THE CRYSTAL STRUCTURE OF NEYITE, $Ag_2Cu_6Pb_{25}Bi_{26}S_{68}$

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ABSTRACT

The crystal structure of type neyite from Alice Arm, British Columbia, was determined from single-crystal X-ray diffraction data with the agreement factors $R_1 = 0.037$ (0.072 for all) and $\omega R_2 = 0.078$. The structural formula supported by the new electron-microprobe data is $AgCu_3Pb_{12.5}Bi_{13}S_{34}$ ($Z = 4$); the lattice parameters are a 37.527(6), b 4.0705(6), c 43.701(7) Å, β 108.801(2)°, space group $C2/m$. The structure contains 26 independent large-cation polyhedra, one Ag site and three Cu sites. It can be described as an alternation of triple-octahedron $(111)_{PbS}$-like layers with $(100)_{PbS}$-like layers two atomic planes thick. Both sets of layers are (a) sheared, giving rise to tetrahedral Cu sites, and (b) truncated by wavy PbS-like layers $(001)_{ney}$, three atomic planes thick. The resulting structure can be described as a box-work of $(100)_{PbS}$-like layers enclosing $(111)_{PbS}$-like fragments. Several hypothetical structures based on the neyite principle have been derived.

Keywords: neyite, crystal structure, sulfosalt, Alice Arm, British Columbia.

SOMMAIRE

Nous avons déterminé la structure cristalline de la neyite provenant de la localité-type, Alice Arm, en Colombie-Britannique, à partir de données en diffraction X prélevées sur cristal unique, jusqu'à un résidu $R_1 = 0.037$ (0.072 pour toutes les réflexions) et $\omega R_2 = 0.078$. La formule structurale qui répond aux nouvelles données de microsonde électronique est $AgCu_3Pb_{12.5}Bi_{13}S_{34}$ ($Z = 4$); les paramètres réticulaires sont a 37.527(6), b 4.0705(6), c 43.701(7) Å, β 108.801(2)°, groupe spatial $C2/m$. La structure contient 26 polyèdres contenant un cation à large rayon, un site Ag et trois sites occupés par le Cu. On peut la décrire en termes d'une alternance de couches ressemblant à $(111)_{PbS}$ à multiples de trois octaèdres et des couches ressemblant à $(100)_{PbS}$ ayant une épaisseur de deux plans d'atomes. Les deux séries de couches sont (a) cisaillées, ce qui donne des sites tétraédriques occupés par le Cu, et (b) terminées par des couches ondulantes ressemblant au PbS le long de $(001)_{ney}$, d'une épaisseur de trois plans d'atomes. On décrit la structure qui en résulte comme un agencement en boîtes de couches ressemblant à $(100)_{PbS}$ et renfermant des fragments de couches rappelant $(111)_{PbS}$. Nous dérivons plusieurs structures hypothétiques à partir du principe de la neyite.

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Mots-clés: neyite, structure cristalline, sulfosel, Alice Arm, Colombie-Britannique.

INTRODUCTION

Neyite was described in 1969 by Drummond *et al.* as a new sulfosalt from Alice Arm, British Columbia, with a composition $(Cu,Ag)_2Pb_7Bi_6S_{17}$ and a remarkably large unit-cell: a 37.5, b 4.07, c 41.6 Å, β 96.8°, space group $C2/m$. In addition to an occurrence at the Alaska mine, Colorado (Karup-Møller & Makovicky 1992), neyite was also reported from Benson, Arizona (Gaines *et al.* 1997), Chishawasha, Zimbabwe (Kalbskopf & Ncube 1983), and Vale das Gatas, Portu-gal (Gaspar & Bowles 1985), and it was recently found by us at Felbertal, Austria (unpubl. data). Still, its crystal structure remained unknown, and its chemical formula, uncertain.

The current determination of the crystal structure of neyite was performed on a crystal extracted from the type specimen (National Mineral Collection of Canada, No. 68067), collected in the Lime Creek BC molybdenum mine, at Alice Arm. The sample studied was kindly provided by Mr. A.C. Roberts, of the Geological Survey of Canada, Ottawa.

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Experimental

The chemical composition of the type neyite was determined by analyzing the other half of the elongate crystal used for structure analysis. It was embedded in epoxy and polished for a wavelength-dispersion electron-microprobe analysis. The JEOL–8600 apparatus at the University of Salzburg was used. It is equipped with Link EXL detector used with an on-line ZAF–4 correction program. Experimental conditions and analytical results are summarized in Table 1.

The electron-microprobe results differ significantly from the original chemical data reported in the contents of Pb, Bi and, to a lesser degree, sulfur. However, the crystallographic data confirm the identity of the crystal investigated as neyite, *i.e.*, we assume that there was a small admixture of other sulfosalts in the bulk material prepared for the standard chemical analysis by Drummond *et al.* (1969). Inspection of Table 1 reveals that the new composition of type-locality neyite is close to the ideal formula $Ag_2Cu_6Pb_{25}Bi_{26}S_{68}$. Without considering Ag and Bi substituting for Pb, this large structure requires 26 (Bi + Pb) sites, one site occupied by silver and three distinct Cu sites in an asymmetric unit. The amount of Ag in neyite is not fixed at two atoms per formula unit (*apfu*); in the neyite from Felbertal, it reaches only 1 *apfu*, whereas in the material from the Alaska mine, Colorado, it attains 4 *apfu* Ag. Both samples have crystallographic properties identical to those of the type neyite.

A crystal with a needle-like shape and dimensions $0.15 \times 0.035 \times 0.015$ mm was measured on a Bruker–AXS four-circle diffractometer equipped with CCD 1000K area detector (6.25 cm × 6.25 cm active detection area, 512 × 512 pixels) and a flat graphite monochromator using $MoK\alpha$ radiation from a fine-focus sealed X-ray tube. The distance from sample to detector was 6 cm. We made 1800 exposures 0.3° apart, with measurement time 45 s in each case. A total of 19063 reflections with 2θ between 4° and 53° and Miller indices covering the range $\overline{45} \leq h \leq 43$, $\overline{5} \leq k \leq 4$, $\overline{49} \leq l \leq 53$ were measured, giving 6809 unique ones, of which 4324 with $I > 2\sigma_I$ were classified as observed. The SMART system of programs was used for unit-cell determination and data collection, SAINT+ for the calculation of integrated intensities and lattice refinement, and SHELXTL for the structure solution and refinement (all Bruker–AXS products). For the empirical absorption-correction based on reflection measurements at different azimuthal angles, and measurements of equivalent reflections, the program XPREP from the SHELXTL package was used. It yielded a merging R_{INT} factor (for equivalent reflections) of 0.0551 compared to 0.1454 before the absorption correction. Minimum and maximum transmission factors were 0.0140 and 0.0558, respectively. The only systematic absences were those of a *C*-centered Bravais lattice. In accordance with the monoclinic symmetry of lattice and intensity statistics ($|E*E - 1| = 1.145$), the centrosymmetric $C2/m$ space group was chosen. The positions of the metal atoms were found by direct methods. In subsequent refinements, the positions of S atoms were deduced from the difference-Fourier syntheses.

