MINERALOGICAL CRYSTALLOGRAPHY AND CRYSTAL CHEMISTRY

New Data on the Composition and Crystal Structure of Galkhaite $(Hg,Cu)_6(Cs,Tl)(As,Sb)_4S_{12}$

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Abstract—The composition of galkhaite from the Gal-Khaya deposit (Yakutia, Russia) and Chauvay Mine (Kyrgyzstan) has been examined by electron microprobe. A significant Cs content (up to 6.64 wt %) has been established in the mineral from both deposits; earlier, it had been not detected by either chemical or spectral analyses. The empirical formulas of galkhaite are $(Hg_{4.89}Cu_{0.92}Zn_{0.07})_{5.88}(Cs_{0.71}Tl_{0.17})_{0.88}(As_{3.98}Sb_{0.17})_{4.15}S_{12.10}$ and $(Hg_{4.64}Cu_{0.98}Zn_{0.34})_{5.96}(Cs_{0.85}Tl_{0.04})_{0.89}(As_{3.68}Sb_{0.42})_{4.10}S_{12.05}$ at the Gal-Khaya deposit and Chauvay Mine, respectively. The crystal structure of galkhaite from the Chauvay Mine (cubic, $I43m$, $a = 10.4144(1)$ Å, $V = 1129.5(2)$ Å^3, $Z = 2$) for the composition $[Hg_{4.83}(Cu,Zn)_{0.98}\square](Cs_{0.71}Tl_{0.14}\square)(As_{3.44}Sb_{0.56})S_{12}$ has been determined by direct methods and refined to $R = 0.0203$. The structure of galkhaite is a framework consisting of vertex-shared $[(Hg,Cu)-S_4 \; 2.5068(3)$ Å] tetrahedrons of the same orientation as large cavities formed in the initial sphalerite structural type due to eight anion vacancies: two $[S_4]-$ tetrahedrons at the point of origin and at the center of the I-cell and 12 cation vacancies as 2 cation octahedrons around the 000 and ½½½ sites.

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Galkhaite was discovered from ores of the Gal-Khaya, Russia, and Khaydarkan, Kyrgyzstan, mercury deposits (Gruzdev et al., 1972). Despite the complex composition of the mineral, the authors preferred the idealized formula $HgAsS_2$ having excluded Cu, Zn, Tl, and Sb from the empirical version, suggesting that they are sporadic isomorphic admixtures. Botinelli et al. (1973) reported the second finding of galkhaite at the Getchel Mine in the United States and gave the extended formula taking into account the aforementioned elements: $(Hg,Cu,Tl,Zn)(As,Sb)S_2$.

The structural data on galkhaite from the Getchel Mine (Divjaković and Nowacki, 1975) and Gal-Khaya deposit (Kaplunnik et al., 1975) were published almost simultaneously. It should be noted that the distinct formula $[Hg_{0.76}(Cu,Zn)_{0.24}]_{12}Tl_{0.96}(AsS_3)_8$ was given for galkhaite from the Getchel Mine. Formula $HgAsS_2$ was used to resolve the mineral structure from the Gal-Khaya deposit. Later on, galkhaite was identified in the ore of the Chauvay Hg deposit (Volgin et al., 1981), but the complete composition of the mineral was not published.

The composition of galkhaite from type deposits and Chauvay was previously determined by chemical analysis, which did not allow ascertaining concentration, partitioning, and correlation of the major components. Therefore, in the early 1981, we examined the chemical composition of galkhaite from the Gal-Khaya type deposits on an electron microprobe[1]. It turned out that the mineral contains much more Tl than was previously reported by Gruzdev et al. (1972) and Cs is predominant. Therefore, we anticipated the presence of Cs in galkhaite from the Khaydarkan and Chauvay deposits, which required verification. In the same year, Chen and Szymański (1981) studied in detail galkhaite from the Getchel Mine. According to electron microprobe data, the mineral contains variable amounts of Cs, whose content is identical to that of Tl or two to seven times higher than the latter. The authors suggested one more version of the galkhaite formula $(Hg,Cu,Zn,Tl,Fe,\square)_6(Cs,Tl,\square)(As,Sb)_4S_{12}$. A short time later, Chen and Szymański (1982) compared the properties and chemical composition of galkhaite from the Getchel Mine and Khaydarkan deposit. A relatively high Cs content and very low Tl concentration (lower than previously reported) was established in galkhaite from the latter deposit. In 1986, we specified the chemical composition of galkhaite from the Chauvay deposit[2] by electron microprobe and verified a Cs content of 5.86–6.64 wt % in the mineral (Table 1). It should be noted that before

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[1] The samples of the mineral were donated by V.S. Gruzdev.
[2] The galkhaite ore samples were found by N.K. Mortsev during field work at the deposit.

