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Crystal structure of owyheeite, $Ag_{1.5}Pb_{4.43}Sb_{6.07}S_{14}$: refinement from powder synchrotron X-ray diffraction

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Abstract: The crystal structure of owyheeite, a natural Ag-Pb-Sb sulphosalt from hydrothermal veins at Kutná Hora in central Bohemia, Czech Republic has been refined from powder X-ray synchrotron data, with a final R_{wp} = 4.1 %. The symmetry is monoclinic, space group $P2_1/c$, with a = 4.1035(1), b = 27.3144(3), c = 22.9366(3) Å, β = 90.359(1)°. The structural formula is $Ag_{1.5}Pb_{4.43}Sb_{6.07}S_{14}$, with Z = 4. The structure of owyheeite contains 26 independent atoms: four Pb sites, one mixed Pb/Sb site, five Sb sites, one Ag site, one mixed Ag/Sb site and 14 S sites. All of them are in general Wyckoff position 4e of the space group $P2_1/c$; no special positions are occupied. The powder synchrotron diffraction pattern showed weak diffraction reflections indicative of a 2a superstructure. Three types of aggregates of coordination polyhedra can be recognized: three-fold columns of bicapped trigonal coordination prisms of Pb, two-strand ribbons of Sb and four-strand ribbons of 2 Sb atoms and 2 mixed sites Sb/Ag and Pb/Sb. A typical feature of the owyheeite structure is an ordering of Sb atoms to form lone electron pair micelles. Electron probe microanalysis gives (mean of 10 point analyses in wt. %): Ag 6.51(12), Cu 0.18(2), Pb 45.03(24), Sb 28.69(33), S 19.66(19), Total 100.08. Owyheeite belongs to a broad family of rod-based sulphosalt structures with the chess-board arrangement of the rods.

Key-words: owyheeite, crystal structure, Pb-Ag-Sb sulphosalt, Rietveld refinement, synchrotron powder data, Kutná Hora, Czech Republic.

Introduction

Owyheeite is a rare sulphosalt mineral of Pb, Ag and Sb which was first described by Burton in 1868 as argentiferous jamesonite from Owyhee Co., Idaho, US. Subsequently this material was analysed and described by Shannon (1921), who gave it the name owyheeite. Shannon established the formula as $Ag_2Pb_5Sb_6S_{15}$. Robinson (1949) measured rotation photographs about c axis showing strong layer lines and very weak intermediate layer lines yielding a pseudo-period $c' = c/2 = 4.095$ Å. He determined cell parameters from Weissenberg photographs as a = 22.82, b = 27.20 and c = 8.19 Å and suggested orthorhombic space group *Pnam*. In 1967 Timofeeevski described from the East Trans-Baikal region of Russia a variety of owyheeite with a decreased Ag content with the formula $(Ag,Cu)_2Pb_{7.07}Sb_{7.91}S_{19.99}$ and cell parameters a = 22.58, b = 26.68, c = 4.08 Å. He called his Ag-poor variety teremkovite. After recalculation to 26 atoms, his formula $Ag_{1.4}Pb_{4.9}Sb_{5.6}S_{14}$ is close to the structural composition described in this article.

Moëlo *et al.* (1984) carried out comparative electron microprobe study of owyheeites from thirteen ore deposits which showed a limited solid-solution field following the substitution $2Pb^{2+} \leftrightarrow Ag^{+}+Sb^{3+}$. The solid solution includes the composition of the variety "teremkovite", but excludes the initial formula proposed by Shannon. Their formula $Ag_{3+x}Pb_{10-2x}Sb_{11+x}S_{28}$ ($-0.36 \leqslant x \leqslant +0.20$) described compositional variations of members with the highest Ag/Sb ratio. Moëlo *et al.* (1984) observed the absence of elements such as Fe, Zn, Cd, Hg and Mn and concluded that this indicated the absence of corresponding tetrahedral positions in the structure of owyheeite.

Shannon suggested in his original description that the true periodicity of owyheeite is 8 Å and not 4 Å. Moëlo *et al.* (1984) determined approximate crystallography of four samples of owyheeite from different localities by means of electron diffraction. All of them had the a parameter equal to approximately 23 Å and the b parameter equal to 27 Å. All of them displayed superstructure reflections indicating 8 Å periodicity along the [001] direction (their setting differs from ours).

The superstructure reflections were very strong and sharp on samples with lowest (Ag+Cu) concentration (5.1 at % of Ag+Cu for owyheeite from Rajpura-Dariba, India) and became weaker and more diffuse with increasing concentrations of these elements (5.9 at % Ag+Cu for samples

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from Chucunio, Bolivia). This suggests a different degree of compositional and configurational ordering as a function of substitutions in certain structure sites. Moëlo *et al.* (1984) suggested that the most disordered owyheeite has the highest concentration of (Ag+Cu) and that the most ordered samples are those exhibiting under microscope the best developed twinning domains.

The hydrothermal veins of the Kutná Hora Ag-Pb-Zn polymetallic deposit in the Czech Republic played an important role in the history of owyheeite. It was here where the first European occurrence of owyheeite was reported by Hoffman & Trdlička (1978) who described the mineral from two different lodes (Roveň and Skalka Lodes) of the deposit. The refinement of the crystal structure of owyheeite presented in this article was carried out on a sample of owyheeite from the Turkaňk Lode of the Kutná Hora deposit. The vein with megascopic owyheeite was discovered in 1999 in medieval workings on the uppermost level. Owyheeite forms massive grain aggregates in quartz associated and/or intergrown with galena, stannite, pyrite, boulangerite, jamesonite, sphalerite and arsenopyrite. No other silver minerals are present in the paragenesis. The colour is very light silvery white, metallic lustre, brownish streak. Maximum size of owyheeite aggregates is 20 × 20 mm.