Owing to a very small difference in their atomic number, the distribution of Pb and Bi among the heavy atom positions cannot be derived from conventional diffraction measurements and had to be inferred on the basis of crystal-chemical considerations. According to the coordination characteristics, some heavy-atom positions were assumed to be filled with Pb, some others, with Bi, and others to represent mixed Pb,Bi occupancies. During the refinement, each position was assigned a Pb or a Bi scattering factor according to its coordination characteristics. As evidence of the incorporation of Ag at some Pb,Bi positions was also found, the occupancies of all heavy cation sites were released during the refinement. Only for four positions was less than full occupancy registered, and for them also, the partial occupancy of Ag was refined. The distribution of Pb and Bi over the mixed-occupancy positions was based on specific crystal-chemical calculations described later in the text, and was completed after the refinement. After the final refinement based on F^2 with anisotropic displacement-factors for all atoms, the highest residual maximum and minimum were 2.04 $e/Å^3$ and –2.01 $e/Å^3$, respectively. The reliability factors obtained are: $\Sigma(wF_c^2 - wF_o^2)/<wF_c^2> = 0.078$; $\Sigma(F_c - F_o)/<F_c> = 0.037$ (for $F_o > 4\sigma_{Fo}$), (0.072 for all); goodness of fit: $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2} = 0.881$ for *m* observations and *n* parameters with the weighting factors $w = 1/\{\sigma_{F_0}^2 + [0.0244(Max(F_o^2,0) + 2F_c^2)/3]\}$.

TABLE 1. ELECTRON-MICROPROBE DATA FOR NEYITE FROM ALICE ARM, BRITISH COLUMBIA

	Measured[6]					Calculated	
	wt.%[1]	at.%[1]	wt.%[2]	at.%[2]	wt.%[3]	wt.%[4]	wt.%[5]
Bi	40.4(1)	20.5(1)	40.4(1)	20.1(1)	36.62	38.7	40.6
Pb	37.9(1)	19.3(1)	37.8(2)	19.0(1)	41.76	41.5	38.7
Cu	2.90(3)	4.84(5)	2.91(2)	4.77(4)	2.84	2.83	2.85
Ag	1.58(3)	1.55(3)	1.56(6)	1.50(5)	1.52	0.8	1.61
Sb	0.10(3)	0.08(3)	0.11(2)	0.10(2)	-	-	-
Cd	0.30(6)	0.28(5)	0.31(6)	0.28(6)	-	-	-
S	16.2(1)	53.5(1)	16.7(1)	54.2(2)	15.65	16.2	16.3
Total	99.4(3)		99.8(3)			98.39	100.0	100.0

Analytical conditions: accelerating voltage 25 kV, sample current 35 nA, analytical time 20 s. Wavelength and standards: Bi*L*α (Bi₂S₃), Sb*L*α (Sb₂S₃), Pb*L*α (PbS), Cd*L*α (CdTe), Ag*L*α (Ag), Cu*K*α (CuFeS₂); S*K*α; sulfur was alternatively calculated using (1) Bi₂S₃ and (2) PbS as reference standard.
(3) Chemical composition of type-locality neyite from analysis by H.V. Sharples in Drummond *et al.* (1969).
(4) Chemical composition expected for the model formula AgCu₆Pb₂₇Bi₂₅S₆₈.
(5) Chemical composition expected for the model formula Ag₂Cu₆Pb₂₅Bi₂₆S₆₈.
(6) The mean analysis gives Ag₁.₉Cu₆.₁Pb₂₄.₃Cd₀.₄Bi₂₅.₈Sb₀.₁S₆₈.₄ calculated for 127 atoms.

TABLE 2. CRYSTAL DATA FOR NEYITE

Formula:	AgCu₃Pb₁₂.₅Bi₁₃S₃₄ (Z = 4)
Formula:	$AgCu_3Pb_{12.5}Bi_{13}S_{34}$ ($Z = 4$)
Measurement temperature:	298 K
Space group:	$C2/m$ (No. 12)
Unit-cell parameters:	
a	37.527(6) Å
b	4.0705(6) Å
c	43.701(7) Å
β	108.801(2)°
V_{uc} (refined from 4523 reflections with I>10σ$_I$)	6319(3) Å³
ρ_c	7.037 g/cm³
μ	71.62 mm⁻¹

The results of the refinement are represented in Tables 2 and 3. Tables of structure factors and interatomic distances and angles may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Besides the $C2/m$ unit cell with β 108.8° and c 43.70 Å used here (Table 2), an $F2/m$ cell can be chosen, with β 96.5° and c/2 equal to 41.56 Å. Such a choice explains the difference between the current unit-cell data and those of Drummond *et al.* (1969), who overlooked the F-centering, mistaking it for C-centering.

DESCRIPTION OF THE STRUCTURE

Atom positions

The structure of neyite contains 26 independent large cation polyhedra, one silver position and three copper sites, together with 34 independent sulfur sites (Figs. 1, 2, Table 3). It is therefore one of the largest sulfosalt structures, alongside izoklakeite (Makovicky & Mumme 1986, Armbruster & Hummel 1987), hodrushite (Kupčík & Makovicky 1968), weibullite (Mumme 1980), and scainiite (Moëlo *et al.* 2000).

Over 50% of large cation positions are mixed-occupancy positions (Figs. 1, 2, Table 4); positions occupied by Ag and Cu do not indicate mixed occupancies. These characteristics are also reflected in the interatomic distances and other coordination parameters (Table 4).

The coordination volumes for cations of coordination number (CN) 6 are closely related to the proportion of Pb and Bi in the mixed-occupancy sites, a fact used in the occupancy analysis below. Volume-based distortions ν (Makovicky & Balić-Žunić 1998) calculated from comparisons with ideal octahedra deviate by generally less than 2% of the polyhedral volumes, with the exception of Me21 and Ag1. As usual for sulfosalts, Bi shows in general larger eccentricity Δ than Pb in the same type of coordination. CN7 polyhedra are close to the type described as "split octahedron" (Makovicky & Balić-Žunić 1998), as witnessed by their volume-based distortions (calculated from the comparison with an ideal pentagonal bipyramid as the CN7 polyhedron with the maximum effective volume). For the ideal "split

octahedron", ν is equal to 0.1333, whereas for an ideal monocapped trigonal prism, ν is equal to 0.1590 (Makovicky & Balić-Žunić 1998).

The structure of neyite is best described by referring to building units larger than individual polyhedra and to the structure of PbS as an archetypal structure.

Polyhedra and their aggregates

As is the case with many Pb–Bi sulfosalts, the fundamental features of the neyite structure can be described by referring to the modules cut out of the archetypal PbS structure. Thus, this structure contains (111)$_{PbS}$ slabs three octahedra thick parallel to $\vec{d}_{001}$ of the neyite lattice (ruled in Fig. 3), alternating with (100)$_{PbS}$ slabs two atomic layers thick (stippled in Fig. 3). This stack of alternating slabs with pseudohexagonal and pseudotetragonal surfaces is periodically sheared by a step one octahedron high at $z = 0$ which, for the (100)$_{PbS}$ layer, creates an empty octahedrally coordinated position flanked by two tetrahedra populated asymmetrically by Cu1 (Cu–Cu = 2.77 Å). This is matched by a simple slip the height of one octahedron in the (111)$_{PbS}$ layers. The step configuration and the adjacent straight-layer portions correspond almost entirely to the hypothetical third homologue of the stepped layer structure of the junoite–felbertalite homologous series (Topa *et al.* 2000), junoite having single, felbertalite double and the current structure triple (111)$_{PbS}$ layers. Furthermore, the stack of alternating slabs is periodically interrupted, sheared and separated by corrugated PbS-like (922)$_{PbS}$ layers at $z = ½$; these are parallel to (001) of neyite. The latter layers are three to four atomic layers thick, their corrugation proceeds as a result of differences in size and coordination between the tetrahedrally coordinated Cu3 and the opposing Me14 (Figs. 1, 2, 3). Further problems in accommodation are addressed in these layers by incorporation of a single, flattened-octahedron site of Ag1 in their straight portion.

