should elucidate the distribution of cation vacancies, Pb–Bi ordering or disorder, the cation sites influenced by Ag and Bi substitution, as well as deformations of the ideal heyrovskyite framework connected with these phenomena. Furthermore, the changes in the bonding scheme of Bi as a result of substitution processes will be examined.

As the first contribution in this series, the crystal structure of Ag- and Bi-substituted heyrovskyite from La Roche Balue (Loire Valley, France) is described.

TABLE 1. CHEMICAL AND CRYSTALLOGRAPHIC DATA FOR HEYROVSKYITE(50)

Space group:	Cmcm	Radiation	MoKα
Unit cell:	a = 4.110(1) Å b = 13.600(3) Å c = 30.485(12) Å	μ:	657
		No. of reflections:	1138 [341 with I ≥ 3σ(I)]
Z:	4		
Chemical formula:	$Pb_{3.67}Cd_{0.05}Ag_{1.15}Bi_{3.13}S_{9.19}$	Structural formula:	$Pb_{3.36}Ag_{1.32}Bi_{3.32}S_9$

EXPERIMENTAL

The analyzed crystals have been extracted from a polished section used in the study of the W–As–(Pb,Bi,Ag) mineralization at La Roche Balue, west of Nantes, France by Moëlo *et al.* (1987). At this deposit, heyrovskyite (with traces of eskimoite) has been deposited together with quartz, scheelite, arsenopyrite, gustavite, vikingite and galena at 350–400°C. The average of five microprobe analyses, closely spaced within the area Hey_{43}–Hey_{54} of the phase diagram Pb_2S_2–Bi_2S_3–Ag_2S, gives (in wt.%): Pb 41.24, Cd 0.27, Ag 6.73, Bi 35.52, Sb 0.04, S 15.96, Se 0.03, total 99.79, giving a formula $Pb_{3.67}Cd_{0.05}Ag_{1.15}Bi_{3.13}S_{9.19}$ (Moëlo *et al.* 1987, Table III), which corresponds to $N = 6.97$ and 44.6% Ag- and Bi-substitution if Cd^{2+} is added to Pb^{2+}.

A Weissenberg study of heyrovskyite crystals gave starting unit-cell parameters values: *a* 13.61(1), *b* 30.47(2) and *c* 4.08(2) Å. From extinction rules and relationships among X-ray intensities, the applicable space-groups are *Bbmm* and *Bb*2_1*m* (Moëlo *et al.* 1987).

X-ray intensities were collected on an Enraf–Nonius CAD–4F diffractometer at the University of Melbourne with graphite-monochromated Mo radiation (λ 0.710687 A) using the ω/2θ mode. A total of 1988 measured reflections were merged into 1138 unique reflections (agreement factor $R_{int} = \Sigma|I_{obs} - I_{aver}| \,/\, \Sigma\, I_{obs}$ is equal to 4.7%). Application of absorption corrections for the crystal examined (0.04 × 0.10 × 0.01 mm) did not improve the subsequent refinement; therefore, no absorption correction for the final set of data was undertaken. Unit-cell parameters were refined using 25 reflections.

The refined unit-cell parameters and the space group used are listed in Table 1. The crystal structure of heyrovskyite solid-solution approximates closely a PbS-like array twinned periodically on $(311)_{PbS}$ (Otto & Strunz 1968, Takéuchi & Takagi 1974, Makovicky & Karup-Møller 1977a). Therefore, its weighted reciprocal lattice displays strong- to medium-intensity reflections at the loci of nodes of the two "twin-related" PbS-like reciprocal sublattices, and weak to very weak reflections for the majority of the true-lattice nodes (Fig. 4 in Makovicky & Karup-Møller 1977a). In this situation, all 1138 unique reflections were used throughout the refinement except for the final cycle, where only 341 reflections with the cut-off value I ≥ 3σ (I) were used.

Initial positional parameters used for the refinement were those given for $Pb_{5.4}Ag_{0.4}Bi_{2.2}S_9$ by Takéuchi & Takagi (1974). The program set SHELX76 (Sheldrick 1976) was used for the refinement, and corrections for anomalous dispersion were included. Fourier and difference-Fourier maps were used in the search for possible Ag positions outside those occupied in Ag-poor heyrovskyite; suspect peaks have all been tried in the least-squares refinement. No additional positions for cations (or anions) have been found.