Kutná Hora Ag-Pb-Zn polymetallic deposit (60 km east of Prague, Central Bohemia, Czech Republic) is a hydrothermal vein type deposit of the Variscan age. It was one of the main European producers of silver in the 14th to 16th century with hundreds of mines on some twelve major lodes. This silver-rich ore deposit is a representative of polymetallic ores with prevailing sulfides and sulphosalts of Ag, Pb, Zn, Cu, Fe, Sb, and As (and in the northern part also of Sn and Bi). Geologically and mineralogically, two mineral assemblages are present in the deposit, one “silver-rich” in the southern part of the deposit and one “pyrite-rich” in the northern part. The silver-rich assemblage consists mainly of freibergite, miargyrite, pyrargyrite, native silver, allargentum, galena, tetrahedrite, pyrite, sphalerite, berthierite and Pb-Sb(-Ag) sulphosalts in quartz-kutnohorite gangue. The pyrite-rich assemblage consists mainly of Ag-bearing galena, pyrite, chalcopyrite, arsenopyrite, sphalerite, pyrrhotite, marcasite, freibergite/tetrahedrite, stannite and Pb-Sb(-Ag) sulphosalts in quartz gangue and no kutnohorite. Typical of this assemblage is the presence of Bi and Sn, completely absent in the “silver-rich” assemblage in the southern part of the deposit, making space for a whole suite of Pb-Bi-Sb-Ag(-Cu) sulphosalts not known from elsewhere in the Czech Republic (megascopic lillianite homologues such as gustavite, vikingite, treasurite, eskimoite; aramayoite; matildite; izoklakeite-giessenite) and a paragenesis resembling Ag-Sn mineralization in Bolivia: megascopic epithermal, radially spherical cassiterite associated with acanthite/argentite and galena. Historically, similar amounts of silver have been exploited from either part (or assemblage) of the deposit. Owyheeite was found in various parageneses in veins of both assemblages: at two different “silver-rich” lodes in the southern part of the deposit and at four different ”pyrite-rich” lodes in the northern part.

Table 1. Chemical composition of owyheeite from Kutná Hora, Turkaňk Lode, Czech Republic.

	owyheeit O5C Kutná Hora		
	mean (wt.%)	range (wt.%)	x
Ag	6.51	6.25-6.70	1.39
Cu	0.18	0.16-0.21	0.07
Pb	45.03	44.66-45.38	5.01
Sb	28.69	28.24-29.33	5.43
S	19.66	19.35-19.96	14.11
Suma	100.08		26.01

x-coefficients on the basis of 26 atoms per formula unit (apfu), $Z = 4$ owyheeit sample O5C, Kutná Hora, Turkaňk Lode: $(Ag_{1,39}Cu_{0,07})_{\Sigma=1,46}Pb_{5,01}Sb_{5,43}S_{14,11}$ (Analysis by Dr. D. Topa, University of Salzburg)

1. Experimental

1.1. Chemical composition

Quantitative chemical analysis was performed with a JEOL JXA-8600 electron microprobe (EMP), controlled by a LINK*eXL* system, operated at 25 kV, 35 nA, and 20 s counting time for peaks and 7 s for background, and a beam diameter of 5 μm. The following standards and X-ray lines were used: galena (PbS: Pb$M\alpha$), Ag metal (Ag$L\alpha$), stibnite (Sb_2S_3: Sb$L\alpha$), and chalcopyrite ($CuFeS_2$: Fe$K\alpha$, Cu$K\alpha$). Raw data were corrected with an online ZAF-4 procedure.

Chemical composition of the examined sample of owyheeite from the Turkaňk Lode of the Kutná Hora Ag-Pb-Zn polymetallic deposit (10 point analyses) yielded the empirical formula $(Ag_{1,39}Cu_{0,07})_{\Sigma=1,46}Pb_{5,01}Sb_{5,43}S_{14,11}$ calculated on the basis of 26 atoms per formula unit (Table 1). Minor contents of Cu (mean 0.18 wt %) were present in all measured points. No other trace elements were detected. This composition differs from the structure-derived formula $Ag_{1.5}Pb_{4.43}Sb_{6.07}S_{14}$, but it is within the solid solution compositional field defined by Moëlo *et al.* (1984) who established the formula $Ag_{3+x}Pb_{10-2x}Sb_{11+x}S_{28}$ ($-0.13 \leqslant x \leqslant +0.20$). The discrepancy between chemical composition and structural formula is probably related to the superstructure nature of the owyheeite under study, *i.e.* averaging of two coordination polyhedra in each independent site in the 4 Å structure (see below). The density calculated from the structure is 5.86 g/cm^3, the measured density is 5.66 g/cm^3, the density calculated from the chemical composition is 5.96 g/cm^3. All these values are under 6 which contradicts the previously reported values of 6.22–6.51 g/cm^3.

1.2. Data Collection

The attempts made in the past to solve and refine the crystal structure of owyheeite from single crystals were only partly successful. It seems extremely difficult to find single crystals suitable for single-crystal X-ray diffraction experiments. All hitherto measured natural crystals of owyheeite from various localities appeared to be mosaic-like, multiple twins by pseudomerohedry. Also, no attempt to synthesize owyheeite has been, to our knowledge, successful. Thus, we decided to perform a synchrotron diffraction experiment with high resolution on a powder sample of natural material.

An initial X-ray diffraction pattern was collected on laboratory diffractometer Philips X'Pert MPD using CuKα radiation. The powder data for owyheeite were collected from 4° to 80° 2θ with a step size of 0.02 $2\theta°$ and an exposure of 20 s per step. To minimize background, the sample was placed on a flat low-background silicon wafer. 11 different samples of owyheeite were measured before a sample suitable for synchrotron measurement was selected.

The high-resolution X-ray diffraction data were collected on the Swiss-Norwegian diffractometer BM1B at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The sample was placed in a rotating glass capillary (diameter 0.3 mm). An Si (111) double-crystal monochromator selected a wavelength of 0.49953 Å from the white beam. Six NaI scintillation counters were used as detectors. An Si (111) analyser crystal mounted in front of each detector was employed for data collection.