Altogether, the (111)$_{PbS}$ slabs contain 12 unique, regular to slightly distorted octahedrally coordinated sites (Me1 – Me12). Two bicapped trigonal prismatic sites are shared with (100)$_{PbS}$ slabs (Me24), and (922)$_{PbS}$ layers (Me26). The square-pyramidal Me coordinations in the (100)$_{PbS}$ slabs that form sheared "partitions" perpendicular to [100]$_{ney}$ are completed by interslab Me–S bonds (distances) into coordination octahedra (Me17, Me21) or into lying (Me19, Me23) or standing (Me18, Me20) monocapped ("split octahedra") or bicapped trigonal prisms (Me22, Me24) (Fig. 2). There are nine unique cation positions in these layers, one of which is the Cu1 position, and two are shared either with the (111)$_{PbS}$ slabs (Me24) or with the (001)$_{ney}$ layers (Me23).

The interlayer space and the polyhedra involved correspond fully to those in junoite CuPb₃Bi₇(S,Se)₁₄ (Mumme 1980). The Cu2 and Cu3 positions are confined to tetrahedral voids in the extension of this space;

TABLE 3. ATOMIC COORDINATES, ANISOTROPIC DISPLACEMENT FACTORS, AND EQUIVALENT ISOTROPIC FACTORS FOR NEYITE

Atom	sf	occ	x	z	U_{11}	U_{22}	U_{33}	U_{13}	U_{eq}	Atom	x	z	U_{11}	U_{22}	U_{33}	U_{13}	U_{eq}
Me1	Bi	1.000	0.09485	0.94977	0.02940	0.02369	0.02781	0.01082	0.02658	S1	0.06509	-0.00405	0.03437	0.02061	0.02830	0.02029	0.02532
			0.00002	0.00002	0.00049	0.00043	0.00063	0.00044	0.00023		0.00016	0.00016	0.00327	0.00270	0.00407	0.00303	0.00140
Me2	Bi	1.000	0.43197	0.13675	0.03259	0.02462	0.02950	0.01038	0.02881	S2	0.45381	0.08328	0.02563	0.02987	0.02693	0.01151	0.02675
			0.00003	0.00003	0.00050	0.00043	0.00063	0.00045	0.00023		0.00015	0.00016	0.00307	0.00297	0.00405	0.00291	0.00143
Me3	Pb	1.000	0.31775	0.07448	0.03180	0.02571	0.03291	0.00858	0.03058	S3	0.35138	0.01729	0.02988	0.02977	0.03741	0.00411	0.03397
			0.00002	0.00003	0.00051	0.00045	0.00067	0.00046	0.00024		0.00016	0.00018	0.00333	0.00311	0.00467	0.00316	0.00163
Me4	Pb	1.000	0.20505	0.01414	0.03017	0.02364	0.02947	0.00783	0.02819	S4	0.02053	0.83397	0.02788	0.02845	0.03684	0.00907	0.03138
			0.00002	0.00003	0.00048	0.00042	0.00064	0.00044	0.00023		0.00016	0.00017	0.00322	0.00303	0.00457	0.00308	0.00157
Me5	Bi	1.000	0.04111	0.77668	0.02971	0.02479	0.03062	0.00939	0.02845	S5	0.12798	0.89323	0.02887	0.02965	0.03067	0.01017	0.02959
			0.00002	0.00003	0.00049	0.00044	0.00065	0.00045	0.00023		0.00016	0.00017	0.00324	0.00301	0.00433	0.00301	0.00150
Me6	Pb	0.904	0.15591	0.83870	0.03044	0.02626	0.02916	0.01113	0.02825	S6	0.24064	0.95702	0.03161	0.03263	0.03362	0.01346	0.03191
		0.008	0.00003	0.00003	0.00060	0.00054	0.00075	0.00048	0.00039		0.00017	0.00017	0.00333	0.00310	0.00441	0.00314	0.00153
Me6	Ag	0.096	0.15591	0.83870	0.03044	0.02626	0.02916	0.01113	0.02825	S7	0.49131	0.74704	0.02811	0.03496	0.03601	0.00979	0.03316
		0.008	0.00003	0.00003	0.00060	0.00054	0.00075	0.00048	0.00039		0.00016	0.00018	0.00326	0.00318	0.00463	0.00312	0.00160
Me7	Pb	1.000	0.27003	0.90052	0.03404	0.02748	0.03314	0.01085	0.03155	S8	0.39963	0.19231	0.02930	0.02925	0.03025	0.01275	0.02885
			0.00003	0.00003	0.00052	0.00046	0.00067	0.00048	0.00024		0.00016	0.00017	0.00321	0.00297	0.00420	0.00302	0.00146
Me8	Bi	1.000	0.48389	0.30940	0.02786	0.02338	0.03039	0.00837	0.02746	S9	0.28778	0.12866	0.03069	0.02694	0.02876	0.01204	0.02820
			0.00002	0.00003	0.00048	0.00042	0.00064	0.00045	0.00023		0.00016	0.00016	0.00320	0.00290	0.00418	0.00294	0.00145
Me9	Pb	0.895	0.37102	0.24759	0.02831	0.02491	0.03309	0.00922	0.02893	S10	0.17830	0.06508	0.02837	0.02279	0.04126	0.01771	0.02925
		0.008	0.00003	0.00003	0.00061	0.00054	0.00077	0.00049	0.00040		0.00016	0.00017	0.00320	0.00281	0.00468	0.00318	0.00154
Me9	Ag	0.105	0.37102	0.24759	0.02831	0.02491	0.03309	0.00922	0.02893	S11	0.03077	0.33529	0.02492	0.02256	0.03777	0.00457	0.02974
		0.008	0.00003	0.00003	0.00061	0.00054	0.00077	0.00049	0.00040		0.00016	0.00017	0.00307	0.00283	0.00453	0.00298	0.00155
Me10	Bi	1.000	0.25656	0.18688	0.03329	0.02543	0.03106	0.01075	0.02984	S12	0.07383	0.72412	0.02480	0.02734	0.03125	0.00530	0.02869
			0.00003	0.00003	0.00051	0.00044	0.00065	0.00046	0.00023		0.00016	0.00017	0.00305	0.00289	0.00427	0.00289	0.00148
Me11	Bi	0.801	0.09861	0.66520	0.03421	0.02729	0.03160	0.01014	0.03115	S13	0.18465	0.78494	0.03292	0.02875	0.03438	0.01708	0.03052
		0.008	0.00003	0.00003	0.00068	0.00058	0.00083	0.00054	0.00043		0.00017	0.00017	0.00334	0.00300	0.00442	0.00315	0.00152
Me11	Ag	0.199	0.09861	0.66520	0.03421	0.02729	0.03160	0.01014	0.03115	S14	0.29140	0.84375	0.02667	0.03315	0.03760	0.01492	0.03138
		0.008	0.00003	0.00003	0.00068	0.00058	0.00083	0.00054	0.00043		0.00016	0.00017	0.00321	0.00318	0.00460	0.00310	0.00156
Me12	Bi	1.000	0.21150	0.72539	0.03095	0.02523	0.02981	0.01366	0.02773	S15	0.45320	0.35905	0.02479	0.03417	0.02797	0.00785	0.02913
			0.00002	0.00003	0.00049	0.00043	0.00064	0.00045	0.00023		0.00016	0.00017	0.00306	0.00312	0.00411	0.00286	0.00146
Me13	Bi	1.000	0.40313	0.52831	0.02756	0.02246	0.02770	0.00876	0.02594	S16	0.34311	0.30519	0.02638	0.02703	0.03696	0.00106	0.03231
			0.00002	0.00002	0.00047	0.00041	0.00061	0.00044	0.00022		0.00016	0.00017	0.00321	0.00299	0.00464	0.00309	0.00164
Me14	Pb	1.000	0.29628	0.54313	0.03273	0.02698	0.03488	0.01244	0.03116	S17	0.23804	0.24290	0.02606	0.02601	0.02953	0.00797	0.02744
			0.00003	0.00003	0.00051	0.00044	0.00068	0.00048	0.00024		0.00016	0.00016	0.00306	0.00280	0.00414	0.00289	0.00144
Me15	Bi	1.000	0.18405	0.53673	0.02807	0.02379	0.02739	0.00811	0.02661	S18	0.05158	0.47919	0.02802	0.02600	0.02709	0.00904	0.02700
			0.00002	0.00002	0.00048	0.00042	0.00063	0.00044	0.00023		0.00016	0.00016	0.00311	0.00288	0.00407	0.00291	0.00143
Me16	Bi	0.863	0.08231	0.55326	0.03376	0.02467	0.04061	0.01830	0.03150	S19	0.14986	0.46080	0.02996	0.02623	0.02506	0.01033	0.02673
		0.008	0.00003	0.00003	0.00066	0.00055	0.00085	0.00055	0.00042		0.00016	0.00016	0.00321	0.00283	0.00397	0.00288	0.00142
Me16	Ag	0.137	0.08231	0.55326	0.03376	0.02467	0.04061	0.01830	0.03150	S20	0.26838	0.47394	0.02964	0.02589	0.02856	0.01438	0.02683
		0.008	0.00003	0.00003	0.00066	0.00055	0.00085	0.00055	0.00042		0.00016	0.00016	0.00323	0.00285	0.00410	0.00296	0.00143
Me17	Bi	1.000	0.37470	0.85626	0.03488	0.02888	0.03594	0.01166	0.03317	S21	0.36281	0.45286	0.02871	0.01965	0.05161	0.01793	0.03213
			0.00003	0.00003	0.00053	0.00046	0.00070	0.00049	0.00025		0.00016	0.00018	0.00323	0.00273	0.00511	0.00330	0.00164
Me18	Pb	1.000	0.33236	0.75102	0.03931	0.02629	0.03668	0.01034	0.03455	S22	0.46661	0.44262	0.03523	0.03165	0.03123	0.01018	0.03283
			0.00003	0.00003	0.00056	0.00045	0.00071	0.00051	0.00026		0.00017	0.00017	0.00347	0.00309	0.00438	0.00318	0.00156
Me19	Bi	1.000	0.31808	0.65130	0.03385	0.02470	0.03407	0.01360	0.03024	S23	0.10346	0.09562	0.03551	0.02531	0.03297	0.01055	0.03138
			0.00003	0.00003	0.00051	0.00044	0.00068	0.00048	0.00024		0.00017	0.00017	0.00348	0.00288	0.00442	0.00316	0.00154
Me20	Bi	1.000	0.02902	0.08656	0.04216	0.02745	0.03636	0.00574	0.03698	S24	0.13871	0.19270	0.02688	0.02404	0.02803	0.00784	0.02656
			0.00003	0.00003	0.00058	0.00046	0.00071	0.00051	0.00027		0.00016	0.00016	0.00309	0.00276	0.00410	0.00288	0.00143
Me21	Bi	1.000	0.06808	0.19264	0.03612	0.02708	0.03431	0.01078	0.03264	S25	0.16670	0.29547	0.02870	0.02890	0.03290	0.00784	0.03067
			0.00003	0.00003	0.00053	0.00046	0.00068	0.00049	0.00025		0.00016	0.00017	0.00323	0.00302	0.00439	0.00305	0.00153