In order to reduce the relative weight of the strongest reflections, the weights *w* used in the refinement were taken to be inversely proportional to $\sigma^2(F) + 0.001F^2$. This weighting scheme equalized substantially the distribution of $w(\Delta F)^2$ over the F/F_{max} categories. In the final cycles, for 1138 reflections, an approximately even distribution of $w(\Delta F)^2$ for all reflections $F/F_{max} > 0.04$ was achieved ($R = 0.20$, weighted $R = 0.10$), which was considered justified in light of the large σ(I)/I for the very weak reflections. In the final step of the refinement, a very even distribution of $w(\Delta F)^2$ over the entire range F/F_{max} was achieved, except for the sixty strongest reflections, which were assigned values of $w(\Delta F)^2$ larger by about 1/3 than the rest. This difference is considered negligible because the final agreement factor *R* for 341 nonequivalent observed reflections is 0.062, compared to weighted $R_w = 0.060$. Anisotropic temperature-factors were refined for metal atoms; only isotropic temperature-factors were used for sulfur. Atomic parameters are given in Table 2, RMS displacements for metal atoms in Table 3, and interatomic angles and distances in Table 4. Tables of structure factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Canada K1A 0S2.

TABLE 2. ATOMIC COORDINATES, OCCUPANCIES, AND U VALUES (Å^2) FOR HEYROVSKYITE(50) WITH THEIR STANDARD DEVIATIONS

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Me1	.0000	.4028	.2500	.0150	.0262	.0478	.0000	.0000	.0000
Pb	.0000	.0007	.0000	.0041	.0044	.0061	.0000	.0000	.0000
Me2	.0000	.5000	.0000	.0092	.0153	.0324	.0005	.0000	.0000
(1)	.0000	.0000	.0000	.0033	.0036	.0047	.0030	.0000	.0000
Me3	.0000	.2284	.0599	.0099	.0116	.0370	.0020	.0000	.0000
(1)	.0000	.0004	.0002	.0022	.0020	.0032	.0020	.0000	.0000
Me4	.5000	.1729	.1778	.0098	.0243	.0176	.0091	.0000	.0000
(2)	.0000	.0006	.0002	.0040	.0046	.0048	.0031	.0000	.0000
Me5	.5000	.4544	.1217	.0114	.0146	.0185	.0014	.0000	.0000
Bi	.0000	.0004	.0002	.0025	.0027	.0029	.0020	.0000	.0000
S 1	.0000	.0433	.1950	.0196					
	.0000	.0027	.0011	.0069					
S 2	.5000	.0888	.0853	.0217					
	.0000	.0024	.0013	.0079					
S 3	.5000	.2567	.2500	.0328					
	.0000	.0039	.0000	.0133					
S 4	.0000	.3273	.1501	.0165					
	.0000	.0022	.0011	.0065					
S 5	.5000	.3590	.0251	.0102					
	.0000	.0021	.0010	.0055					

(1) Occupancy 0.80 Pb + 0.20 Bi.
(2) Occupancy refined as 0.657 ± .027 Ag while constrained as Ag + Bi = 1.0.

TABLE 4. BOND LENGTHS (Å) AND ANGLES (°) IN HEYROVSKYITE(50)