1.3. Structure determination

1.3.1. Search for a structural model

The powder X-ray synchrotron diffraction pattern was indexed using 25 first reflections with the automatic indexing program DICVOL04 (Louer & Boultif, 2004) implemented in the program WinPlotr (Carvajal 2005). This program found a monoclinic cell with the lattice parameters a = 22.929(8), b = 27.309(5), c = 4.4.1020(8) Å, β = 90.15(10)°. The figures of merit M_{20} and F_{20} (de Wolff, 1968; Smith & Snyder, 1979) for assessing the quality of the solution were $M_{20} = 37$, $F_{20} = 267$ (0.0014, 53).

In order to determine the space group, these initial lattice parameters, together with zero- shift, three profile parameters [pseudo-Voigt function (Snyder 1993)] and one Bérar & Baldinozzi (1993) asymmetry parameter were refined using the iterative decomposition algorithm introduced first by Le Bail (1988; full powder refinement without structural constraints) implemented in the program FullProf (Rodriguez-Carvajal, 2006). The space group was set to $P2/m$. The final profile residual of this procedure converged to $R_{\mathrm{wp}} = 3.14$ %.

Systematic absences of $h0l$ reflections with l odd and $0k0$ reflections with k odd unambiguously determined the space group $P2_1/c$.

To obtain a starting structural model, Monte Carlo simulated-annealing calculations were attempted with the global optimization program FOX (Favre-Nicolin & Černý, 2002) but it always failed. In all cases, the agreement between the simulated pattern and the experimental one remained unsatisfactory. Direct methods implemented in the program EXPO2004 (Altomare *et al.* 2004) for the solution of crystal structures from powder data were also used but no sensible solution was obtained.

Because traditional approaches to find the starting structural model from powder data were not successful, we had to use data obtained from an older single crystal measurement of an owyheeite crystal (Makovicky *et al.*, 1998). By applying direct methods implemented in the program SHELXTL (Sheldrick, 1997) to this dataset these authors extracted a basic structural model which had very similar unit cell parameters and the same space group as determined from the synchrotron powder study (this article). The starting model consisted of 26 independent atoms, 4 pure Pb sites, 5 pure Sb sites, 2 pure Ag sites, one mixed Pb/Sb site and 14 S sites. But this model could not be refined to satisfactory R factors because of the above mentioned twinning. Thus, we decided to use this partially refined single-crystal structural model as a starting structure model in our powder synchrotron study.

1.3.2. Rietveld Refinement

The starting structural model was then introduced in the program FullProf (Rodriguez-Carvajal, 2006) for Rietveld analysis. The Rietveld refinement was carried out in the angular range 2.47–30.71 $2\theta°$ containing 3304 reflections. Intensities were corrected for absorption by applying absorption correction coefficient μR (see FullProf Manual for details).

A pseudo-Voigt function (Snyder 2000) was selected to describe individual line profiles, with a variation of the mixing factor η defining the Lorentzian and the Gaussian character of the peaks shape. Corrections taking into account the asymmetry of the peaks caused by axial divergence were used according to Bérar & Baldinozzi (1993). The angular variation of the line width was accounted for by using the Cagliotti function (Cagliotti *et al.*, 1958). Intensities within 15 times the full width at half maximum of a peak were considered to contribute to the central reflection. The background was determined by linear interpolation between consecutive breakpoints in the pattern. The convergence criterion, ε, forcing the termination of the refinement when parameter shifts $< \varepsilon \times \sigma$, was set to 0.05. The corrections for the anomalous dispersion of Pb, Ag, and Sb atoms were applied according to the program DISPANO (Laugier, 1999).

The refinement was done in consecutive steps with the atomic coordinates and thermal parameters held fixed in the initial calculations. They were allowed to vary after the scale factor, zero-shift, peak shape parameters and lattice parameters were close to convergence to their optimum values. The isotropic temperature factors (B_{iso}) for like atoms were constrained to be equal.

During the refinement of atom positions, a soft constraint for the Sb7-S6 bond was applied assuming an Sb-S distance of 2.50 Å. A low weight was given to this soft constraint by applying sigma values of 0.01 to the prescribed Sb-S distance. Without this soft constraint this value refines to unrealistic short value of 2.36 Å.

Table 2. Details of Rietveld refinement for owyheiite.*R* agreement factors defined according to McCuster *et al.* (1999) and Rodriguez-Carvajal (2006).

Formula	$Ag_{1.5}Pb_{4.43}Sb_{6.07}S_{14}$
Crystal system	Monoclinic
Space group	$P2_1/c$
a(Å)	4.1035(1)
b(Å)	27.3144(3)
c(Å)	22.9366(3)
β (°)	90.359(1)
V(Å^3)	2570.79(8)
Z	4
D_c(g/cm^3)	5.86
2θ range (°)	2.470–30.710
Step size (°)	0.004
2θ FWHM (°)	0.019–0.053
Wavelength (Å)	0.49954
Linear absorption coef. (cm^{-1})	163
No. of atoms in asym.unit	26
No. of contributing reflections	3304
No. of structural parameters	78
No. of profile parameters	5
R_p	0.0314
R_{wp}	0.0409
R_{exp}	0.0191
χ^2	4.59
R_B	0.0352
R_F	0.0388
Largest diff. peak/hole (e$^-$.Å^{-3})	0.78/–1.08

When the occupancy factor of the Pb5/Sb5 position was refined, temperature factors were held fixed and refinement was performed varying only the scale factor, occupancy factor and atomic coordinates. This procedure was followed in order to reduce the possible correlations between the temperature and occupancy factors.

Similarly to structure determinations of complex Pb-Sb sulphosalts such as pillaite (Meerschaut *et al.*, 2001), pellouxite (Palvadeau *et al.*, 2004), rouxelite (Orlandi *et al.*, 2005), we attempted to adjust the structural formula to the chemical composition from the electron microprobe. To do this we adjusted site occupancies resulting from the Rietveld refinement to fit the chemical composition given by electron microprobe analysis (especially Pb/Sb ratio). However, this has led in all cases but one to the rapid worsening of the agreement factors. Nevertheless, in the case of originally pure Sb2 site, the refinement of occupancy disclosed a mixed Ag2/Sb2 site. The occupancy of this site was set to correspond to the silver content according to the microprobe analysis.