TABLE 3. ATOMIC COORDINATES, ANISOTROPIC DISPLACEMENT FACTORS, AND EQUIVALENT ISOTROPIC FACTORS FOR NEYITE

Atom	sf	occ	x	z	U_{11}	U_{22}	U_{33}	U_{13}	U_{eq}
Me22	Pb	1.000	0.07804	0.28881	0.05235	0.02915	0.03493	0.01064	0.03963
			0.00003	0.00003	0.00064	0.00048	0.00072	0.00055	0.00027
Me23	Pb	1.000	0.10255	0.38733	0.03386	0.02364	0.03605	0.01148	0.03113
			0.00003	0.00003	0.00052	0.00044	0.00069	0.00048	0.00025
Me24	Pb	1.000	0.38789	0.95725	0.05105	0.03752	0.04466	0.00092	0.04788
			0.00003	0.00003	0.00067	0.00056	0.00084	0.00060	0.00032
Me25	Pb	1.000	0.00264	0.41019	0.03531	0.03068	0.05300	0.00681	0.04144
			0.00003	0.00003	0.00055	0.00049	0.00085	0.00054	0.00029
Me26	Pb	1.000	0.32008	0.37164	0.04594	0.03660	0.05878	0.02089	0.04614
			0.00003	0.00003	0.00063	0.00054	0.00091	0.00061	0.00031
Ag1			0.50000	0.50000	0.05235	0.08567	0.03271	0.00844	0.05817
			0.00000	0.00000	0.00198	0.00239	0.00221	0.00168	0.00094
Cu1			0.46888	0.01065	0.03832	0.04203	0.04918	0.00881	0.04445
			0.00009	0.00009	0.00182	0.00178	0.00267	0.00177	0.00092
Cu2			0.23194	0.30895	0.03775	0.03468	0.05888	0.01476	0.04397
			0.00009	0.00009	0.00183	0.00166	0.00284	0.00182	0.00094
Cu3			0.74956	0.59064	0.03167	0.03338	0.05584	0.01017	0.04124
			0.00008	0.00009	0.00169	0.00161	0.00274	0.00172	0.00091
S26			0.18636	0.39239	0.02668	0.03133	0.02923	0.01101	0.02860
			0.00016	0.00017	0.00311	0.00298	0.00419	0.00295	0.00146
S27			0.47100	0.95417	0.02853	0.02457	0.03150	0.01053	0.02799
			0.00016	0.00017	0.00314	0.00283	0.00426	0.00295	0.00146
S28			0.44556	0.85669	0.02891	0.02503	0.03177	0.01099	0.02828
			0.00016	0.00017	0.00321	0.00284	0.00425	0.00300	0.00147
S29			0.40732	0.76003	0.02768	0.02508	0.02912	0.01145	0.02674
			0.00016	0.00016	0.00310	0.00281	0.00411	0.00289	0.00142
S30			0.39053	0.66252	0.02958	0.02170	0.02377	0.00963	0.02477
			0.00015	0.00016	0.00317	0.00269	0.00391	0.00286	0.00138
S31			0.44003	0.59079	0.02516	0.02205	0.02852	0.00964	0.02500
			0.00015	0.00016	0.00302	0.00271	0.00410	0.00284	0.00141
S32			0.22310	0.59748	0.02695	0.02212	0.02742	0.00945	0.02534
			0.00016	0.00016	0.00306	0.00271	0.00399	0.00285	0.00139
S33			0.12364	0.61611	0.02472	0.03417	0.03490	0.01179	0.03074
			0.00016	0.00017	0.00314	0.00316	0.00446	0.00303	0.00154
S34			0.23842	0.67783	0.03210	0.02711	0.03117	0.01607	0.02872
			0.00016	0.00017	0.00333	0.00294	0.00427	0.00309	0.00149

Note that y, U_{12}, and U_{23} are equal to 0 for all atoms. For the heavy atoms ($Me1 - Me26$), the scattering factors used (sf) and the occupancies (occ) also are shown.