Me1	S3	2.858 × 2	S3-Me1-S3	91.92
Me1	S1	3.269 × 4	S1-Me1-S1	77.90
Me1	S4	3.214 × 2	S1-Me1-S1	61.72
			S1-Me1-S3	87.39
			S4-Me1-S4	142.73
			S1-Me1-S4	72.59
			S3-Me1-S4	77.17
Me2	S2	2.867 × 2	S5-Me2-S5	89.73
Me2	S5	2.913 × 4	S2-Me2-S5	92.24
Me3	S5	2.916 × 2	S5-Me3-S5	89.61
Me3	S2	2.903 × 2	S2-Me3-S2	90.12
Me3	S4	3.061	S4-Me3-S5	178.58
Me3	S5	2.851	S4-Me3-S5	93.39
			S5-Me3-S5	85.60
			S4-Me3-S2	92.74
			S2-Me3-S5	88.27
Me4	S4	3.057 × 2	S4-Me4-S4	84.47
Me4	S1	2.758 × 2	S1-Me4-S1	96.35
Me4	S3	2.479	S2-Me4-S3	174.70
Me4	S2	3.043	S3-Me4-S4	85.95
			S2-Me4-S4	90.13
			S3-Me4-S1	97.18
			S2-Me4-S1	86.33
Me5	S2	2.966 × 2	S2-Me5-S2	87.72
Me5	S4	2.821 × 2	S4-Me5-S4	93.49
Me5	S1	2.541	S5-Me5-S1	175.36
Me5	S5	3.218	S2-Me5-S1	92.05
			S2-Me5-S5	84.61
			S4-Me5-S1	91.24
			S4-Me5-S5	91.94

Estimated standard deviation for bond distances is 0.030 Å; for bond angles 0.9°.

DESCRIPTION OF THE STRUCTURE

The crystal structure of heyrovskyite (Fig. 1) has five independent cation sites, four of which are octahedral or quasi-octahedral; the fifth site represents a bicapped trigonal coordination prism. The numbering scheme of the sites used here is that used by Takéuchi & Takagi (1974) for Ag-poor heyrovskyite.

The bicapped coordination prism (site *Me*1) is situated on the planes (311) of unit-cell twinning of the archetypal PbS structure. It is surrounded by the coordination polyhedra of *Me*4, in which the Ag–Bi substitution in heyrovskyite(50) takes place. This substitution appears to influence the position of S4 atoms, which cap the prism so that the distance *Me*1–S4 is equal to 3.21 Å instead of 3.48 Å observed by Takéuchi & Takagi (1974) in the Ag-poor structure. It also influences the S3 atoms, which acquire high "temperature-factors", *i.e.*, positional disorder. The RMS displacement for *Me*1 is appreciable in the direction perpendicular to vertical mirror planes, similar to the results of Takéuchi & Takagi (1974) for heyrovskyite and to those of Takagi & Takéuchi (1972) for lillianite.

TABLE 3. THERMAL AND DISORDER ELLIPSOIDS IN HEYROVSKYITE(50)

	Angle to a	Angle to b	Angle to c	RMS displacement
Me1	180	90	90	0.1225
	90	180	90	0.1622
	90	90	0	0.2186
Me2	180	90	90	0.0959
	90	1.6	88.4	0.1236
	90	91.7	1.7	0.1800
Me3	180	90	90	0.0995
	90	175.6	85.6	0.1070
	90	85.5	4.5	0.1928
Me4	180	90	90	0.0990
	90	124.9	34.9	0.1061
	90	34.9	55.1	0.1751
Me5	180	90	90	0.1068
	90	162.2	72.2	0.1190
	90	72.2	17.8	0.1377

In $Pb_{5.4}Ag_{0.4}Bi_{2.2}S_9$ (Takéuchi & Takagi 1974), the central zone of the PbS-like slab is occupied by lead atoms; the averages of six *Me*–S distances are 2.94 A and 2.97 A for *Me*2 and *Me*3, respectively. The situation is altered for both sites in the present structure of heyrovskyite(50). The respective averages are smaller, 2.90 Å for *Me*2 and 2.93 Å for *Me*3. The shortest *Me*–S distances are appreciably shorter as well: 2.87(× 2) Å for *Me*2 and 2.85(× 1) Å for *Me*3–S5. Averages of three shortest distances are 2.88 Å for *Me*2 and 2.89 Å for *Me*3. Therefore, besides accommodating potentially the trace amounts of Cd detected in microprobe analyses (this assignment can be disputed), these positions display partial Bi replacement for Pb. The conclusion is supported by higher appropriate mean-square displacements (Table 3) and a higher "temperature-factor" of S2. Such a replacement brings about a reduction in the size of *Me*2 and