For the last Rietveld cycles, 93 parameters were refined, as follows: 1 scale factor, 1 zero-point, 4 cell parameters, 4 profile parameters, 1 asymmetry parameter, 4 isotropic thermal parameters (the isotropic temperature factors for like atoms were constrained to be equal), 78 coordinates of 26 atoms and a parameter G1 linked to the preferred orientation along [100] according to the March-Dollase (Dollase, 1986) function. The refinement converged to satisfactory residual factors $R_{\text{Bragg}} = 3.55$ %, $R_{\text{wp}} = 4.08$ %. No structurally meaningful residuals were found in the difference Fourier maps and maximum differences were not greater than 1.08 ± e.Å^{-3} (Table 2). The details of the refinement are reported in Table 2. Figure 1 shows the final Rietveld plot.

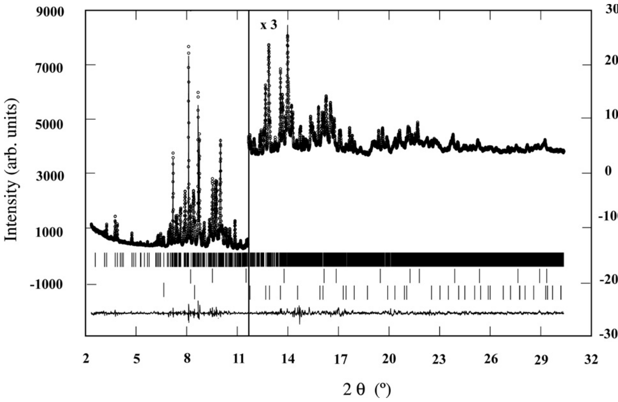

Fig. 1. Final Rietveld plot of owyheeite. Observed data point are indicated by circles, the best-fit profile (upper trace) and the difference pattern (lower trace) are solid lines. The vertical bars indicate the positions of Bragg peaks. The scale splitting of the powder pattern is indicated by the scales on y axes.

2. Structure description

The structure of owyheeite contains 26 independent atoms, four Pb sites, one mixed Pb/Sb site, five Sb sites, one Ag site, one mixed Ag/Sb site and 14 S sites. All of them are in a general Wyckoff position 4*e* of the space group $P2_1/c$; no special positions are occupied. Figure 2 represents a projection along *a* of the crystal structure of owyheeite. Atomic coordinates, site occupancy factors and isotropic displacement parameters U_{iso} are in Table 3.

The refined structure is in fact a 4 Å substructure, parallel to many such refinements of complex Pb-Sb sulphosalts in literature, e.g. pillaite (Meerschaut *et al.*, 2001), pellouxite (Palvadeau *et al.*, 2004), rouxelite (Orlandi *et al.*, 2005). The 8 Å superstructure reflections have been observed in the complex synchrotron powder pattern but they were very weak (Fig. 3). The weak 2*a* superstructure is likely indicative of an ordering along *a* of Pb/Sb and Sb/Ag as well as of two distinct Sb coordinations within the 8 Å period. Because of the scarcity and weakness of the reflections related to the 2*a* superstructure, the crystal structure refinement was limited to the reduced *a* parameter. The Le Bail fit of the 8 Å cell has been performed and confirmed the presence of weak superstructure reflections (Fig. 3).

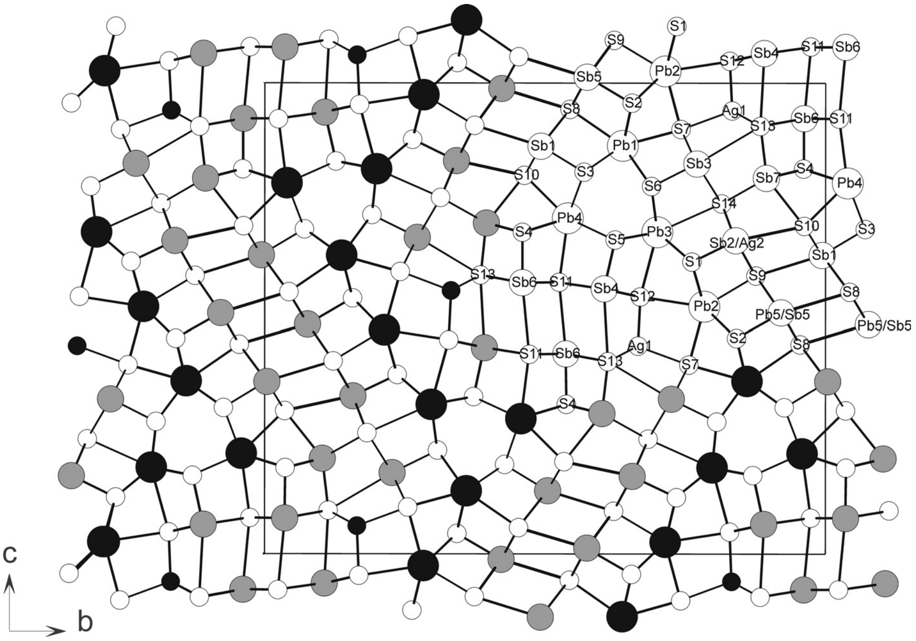

Fig. 2. Projection along *a* of the crystal structure of owyheeite. Atoms in order of decreasing size: Pb (black); Pb/Sb, Sb, Sb/Ag (all grey and the same size), Ag (black), S (white).

Table 3. Site occupancy factors (s.o.f.), atomic coordinates and equivalent isotropic displacement parameters U($_{iso}$) for the crystal structure of owyheeite. Isotropic displacement parameters for like atoms were constrained to be equal.