Cu2 is closer to a trigonal planar coordination, whereas Cu3 is closer to a tetrahedral one (Fig. 2). These Cu atoms cover bases of an empty horizontal coordination prism subparallel to [001] and do not show Cu...Cu interaction.

The third type of building blocks, the distorted layers $(001)_{ney}$ (white in Fig. 3) consist of [010] "rods", which contain twelve cations ($Me13$, 15, 16, 23, 25 and 26) and twelve sulfur atoms (S18, 19, 21, 31, 32, 33) each. These rods are centered on a single flattened octahedron formed around linearly coordinated Ag1; they are interconnected by a pair of "split" Pb14 coordination octahedra, each facing a Cu3 tetrahedron. These latter polyhedra cause periodic changes of direction of the $(001)_{ney}$ layer, warping it in order to fit the varying attachment requirements of pseudohexagonal and pseudotetragonal slabs perpendicular to [001]. This type of layer can also be described as a $(100)_{PbS}$ slab three atomic planes thick, displaced periodically on $(111)_{PbS}$ by an increment equal to $\frac{1}{2}\vec{d}(100)_{PbS}$.

Occupancies of the Pb and Bi positions

An attempt was made to characterize those metal positions in the neyite structure that show characteristics of mixed Pb,Bi occupancy as either Bi-dominated, Pb-dominated or mixed. This attempt is based on several semi-empirical models.

In the first instance, the occupancies were determined from the bond-valence calculations using the formula:

$$s = \exp[(r_O - r)/B]$$

where r_O is an element-specific bond-valence parameter, r the bond distance, and B is a constant equal to 0.37 (Brown & Altermatt 1985). The bond-valence parameters for Bi–S and Pb–S bonds quoted by Brese & O'Keeffe (1991) are the same (2.55), which allows an easy determination of occupancies from the calculated valence-sums for cation positions. For positions that also include Ag, the amount of Ag determined by structure refinement was subtracted first.

Subsequently, the volume of a circumscribed sphere, least-squares-fitted to the cation polyhedron, and the volume of the coordination polyhedron itself, were used to calculate the occupancies. We noted that the heavy cation position No. 3 shows the largest, and the position No. 8, the smallest volume among the CN6 coordinations (Tables 4, 5). The calculated valences for these two positions are 1.95 and 2.93 valence units (vu), and the bond distances also suggest practically full occupancy by Pb and Bi, respectively. Taking their volumes as representative for Pb and Bi in the structure studied, and assuming that the volumes change linearly with the extent of Pb-for-Bi substitution, the observed volumes
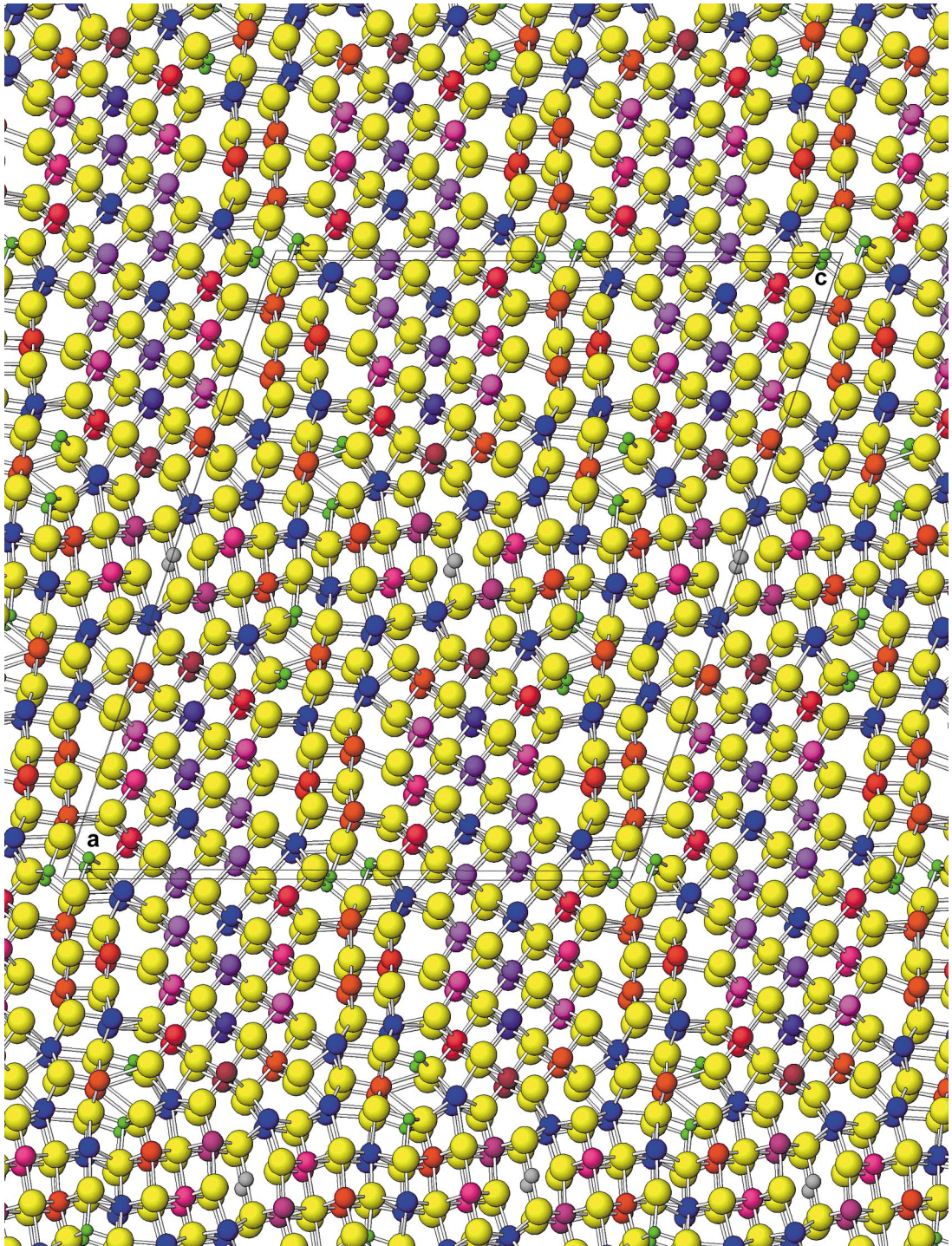
FIG. 1. The crystal structure of neyite. Pb atoms are blue, Bi atoms are red, mixed Pb–Bi positions, purple with shades varying according to the Pb/Bi ratio; Ag atoms are grey, Pb–Bi positions partly substituted by Ag are brown to dark violet, Cu atoms are green, and S atoms are yellow. Oblique projection on (010); four atomic layers parallel to (010) are shown.
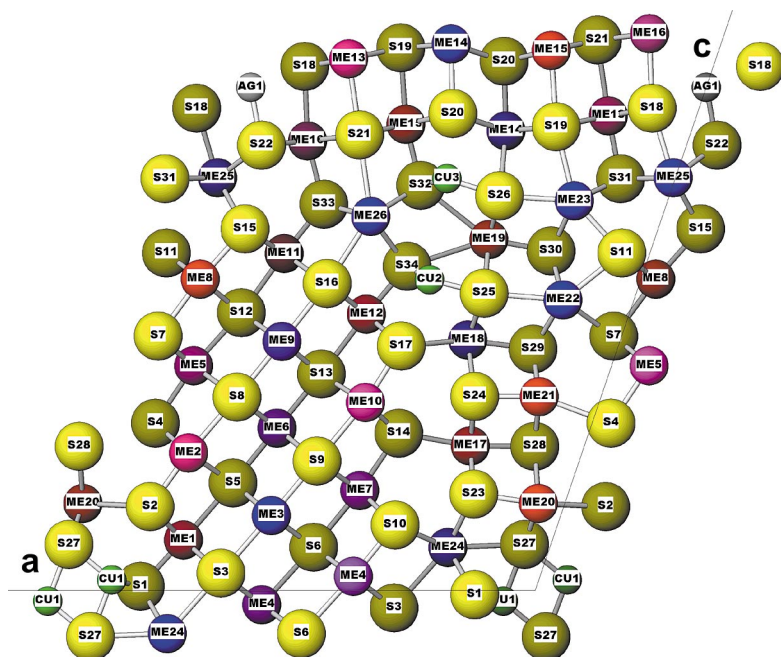
Fig. 2. Asymmetric unit of neyite structure projected parallel to [010], with atomic labels. Atoms at $y = 0$ are unshaded, those at $y = \frac{1}{2}$ are shaded. Color scheme as in Figure 1.