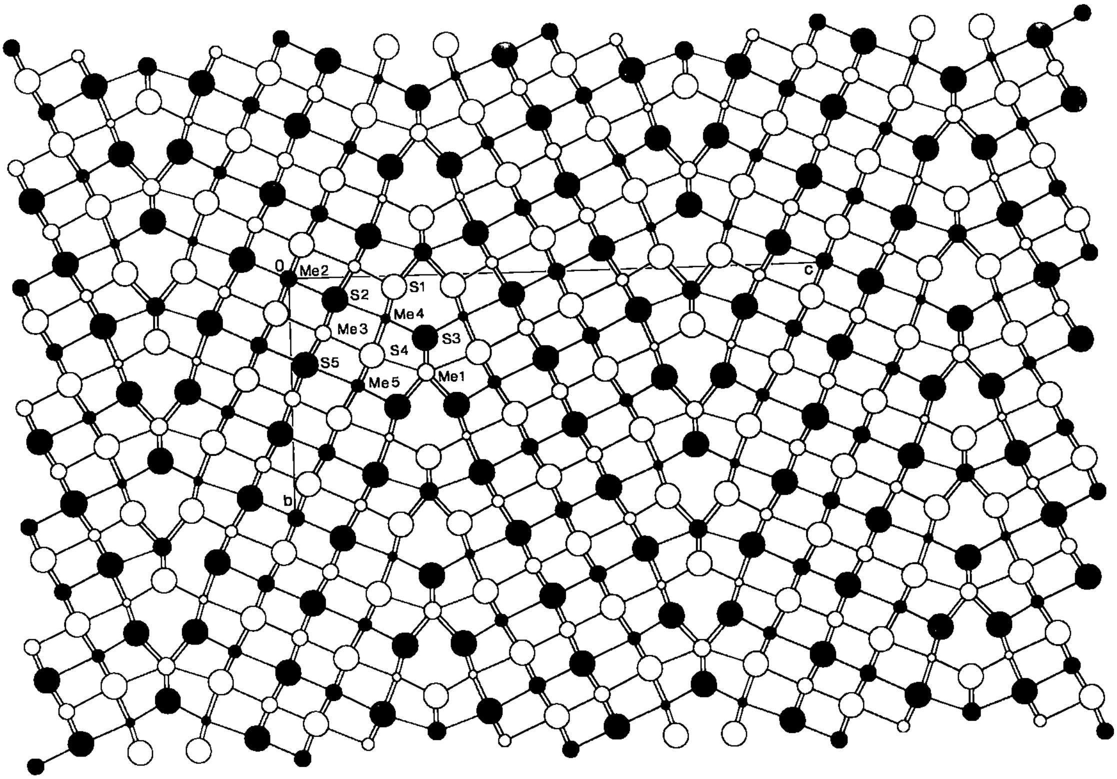

Fig. 1. The crystal structure of Ag-Bi bearing heyrovskyite. In the order of decreasing size, the circles denote atoms of S, Pb (and $Pb_{0.8}Bi_{0.2}$), Bi, and (Ag,Bi). Empty circles denote atoms at $x = 0$, filled circles atoms at $x = 1/2$.

*Me*3 coordination octahedra and may be necessary to alleviate potential misfit.

Toward the slab margins, the next cation site, with the coordination octahedron still wedged between octahedra and the trigonal prismatic site, has been denoted *Me*5 by Takéuchi & Takagi (1974). The average of three shortest distances for this site is 2.73 Å, the shortest (*Me*5–S1) distance is 2.54 Å, whereas the average for the entire coordination octahedron, 2.89 Å, is similar to those of *Me*2 and *Me*3. It represents a pure Bi site, situated within the cluster of pure-Bi sites in the plot of bond-distance ratios devised by Hummel & Armbruster (1987, Fig. 1).

According to the results of the present refinement, all detectable Ag substitution takes place in the site *Me*4, which is the closest to the margin of the PbS-like slab. Only a single maximum was found, refined as 0.657 Ag + 0.343 Bi. Its RMS displacement values are not markedly higher than those of the other atoms (Table 3); the principal displacement occurs along the line of the largest (*Me*4–S2 = 3.04 Å) and shortest (*Me*4–S3 = 2.48 Å) bonds in the coordination quasi-octahedron (Table 4). As mentioned above, S3 displays the largest displacements of all S atoms in the structure, undoubtedly owing to two different cation coordinations in the site *Me*4.