Atom	s.o.f.	*x*	*y*	*z*	*U*(eq/iso)
Pb1	1	0.2736(12)	0.8610(1)	0.3666(1)	0.0500(4)
Pb2	1	0.7306(12)	0.2152(1)	0.4750(2)	0.0500(4)
Pb3	1	0.7265(16)	0.2989(1)	0.3169(1)	0.0500(4)
Pb4	1	0.2896(11)	0.9590(1)	0.2129(1)	0.0500(4)
Pb5	0.43	0.2249(14)	0.0768(2)	0.4882(2)	0.0500(4)
Sb5	0.57	0.2249(14)	0.0768(2)	0.4882(2)	0.0500(4)
Sb1	1	0.7597(21)	0.0056(2)	0.3656(2)	0.0482(8)
Sb2	0.5	0.2311(24)	0.1581(2)	0.3353(3)	0.0482(8)
Ag2	0.5	0.2311(24)	0.1581(2)	0.3353(3)	0.0482(8)
Sb3	1	0.2211(20)	0.2277(2)	0.1721(2)	0.0482(8)
Sb4	1	0.2096(19)	0.1074(2)	0.9377(2)	0.0482(8)
Sb6	1	0.7972(18)	0.0379(2)	0.0756(3)	0.0482(8)
Sb7	1	0.3208(18)	0.1037(2)	0.2026(3)	0.0482(8)
Ag1	1	0.7352(26)	0.1662(2)	0.0590(3)	0.049(3)
S1	1	0.2174(70)	0.2365(7)	0.3804(9)	0.0442(16)
S2	1	0.2102(74)	0.1568(7)	0.5435(10)	0.0442(16)
S3	1	0.7352(69)	0.9287(7)	0.3103(8)	0.0442(16)
S4	1	0.7472(67)	0.0386(7)	0.1826(8)	0.0442(16)
S5	1	0.1916(62)	0.1268(7)	0.8338(8)	0.0442(16)
S6	1	0.2649(67)	0.3085(4)	0.2201(8)	0.0442(16)
S7	1	0.7303(71)	0.2569(7)	0.0991(9)	0.0442(16)
S8	1	0.7576(66)	0.0448(8)	0.5558(8)	0.0442(16)
S9	1	0.6847(64)	0.1235(8)	0.4094(9)	0.0442(16)
S10	1	0.2713(58)	0.0361(7)	0.3041(7)	0.0442(16)
S11	1	0.2349(74)	0.9741(7)	0.0765(9)	0.0442(16)
S12	1	0.7858(69)	0.1702(7)	0.9539(9)	0.0442(16)
S13	1	0.2437(70)	0.1141(7)	0.0923(9)	0.0442(16)
S14	1	0.7551(68)	0.1846(7)	0.2565(8)	0.0442(16)

Unit cell (space group $P2_1/c$): $a = 4.1035(1)$, $b = 27.3144(3)$, $c = 22.9366(3)$ Å, $\beta = 90.359(1)°$, $V = 2570.78(6)$ Å^3

2.1. Aggregates of coordination polyhedra

The 4 Å structure of owyheeite has the following aggregates of coordination polyhedra:

(1) three-fold columns of bicapped trigonal coordination prisms Pb1-Pb3-Pb4 (Fig. 4)
(2) two-strand ribbons of Sb4 and Sb6 (Fig. 4)
(3) four-strand ribbons Sb3- Sb2/Ag2 - Pb5/Sb5 – Sb1 with peculiar Sb7 coordination polyhedra attached laterally and shifted by 2 Å against the cations in this ribbon (Fig. 4).

The three-fold columns of Pb coordination prisms are surrounded by two four-strand ribbons and one two-strand ribbon, approximating only vaguely a trigonal arrangement.

The two-strand [001] ribbons form a lone electron pair micelle (i.e. a common space for their non-bonded electron pair) which is closed at both ends by coordination tetrahedra of Ag12. The same is true for the extended lone electron pair micelle of the four-strand ribbon (sub (3) in the above listing). General organization of the three types of aggregates of coordination polyhedra enhancing the lone electron pair micelles is featured in Fig. 5.

2.2. Coordination polyhedra

The description of the cation coordination is briefly presented taking into account the chemical bonding quantified through bond valence calculations (Tables 4 to 6). Owing to the complexity of the structure, the coordination of S sites will not be detailed. The bond valence calculations were carried out according to the Brese & O'Keeffe (1991) using the program Ivton (Balić-Žunić & Vicković, 1996).

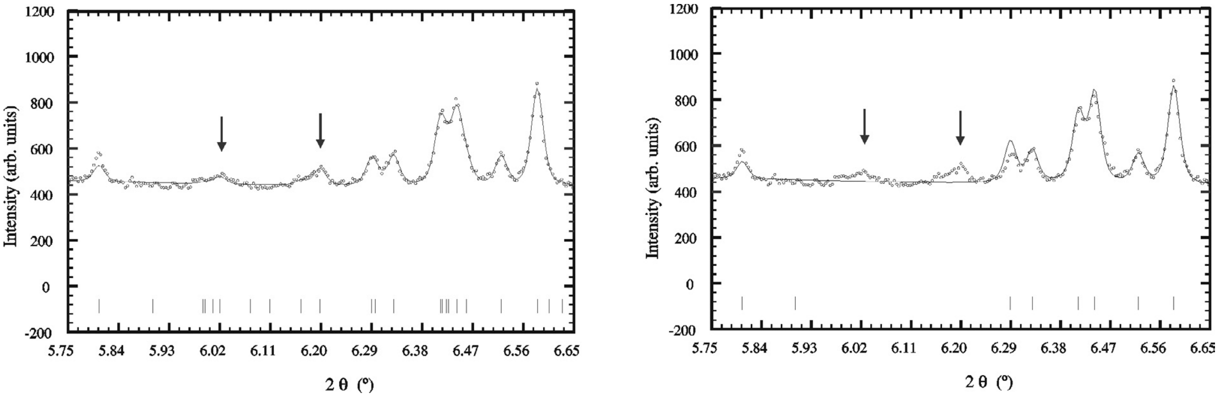

Fig. 3. Le Bail fit of owyheeite indicating the presence of weak superstructure reflections (marked by arrows). The left picture (Le Bail fit of the 8 Å cell) shows good agreement between the observed and calculated patterns, while the right picture (Le Bail fit of the 4 Å) shows that these reflections are not fitted in the 4 Å cell. The vertical bars indicate the positions of Bragg peaks.