can be used to calculate the fractional occupancy of each position by these two elements. For positions with a contribution from Ag, the appropriate volume-contribution by Ag was calculated using the Ag occupancy obtained from the structure refinement, as well as the volumes of the sphere and of the coordination polyhedron for the Ag1 position.

The calculations were done only for the positions with CN6. Similar calculations were attempted for the six positions with CN7, but the calculations did not give satisfactory results. The calculated valences were found to be too low (the same is true for the CN8 positions), and it is hard to define a typical volume for positions occupied exclusively by Pb and Bi. From the experimentally determined composition and the calculated occupancies of CN6 positions, it follows that there are approximately two Bi atoms distributed over the remaining six CN7 and three CN8 positions. Positions 19 and 20, with CN7, have the largest eccentricities (Table 4) and were interpreted to be fully occupied by Bi, and the others, fully occupied by Pb. The largest eccentricities for Pb with CN = 7 occur in the "split octahedra" of $Me14$ and $Me18$. Values of sphericity vary throughout the structure; in general, they are reduced for the cations of the central row of the $(111)_{PbS}$ slab and for the bicapped trigonal prisms of Pb.

The results are represented in Table 5. There is a generally good concordance among results of the various methods of calculation, the largest discrepancy being found in position 21, for which the first two calculations give a significant occupancy by Pb, whereas the volume of the coordination polyhedron suggests that it is practically filled by Bi. The sum obtained from the volumes (V_P) of coordination polyhedra shows the best concordance with the microprobe-established composition, which indicates 12.43 Pb and 13.04 Bi positions, the rest of the positions (0.53) being occupied by Ag.

Four octahedral positions were found to be partly occupied by silver: three of them ($Me6$, $Me9$ and $Me11$) are in the central row of the triple-octahedron layer, and one ($Me16$) is in the distorted $(001)_{ney}$ layer, where two Bi16 positions flank the Ag1 position. In all these cases, the Ag content was modeled as 0.1–0.2 Ag atoms.

Modular character

As mentioned above, the structure of neyite can be described as a stacking of pseudotetragonal $(100)_{PbS}$ and pseudohexagonal $(111)_{PbS}$ slabs that are regularly sheared. Shear by steps that are one octahedron or one pseudotetragonal double layer high, and situated at $z = 0$, alternates in neyite with shear by compositionally

FIG. 3.   Modular interpretation of the neyite structure. Pseudohexagonal blocks $(111)_{PbS}$ are ruled, the interleaved pseudo-
tetragonal slabs $(100)_{PbS}$ are stippled, and the corrugated $(922)_{PbS}$ layers are left unshaded.

non-conservative (001) boundaries at $z = \frac{1}{2}$ (Fig. 3). These non-conservative boundary-layers, 4 to 3 atomic layers wide, are related to the pseudohexagonal blocks by the local unit-cell twinning on $(311)_{PbS}$: two bicapped trigonal coordination prisms of lead (*Me*25 and distorted *Me*26) following each other are situated in this lillianite-like boundary region of the structure (Figs. 1, 2, 3). The local twin-relationship of $(111)_{PbS}$ between the $(001)_{ney}$ layers and $(100)_{PbS}$ slabs is less prominent. The joining of two distinct pseudotetragonal building-blocks creates a "box-work" structure, which accommodates the pseudohexagonal blocks. The latter have a non-commensurate match on both the (111) and the $(1\bar{1}1)_{PbS}$ surfaces (Fig. 3). For the terminology used in this section, we recommend the review by Makovicky (1997a, b) and the references therein.

Because of its complexity, the structure of neyite belongs to a new, "advanced" generation of complex sulfide structures. It is *doubly-non-commensurate*, of a novel *"box-work"* type and of a *highly complex char-acter*. Whereas the typical complex sulfosalt structures with sheared layers or those of the rod-based category (Makovicky 1989, 1993, 1997a, b) have non-commen-surate match on one type (set) of interfaces, neyite and other box-work structures have two types of non-com-

mensurate interfaces, in two sets that are oblique to each other. The best other examples of this category are the recently described sulfosalt pillaite $Pb_9Sb_{10}S_{23}ClO_{0.5}$ (Meerschaut *et al.* 2001) and the rare-earth sulfide $Er_9La_{10}S_{27}$ (Carré & Laruelle 1973, Makovicky 1992).

The majority of complex sulfide structures have one or two kinds of layers or blocks or rods recombined into a large-scale structure. Neyite and other structures of "box-work" type have three such building-blocks: two types of $(100)_{PbS}$ layers/fragments with pseudotetra-gonal character and one type of pseudohexagonal $(111)_{PbS}$ layers/blocks. The two pseudotetragonal ele-ments differ from each other to various degrees in dis-tinct members of the "box-work" family.

Hypothetical derivatives of neyite

Several new structures can be derived from the neyite structure, either by homologous expansion or contraction, or by truncations in either of the two types of sheared areas.

Homologous contraction of pseudohexagonal $(111)_{PbS}$ layers, reducing their thickness respectively, to a single- or a double-octahedron layer, leads to lower homologues, of the order N = 1 and 2, of the neyite