If we select a similarly situated *Me*5 (Bi) from the crystal structure of unsubstituted benjaminite (Herbert & Mumme 1981) as one mixing component for the combined *Me*4 site in heyrovskyite(50), and that of Ag in trechmannite (Matsumoto & Nowacki 1969) as the other component, and weigh the observed maximum in terms of products of occupancies with respective atomic numbers (Makovicky & Nørrestam 1985) [*i.e.*, (0.657 × 47 + 0.343 × 83)/130], the observed position represents, in terms of electron density, 52% Ag and 48% Bi. By multiplying the model *Me*–S distances defined above with these "weighted percentages", we can build a composite model coordination polyhedron and compare it with the observed one. The calculated *Me*4–S4 distance is 3.03 Å, observed 3.04 Å; *Me*4–S1 calc. 2.72 Å, obs. 2.76 Å; *Me*4–S3 calc. 2.63 Å, obs. 2.48 Å; and *Me*4–S2 calc. 2.92 Å, obs. 3.04 Å. Taking into account a rather arbitrary choice of the Ag example, the agreement is satisfactory. On the one hand, rather varied Ag coordinations [3 + 1] are given in the literature, and on the other hand S2 and S3 have large displacement parameters, and *Me*4 atoms show anisotropic displacement along the S2–S3 line. With only averages of the three shortest bonds (2.77 Å for Bi 5 in benjaminite and 2.62 Å for Ag in trechmannite), their weighted average, 2.69 Å, is close to the observed one, 2.67 Å.

The Ag/Bi ratio in the *Me*4 site determines the chemical composition of the analyzed crystal as $Pb_{6.74}Ag_{2.63}Bi_{6.63}S_{18}$, assuming that the traces of Cd are located elsewhere and added in the formula to Pb. Bi from the *Me*5 and *Me*4 sites add up to 5.37 Bi. The remaining 1.26 Bi per formula is distributed among the two *Me*2 and four *Me*3 sites; *Me*1 is assumed to be occupied entirely by Pb. This assumption gives an average occupancy for an octahedron from the central slab portions (*Me*2 or *Me*3) of 79% Pb and 21% Bi, in good quantitative agreement with their *Me*–S distances. Least-squares refinement using these Pb/Bi ratios did not give results that differ significantly from those obtained using pure Pb in these positions.

The extent of Ag- and Bi-substitution derived from the present determination of the crystal structure is 52.6% if the traces of Cd occur in Me^{2+} sites. Comparing this value with the percentage of substitution determined from the electron-microprobe analyses, equal to 45% for the average of all crystals analyzed, a Ag- and Bi-substitution of 50% represents a good estimate for the material studied.

The crystal structure of heyrovskyite(50) is similar to that of Ag-poor heyrovskyite studied by Takéuchi & Takagi (1974) and deviates only a little from the regular PbS archetype. Average sizes of all coordination octahedra are very consistent, except for the marginal *Me*4 site, with an average bond-length of only 2.86 Å. However, without the shortest outwardly directed bond, *Me*4–S3, this polyhedron attains the average bond-length of 2.93 Å. In heyrovskyite(50), as has been generally observed for sulfosalts (Makovicky 1981), for those bond directions that impinge at larger angles upon slab boundaries, an appreciable separation into outward, shorter bonds and inward, longer distances takes place (Table 5), with lone pairs of electrons of (primarily) Bi playing a stereochemical role. Similar separation for bonds running at low angles to the slab boundaries is much less pronounced (Table 5). Further geometrical and structural correlations are deferred until our analysis of the entire span of heyrovskyite structures is completed.

TABLE 5. ME-S BOND DISTANCE SEPARATIONS FOR MARGINAL COORDINATION POLYHEDRA IN HEYROVSKYITE(50)

Atom	Bonds at high angle to slab boundary	Direction relative to slab edge	Bonds at low angle to slab boundary
Me4	S3 2.479 × 1	outward pointing	S1 2.758 × 2
	S2 3.043 × 1	inward pointing	S4 3.057 × 2
Me5	S1 2.541 × 1	outward pointing	S4 2.821 × 2
	S5 3.218 × 1	inward pointing	S2 2.966 × 2

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