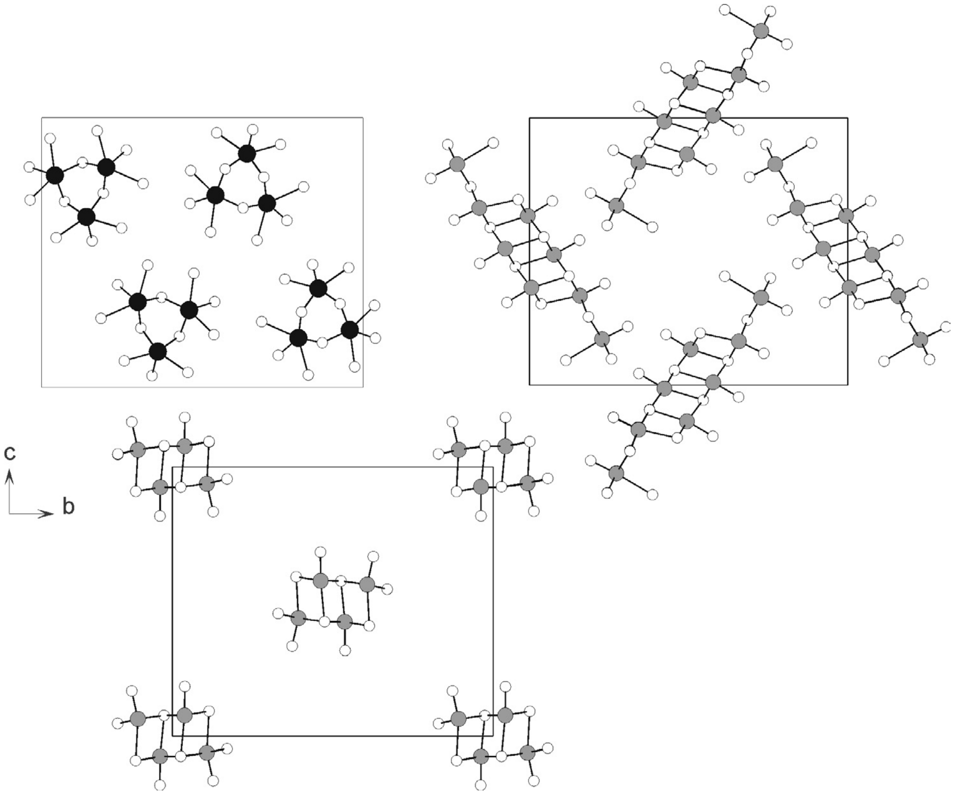

Fig. 4. Aggregates of coordination polyhedra in the structure of owyheeite: three-fold columns of bicapped trigonal coordination prisms Pb1-Pb3-Pb4 (upper left), four-strand ribbons Sb3- Sb2/Ag2 - Pb5/Sb5 – Sb1 (upper right), two-strand ribbons of Sb4 and Sb6 (bottom).

Lead sites (Table 4):

- three Pb1, Pb3, Pb4 polyhedra are typical lead coordination prisms, with all Pb-S distances (Table 4) between 2.81 Å and 3.42 Å. The long distances can occur either inside the coordination prisms (for Pb1 and Pb4) or in the caps (Pb3).
- flat-lying monocapped coordination prism of Pb2, which shares a horizontal edge with the tetrahedron of Ag1, again has distances typical for pure Pb: 2.93 Å to 3.18 Å.

For the above Pb cations the bond valence sums vary between 1.77–2.12 v.u., which is satisfactory considering the approximate nature of bond valence approach.

Antimony sites (Table 5):

- Sb1 site is closest to a regular bond scheme for Sb. The bond to the vertex of the coordination pyramid is the shortest one, 2.46 Å, opposed by the long distance of 3.39 Å across the lone electron pair micelle. The two shorter distances in a base of the pyramid are 2.58 Å and 2.67 Å, opposed by 3.00 Å and 3.12 Å. Thus any

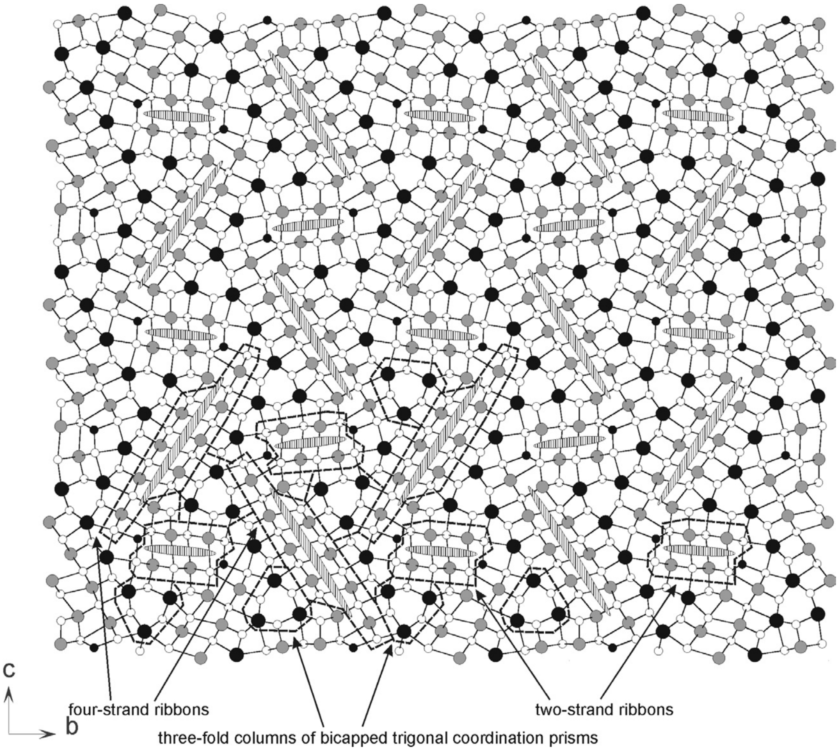

Fig. 5. General organization of the 3 types of the aggregates of coordination polyhedra in the structure of owheeite enhancing lone electron pair micelles.