TABLE 4. COORDINATION CHARACTERISTICS FOR CATION POSITIONS
IN THE STRUCTURE OF NEYITE

	%Pb	%Bi	%Ag	CN	$<d>$	d_{min}	d_{max}	r_s	V_p	v	Δ	σ
$Me1$	13	87	0	6	2.853	2.604	3.105	2.857	30.918	0.0054	0.2497	0.9996
$Me2$	24	76	0	6	2.873	2.713	3.045	2.868	31.441	0.0005	0.2399	0.9937
$Me3$	100	0	0	6	2.974	2.903	3.142	2.977	34.970	0.0059	0.1185	0.9524
$Me4$	60	40	0	6	2.921	2.722	3.188	2.927	33.143	0.0086	0.2294	0.9760
$Me5$	38	62	0	6	2.891	2.785	2.998	2.887	32.071	0.0005	0.1531	0.9976
$Me6$	58	32	10	6	2.918	2.884	2.949	2.918	33.087	0.0008	0.0240	0.9774
$Me7$	56	44	0	6	2.918	2.845	3.011	2.915	32.939	0.0025	0.0992	0.9908
$Me8$	0	100	0	6	2.837	2.690	2.988	2.834	30.300	0.0011	0.2206	0.9972
$Me9$	69	21	10	6	2.933	2.883	3.023	2.934	33.586	0.0026	0.0541	0.9610
$Me10$	33	67	0	6	2.887	2.753	3.124	2.881	31.859	0.0006	0.2288	0.9578
$Me11$	6	74	20	6	2.848	2.604	3.006	2.850	30.691	0.0059	0.2384	0.9633
$Me12$	10	90	0	6	2.849	2.588	3.078	2.852	30.771	0.0055	0.2412	0.9862
$Me13$	27	73	0	6	2.874	2.634	3.152	2.886	31.546	0.0152	0.2968	0.9856
$Me14$	100	0	0	7	3.079	2.865	3.365	3.088	41.166	0.1180	0.2958	0.9530
$Me15$	3	97	0	6	2.843	2.587	3.148	2.853	30.421	0.0170	0.2691	0.9874
$Me16$	24	62	14	6	2.876	2.683	3.066	2.875	31.495	0.0057	0.2261	0.9907
$Me17$	6	94	0	6	2.851	2.655	2.995	2.860	30.575	0.0201	0.1646	0.9705
$Me18$	100	0	0	7	3.074	2.711	3.411	3.088	40.563	0.1311	0.3550	0.9942
$Me19$	0	100	0	7	3.035	2.602	3.582	3.026	39.172	0.1079	0.4686	0.8981
$Me20$	0	100	0	7	3.031	2.694	3.446	3.046	38.812	0.1333	0.4433	0.9363
$Me21$	0	100	0	6	2.875	2.649	3.148	2.896	30.274	0.0647	0.2414	0.9953
$Me22$	100	0	0	8	3.119	2.906	3.227	3.121	53.343	0.0333	0.1611	0.9016
$Me23$	100	0	0	7	3.013	2.911	3.129	3.018	38.724	0.1115	0.1168	0.9648
$Me24$	100	0	0	8	3.138	3.018	3.328	3.14	54.167	0.0365	0.0482	0.9099
$Me25$	100	0	0	7	3.042	2.973	3.149	3.048	39.266	0.1249	0.1109	0.9763
$Me26$	100	0	0	8	3.152	2.858	3.393	3.152	54.776	0.0363	0.1305	0.8374
$Ag1$	0	0	100	6	2.898	2.416	3.139	2.898	30.809	0.0505	0.0007	0.6135
$Cu1$	0	0	0	4	2.379	2.284	2.494	2.363	6.525	0.0369	0.1624	1.0000
$Cu2$	0	0	0	4	2.475	2.302	2.968	2.423	7.262	0.0051	0.5364	1.0000
$Cu3$	0	0	0	4	2.402	2.275	2.68	2.382	6.896	0.0060	0.3321	1.0000

Atomic percentages are determined from the structure refinement (% Ag) and V_p (% Pb,% Bi: see text). CN: coordination number, $<d>$ = average bond-length, d_{min}, d_{max} = minimum and maximum bond-length, r_s: radius of circumscribed sphere, V_p: polyhedron volume, v: volume-based distortion, Δ: volume-based excentricity, σ: volume sphericity. For the description of coordination-distortion parameters, see Makovicky & Balić-Žunić (1998).
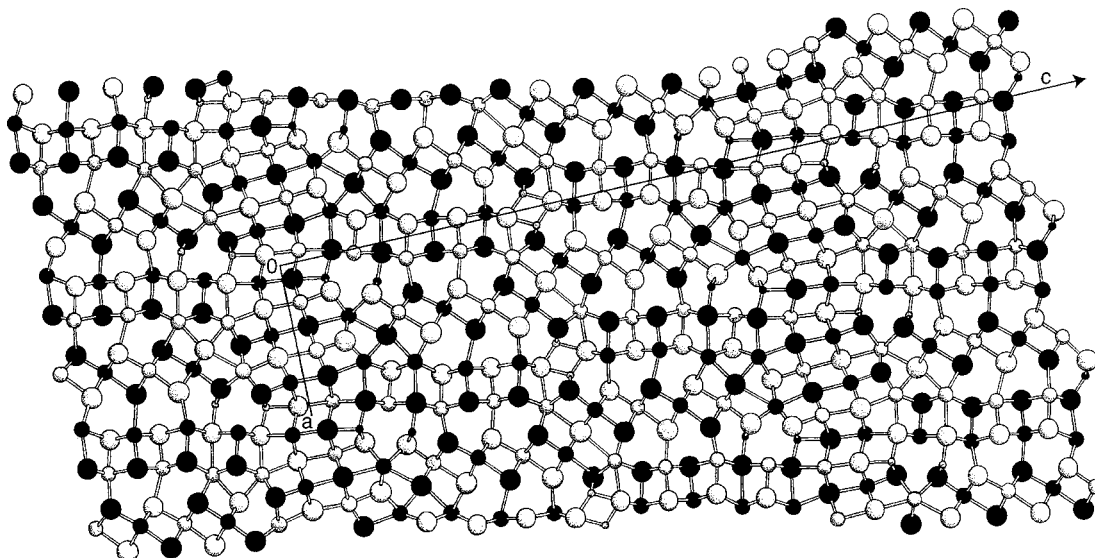

FIG. 4. The hypothetical N = 1 homologue of the neyite homologous series, with the model composition $Cu_6Pb_{12}Bi_{20}S_{45}$. Collage based on homologous contraction of the refined structure of neyite.

TABLE 5. CALCULATED Pb/Bi OCCUPANCIES FOR
THE 26 HEAVY-METAL POSITIONS IN THE STRUCTURE OF NEYITE

Position	CN	$Pb_{val.}$	Pb_{Vs}	Pb_{Vp}	$Bi_{val.}$	Bi_{Vs}	Bi_{Vp}
1	6	0.13	0.16	0.13	0.87	0.84	0.87
2	6	0.3	0.23	0.24	0.7	0.77	0.76
3	6	1.00	1.00	1.00	0	0	0
4	6	0.65	0.64	0.60	0.35	0.36	0.40
5	6	0.54	0.36	0.38	0.46	0.64	0.62
6*	6	0.7	0.53	0.58	0.2	0.37	0.32
7	6	0.76	0.56	0.56	0.24	0.44	0.44
8	6	0.07	0	0	0.93	1.00	1.00
9*	6	0.76	0.64	0.69	0.13	0.26	0.21
10	6	0.42	0.32	0.33	0.58	0.68	0.67
11*	6	0.09	0.03	0.06	0.71	0.77	0.74
12	6	0.1	0.13	0.10	0.90	0.87	0.90
13	6	0.19	0.35	0.27	0.81	0.65	0.73
14	7	1	1	1	0	0	0
15	6	0.02	0.13	0.03	0.98	0.87	0.97
16*	6	0.30	0.22	0.24	0.56	0.64	0.62
17	6	0.23	0.18	0.06	0.77	0.82	0.94
18	7	1	1	1	0	0	0
19	7	0	0	0	1	1	1
20	7	0	0	0	1	1	1
21	6	0.31	0.42	0.00	0.69	0.58	1.00
22	8	1	1	1	0	0	0
23	7	1	1	1	0	0	0
24	8	1	1	1	0	0	0
25	7	1	1	1	0	0	0
26	8	1	1	1	0	0	0
sum		13.57	12.9	12.27	11.88	12.56	13.19

The values indicated follow from bond-valence calculations (val.), volumes of circumscribed spheres (Vs), and volumes of coordination polyhedra (Vp). Positions denoted by asterisks are partially occupied by silver.

structure-type (N = 3). The second homologue displays problems in the interface match and may require a substantial change in at least one (pseudohexagonal) coordination polyhedron in order to materialize. However, the N = 1 homologue, with single-octahedron pseudohexagonal layers of the same length as those in neyite, is a perfectly viable structure. It has model composition $Cu_6Pb_{12}Bi_{20}S_{45}$, space group $A2/m$ (a 12.7, b 4.1, c 85.4 Å, $\beta \approx 90.5°$) (Fig. 4).