Table 4. Owyheeite, interatomic distances around lead atoms with corresponding bond valences (B.V.).

		d (Å)	B.V.			*d* (Å)	B.V.
Pb1	S2	2.91(2)	0.38	Pb2	S9	2.92(2)	0.36
	S3	2.95(2)	0.34		S7	2.94(2)	0.34
	S7	2.95(2)	0.34		S2	2.97(3)	0.32
	S2	2.98(3)	0.31		S1	3.01(2)	0.27
	S6	3.10(2)	0.22		S1	3.07(2)	0.25
	S8	3.13(2)	0.21		S2	3.10(2)	0.23
	S3	3.15(2)	0.2		S12	3.17(2)	0.18
	S6	3.29(2)	0.14			**Sum**	1.95
		Sum	2.14				
Pb3	S5	2.81(2)	0.49	Pb4	S4	2.95(2)	0.33
	S6	2.92(2)	0.37		S10	2.96(2)	0.32
	S1	3.00(3)	0.29		S3	2.99(2)	0.3
	S5	3.01(2)	0.28		S11	3.16(2)	0.19
	S1	3.07(2)	0.24		S4	3.18(3)	0.18
	S6	3.15(2)	0.2		S5	3.24(2)	0.15
	S12	3.26(2)	0.15		S3	3.30(2)	0.13
	S14	3.41(2)	0.1		S5	3.34(2)	0.17
		Sum	2.12			**Sum**	1.77

Table 5. Owyheeite, interatomic distances around antimony atoms with corresponding bond valences (B.V.).

		d (Å)	B.V.			*d* (Å)	B.V.
Sb1	S3	2.45(2)	0.98	Sb3	S6	2.47(2)	0.94
	S10	2.58(2)	0.7		S7	2.73(3)	0.47
	S10	2.66(2)	0.56		S7	2.80(3)	0.39
	S8	3.00(3)	0.23		S14	2.97(3)	0.24
	S8	3.11(3)	0.17		S14	3.14(2)	0.15
	S9	3.38(2)	0.08		S13	3.60(2)	0.04
		Sum	2.72			**Sum**	2.23
Sb4	S5	2.44(2)	1.02	Sb6	S4	2.46(2)	0.96
	S12	2.47(3)	0.94		S11	2.50(2)	0.87
	S11	2.89(2)	0.30		S13	2.79(2)	0.39
	S12	2.94(2)	0.26		S11	2.89(3)	0.3
	S11	3.20(2)	0.13		S13	3.10(2)	0.17
	S13	3.55(2)	0.05		S11	3.50(2)	0.06
		Sum	2.70			**Sum**	2.75
Sb7	S4	2.53(2)	0.79				
	S13	2.56(2)	0.74				
	S10	2.97(2)	0.24				
	S4	2.98(3)	0.24				
	S14	3.09(2)	0.18				
	S14	3.44(2)	0.07				
		Sum	2.26				

splitting of the position in the 4 Å substructure is insignificant.

- The marginal pyramid Sb3 has cation-vertex distance of 2.47 Å. The Sb-S distances in the base of the pyramid follow the same distribution scheme as those of Sb4: 2.73 Å opposed by 3.14 Å and the conjugate 2.80 Å opposed by 2.97 Å.

- Sb4 and Sb6, forming the two-strand ribbon, have an asymmetric square pyramidal coordination. They have a typical Sb-S distance to the vertex of the coordination pyramid (2.44 Å and 2.46 Å, respectively), one more such distance in the base of the pyramid (2.47 Å and 2.50 Å), opposed by a long distance (3.20 Å and 3.10 Å in the two polyhedra). However, the distance conjugate with the short one is 2.89 Å and 2.79 Å, opposed by 2.94 and 2.89 Å. This type of configuration is typical for a split Sb site, with two partial atoms lying in the base of the pyramid, along the 2.8–2.9 Å join. They share the two short distances and the long distances opposing them (Makovicky *et al.*, 2006). Based on the M-S distances observed, a similar scheme can be drawn for the Sb atom in the mixed Pb5/Sb5 site.
- The last cation site is an unusual cation site, designated as Sb7. It is situated 2 Å "below" the rest of cation sites of the four-strand ribbon, on a line connecting S10 and S13, and its S4 ligands deviate from the plane of other S ligands in the ribbon. It has two short M-S distances, 2.53 and 2.56 Å, at about 90° at one another. The remaining distances are 2.98 Å and 2.98 Å as well as 3.09 Å and 3.44 Å across the micelle. Although various partial analogies to this coordination have been invoked, we do not have a reliable one. Especially, because we do not deal with a single position but with at least two overlapping fractional sites.

The formation of the Sb7 site might be a result of compatibility with the antimony Sb6 site in the two-strand ribbon on the one hand and with the distorted PbS-like archetype on which a configuration of the lone electron pair micelles of owyheeite is based on the other hand.

Bond valence sums for antimony atoms fall into two categories. Atoms No 1, 4, 6 have bond valence sums fairly in accordance with the expected valence 3 v.u.. All correspond to variously split positions. A small difference in the expected and calculated bond valence sums confirms the splitting of these atoms.

Sb3 and Sb7 (2.23 and 2.26 v.u.) present a strong deficit from expected values of bond valence sum; obviously, we do not deal with a single position but with at least two overlapping fractional sites which would explain such deficit.

Ag sites (Table 6):

- the Ag1 is a slightly distorted tetrahedron with M-S distances ranging from 2.42 to 2.64 Å. Bond valence sum of 1.31 v.u. in this site can be caused by a small admixture of copper resulting in shortened metal-sulphur distances. After the inclusion of Cu (0.25 at. % or 0.07 atomic coefficients according to the electron microprobe analysis) the calculated bond valence sum for the site decreases to 1.26 v.u.

Mixed sites (Table 6):

- The Pb5/Sb5 site is positioned along the median portion of the four-stranded ribbon and was refined as a mixed site with 0.43 Pb and 0.57 Sb s.o.f.. It displays appropriately shortened M5-S distances. The M5-S2 distance to the vertex of the square coordination prism is 2.53 Å, two shorter distances in the base of this pyramid are 2.62 Å and 2.81 Å, those opposing them are 2.91 Å and 3.12 Å in that order, and the distance spanning the lone electron pair micelle is 3.47 Å.

The calculated average bond valence sum for this mixed position is 2.62 v.u. While the bond valence sums are overestimated for Pb atoms and underestimated for Sb ones, the calculated bond valence sum for this mixed position, taking into account the occupancy factors, is in a good agreement with theoretical ones (Table 6).

- Ag2/Sb2 mixed site was revealed by bond length analysis and confirmed by Rietveld refinement. Although Ag and Sb have close Z values, the X-ray wavelength used, 0.49953 Å, and subsequent corrections for anomalous dispersion enhanced the contrast between these species. The Sb2 polyhedron deviates substantially from the known distribution schemes of Sb-S bonds. In the pyramidal base, a distance of 2.69 Å opposes 2.75 Å, whereas 2.91 Å opposes 3.07 Å. The diamond-like shape of the base reminds of those observed for pure Ag sites in diaphorite (Armbruster *et al.* 2003). For the Ag3 site in this structure, the bond of 2.524 Å is opposed by 2.535 Å whereas 3.032 Å is opposed by 3.232 Å. Perpendicular to this base, 2.676 Å is opposed by 3.232 Å across the lone electron pair micelle of adjacent Sb atoms. The latter pair of distances corresponds to 2.38 Å opposed by 3.41 Å in owyheeite. The Ag4 site in diaphorite is similar: 2.551 Å opposed by 2.582 Å, 3.167 Å *vs.* 3.241 Å in the pyramidal base, and 2.629 Å *vs.* 3.307 Å perpendicular to the base of the coordination pyramid. In freieslebenite (Ito and Nowacki, 1974), the Ag-S bond of 2.522 Å opposes that of 2.535 Å, and 2.687 Å opposes 2.928 Å; the short bond perpendicular to the base is 2.687 Å long.

Based on the comparison with these pure Ag polyhedra, the Sb2 site of the 4 Å substructure was refined as a mixed Sb2/Ag2 site. The occupancy factors were set to correspond to the silver content determined by electron microprobe analysis.

The calculated bond valence sum of 2.02 v.u. corresponds well to the theoretical value of 2 v.u.

Conclusions

The crystal structure of owyheeite contains two types of [100] rods. Both have a simple internal structural arrangement, transitional between that observed in the PbS and SnS archetypes, which were defined for sulphosalts by Makovicky (1997). These rods are based on the above described ribbons of Sb polyhedra, the intervening lone electron pair micelle and the Pb polyhedra which envelop them.

Because of the chess-board arrangement of these rods in the structure, owyheeite belongs to the broad structural family of sulphosalts with such a structural arrangement

Table 6. Owyheeite, interatomic distances around silver atom and two mixed (Pb/Sb), (Ag/Sb) positions with corresponding bond valences (B.V.).

		d (Å)	B.V.(Pb)	B.V.(Sb)			*d* (Å)	B.V.(Ag)	B.V.(Sb)
Pb5/Sb5	S2	2.52(2)	1.06	0.81	Ag2/Sb2	S1	2.37(2)	0.54	1.22
	S8	2.62(2)	0.82	0.63		S9	2.68(2)	0.24	0.53
	S8	2.81(3)	0.49	0.38		S14	2.74(2)	0.2	0.44
	S9	2.91(2)	0.37	0.28		S14	2.90(3)	0.13	0.29
	S9	3.12(2)	0.21	0.16		S9	2.97(2)	0.11	0.24
	S8	3.47(2)	0.08	0.06		S10	3.41(2)	0.03	0.07
		Sum	3.03	2.32			**Sum**	1.25	2.79
	Average/Theor.*		2.62/2.57		**Average/Theor.***			2.02/2.00	

		d (Å)	B.V.
Ag1	S12	2.42(2)	0.48
	S13	2.58(2)	0.3
	S13	2.63(3)	0.27
	S7	2.64(2)	0.26
		Sum	1.31

* According to the s.o.f. Theor.: mean of the basis of valences 2 for Pb, 3 for Sb and 1 for Ag. Average: mean from the bond valence values.

(Makovicky 1993) which contains, among other sulphosalt phases, kobellite (structure by Miehe, 1971), izoklakeite (Makovicky & Mumme, 1986; Armbruster & Hummel, 1987) and eclarite (Kupcik, 1984). In spite of the common chess-board scheme, each of these phases contains specific features (Makovicky, 1993). Thus, owyheeite differs from any of these phases by the position and structural role of the AgS_4 tetrahedron and by a presence of the unique Sb7 polyhedron.

Closest to the owyheeite structure are the structures of $Eu_3Sb_4S_9$ (Lemoine *et al.*, 1981) and the isotypic $Sr_3Sb_4S_9$ (Cordier *et al.*, 1982). Although the structure of owyheeite resembles a higher homologue of these two chess-board structures, the above mentioned polyhedra of Ag and Sb7 do not have counterparts in these structures. These two kinds of polyhedra are necessary in order to accommodate problems arising from the increase in rod diameters against those observed in $Eu_3Sb_4S_9$.

A better understanding of crystal chemistry of owyheeite with relation to the structure arrangement, especially the formation of superstructures in relation to the Ag content, presents an interesting field of research. However, this research is limited by the difficulty in obtaining crystals suitable for single crystal diffraction experiments.

A detailed study of the chemical compositions of owyheeite samples from different lodes of the Kutná Hora polymetallic deposit with relation to the structural arrangement will be a subject of a separate article.

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