Truncation of the structures of neyite homologues (N = 1 to N = 3) by deleting the compositionally non-conservative interlayer leads to sheared layer-structures of the junoite family, such as junoite $CuPb_3Bi_7(S, Se)_{14}$, N = 1 (Mumme 1975) and the newly discovered felbertalite $Cu_2Pb_6Bi_8S_{19}$, N = 2 (Topa et $al.$ 2000, 2001).

Truncation of neyite homologues by deleting the stepped areas at $z_{ney} = 0$ leads to a new homologous series of typical box-work structures. Homologues N = 1 and 3 do not have coordination problems (Figs. 5, 6); the N = 2 homologue experiences the same problems for some coordination polyhedra as those observed in the full, neyite-like N = 2 structure. Homologue N = 1 has space-group symmetry $P2_1/m$, a 12.7, b 4.1, c 30.3 Å, and $\beta \approx 94°$, model formula $Cu_2Pb_5Bi_6S_{15}$. Homologue N = 3 has space-group symmetry $C2/m$, a 37.5, b 4.1, c 30.1 Å, and $\beta \approx 94°$, model formula $AgCu_4Pb_{22}Bi_{13}S_{44}$ if no Ag + Bi substitution for 2Pb is envisaged.
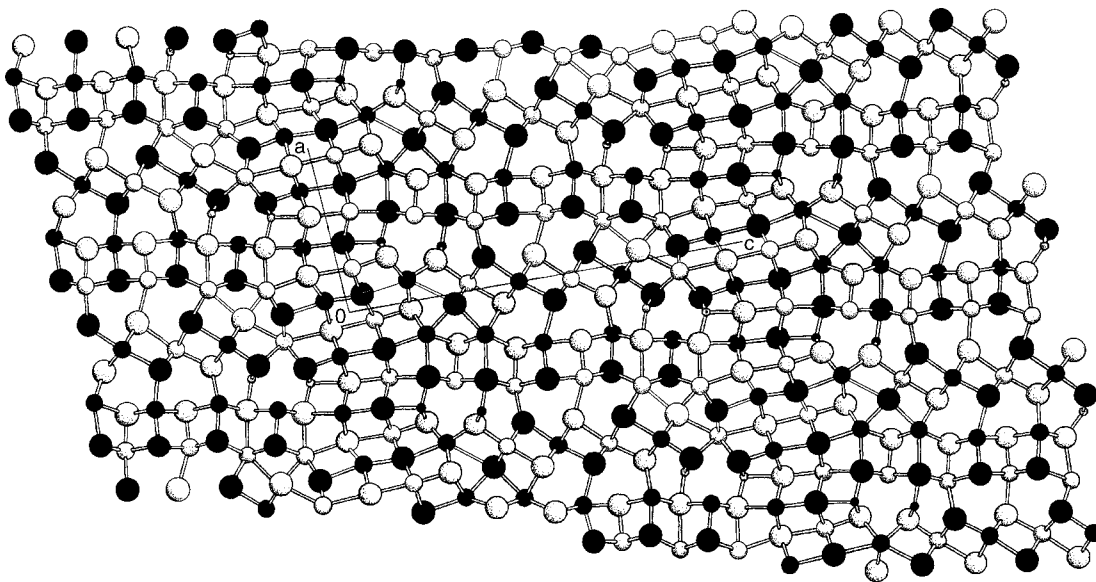

FIG. 5.   The hypothetical N = 1 truncation derivative of the neyite homologous series. Model composition $Cu_2Pb_5Bi_6S_{15}$; collage based on neyite.
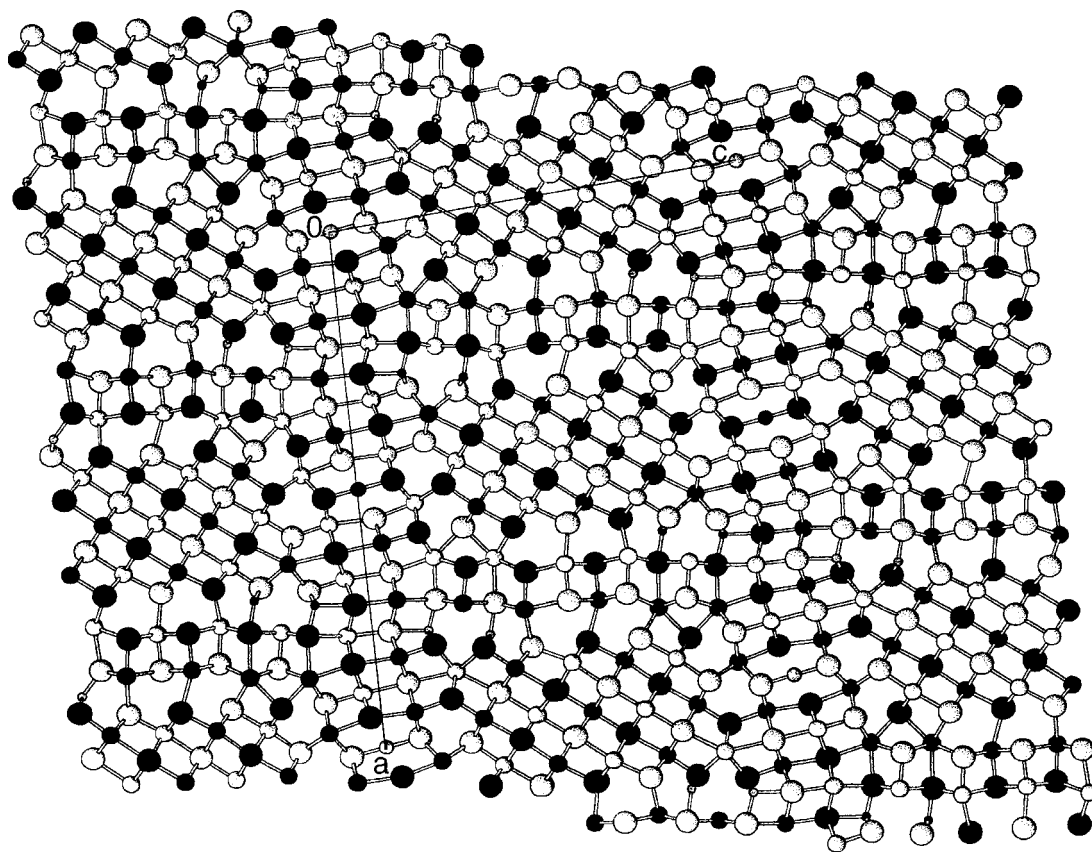
FIG. 6.   The hypothetical N = 3 truncation derivative of neyite. Model composition $AgCu_4Pb_{22}Bi_{13}S_{44}$; collage based on neyite.

Variation of the length of the $(111)_{PbS}$ and $(100)_{PbS}$ elements appears to be restricted. In neyite and the "stepped" neyite homologues, the total, long non-commensurate match can be described approximately as 7½ pseudotetragonal subcells (coordination polyhedra) facing 4½ orthohexagonal subcells (*i.e.,* 8 coordination octahedra and one more such interval for the terminal trigonal coordination prism) (Figs. 2, 3). In the above "box-work" truncation derivatives, four pseudotetragonal subcells match with two and a half orthohexagonal subcells. Other matches were attempted but discarded because they create contradictions either in *x* and *y* or in *z* values of certain atoms. None of these structures have yet been detected; they may require a certain amount of element substitutions away from the model compositions to become stabilized.

ACKNOWLEDGEMENTS

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