Table 1. Chemical composition of galkhaite, wt %

Deposit	Grain number	S	Hg	Zn	Cu	Sb	As	Cs	Tl	Total
Gal-Khaya	1	21.14	53.38	N.d.	3.29	0.41	16.78	5.68	N.d.	100.69
	2	20.92	50.90	0.45	3.15	0.83	16.08	4.89	2.25	99.48
	3	21.37	53.82	N.d.	3.36	0.33	16.84	5.47	0.28	101.46
	4	21.16	51.60	0.58	2.67	0.85	16.06	5.00	2.12	100.04
	5	20.70	52.47	0.16	3.16	0.86	15.60	4.47	2.43	99.83
	6	20.62	50.87	0.39	3.02	1.32	15.54	4.58	3.36	99.70
	7	20.54	53.55	0.34	3.10	0.65	16.01	4.93	2.27	101.40
	8	20.75	52.09	0.24	2.96	1.52	15.19	4.92	1.92	99.60
	9	20.58	53.81	N.d.	3.34	0.36	16.55	5.72	0.33	100.70
	10	19.71	51.06	N.d.	3.32	1.90	15.26	4.70	3.98	99.93
	11	20.44	51.68	0.39	3.04	2.62	15.49	3.96	2.32	99.94
	12	20.40	51.99	0.17	3.07	1.47	15.35	6.08	0.85	99.38
	Average	20.69	52.27	0.23	3.12	1.09	15.90	5.03	1.84	100.17
Chauvay	1	21.04	50.25	1.00	3.45	3.07	14.92	6.04	0.52	100.29
	2	20.84	50.33	1.05	3.43	2.72	15.05	6.12	0.36	100.10
	3	20.85	50.60	0.97	3.48	2.77	15.10	5.88	0.39	100.04
	4	20.67	50.84	1.11	3.33	2.87	14.89	6.11	0.33	100.15
	5	20.82	50.47	1.13	3.56	2.34	15.32	6.44	0.25	100.33
	6	20.82	50.37	1.05	3.46	3.06	14.57	6.02	0.52	99.87
	7	20.96	50.36	1.01	3.48	2.83	14.83	5.95	0.51	99.93
	8	20.71	50.64	1.39	3.54	3.25	14.55	5.88	0.45	100.40
	9	20.80	50.29	1.17	3.42	2.04	14.92	6.57	0.24	99.45
	10	20.92	50.47	0.89	3.46	3.06	14.59	5.86	0.61	99.86
	11	21.09	51.13	1.30	3.32	2.88	14.99	5.88	0.38	100.97
	12	20.94	50.71	1.32	3.24	2.70	14.80	5.99	0.36	100.06
	13	21.09	50.15	1.51	3.41	2.47	15.12	6.43	0.26	100.44
	14	20.90	49.73	1.29	3.28	2.80	14.83	5.91	0.49	99.23
	15	21.01	51.24	1.28	3.32	2.95	14.72	5.87	0.49	100.88
	16	21.13	49.96	1.36	3.24	3.32	15.06	6.08	0.43	100.58
	17	20.81	49.92	1.28	3.28	2.96	14.84	5.99	0.60	99.68
	18	20.95	50.44	1.42	3.14	2.75	14.87	6.07	0.33	99.97
	19	21.31	50.27	1.27	3.24	2.36	15.64	6.64	0.36	101.09
	Average	20.93	50.44	1.20	3.37	2.80	14.93	6.09	0.41	100.17

Note: JXA-5A electron microprobe, analyst L.N. Pospelova, Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences. The empirical formula of galkhaite from Gal-Khaya calculated on the basis of average composition is $(Hg_{4.89}Cu_{0.92}Zn_{0.07})_{5.88}(Cs_{0.71}Tl_{0.17})_{0.88}(As_{3.98}Sb_{0.17})_{4.15}S_{12.10}$. The empirical formula of galkhaite from Gal-Khaya calculated on the basis of average composition is $(Hg_{4.64}Cu_{0.98}Zn_{0.34})_{5.96}(Cs_{0.85}Tl_{0.04})_{0.89}(As_{3.68}Sb_{0.42})_{4.10}S_{12.05}$.

1981, in addition to the elements involved in the proposed empirical and idealized formulas, no significant concentrations of other elements, in particular, Cs, were detected in galkhaite elsewhere.

Pobedimskaya et al. (1991) reported the structure of Ag-bearing galkhaite in a review on classification of sulfides and sulphosalts. Based on the concept of priority anion packing in the organization of the structure elaborated by Belov (1947), the authors studied in detail the topological nuances in the structure of galkhaite variable in composition.

This study is focused on the chemical features of galkhaite from the Gal-Khaya and Chauvay deposits and refines the crystal structure of the mineral from Chauvay. Our investigation of the structures of minerals with heavy cations showed that the structure is

often controlled by the geometry of cation matrices (Borisov et al., 2002). Therefore, this aspect is of interest for galkhaite.

PROPERTIES AND COMPOSITION OF GALKHAITE

Galkahite grains from the Gal-Khaya and Chauvay deposits are identical in morphology to those from the Khaydarkan deposit. The ore of this deposit is dominated by cubic crystals ranging from a few micrometers to 1−3 mm and occasionally up to 1 cm in size, as well as by aggregates of their crystals and impregnation. Gruzdev et al. (1972) and Volgin et al. (1981) described the properties of the mineral in detail. According to our data, the experimental density of galkhaite from the Gal-Haya, Khaydarkan, and Chauvay deposits is 5.4, 5.7, and 5.53 g/cm^3, respectively. The variable density of the mineral is undoubtedly caused by variable composition of the compound. The correct determination of the density requires a choice of grains close in composition, which is hardly feasible due to the variable composition of individual mineral grains noted even at the first stage of investigating the mineral. Galkhaite also varies in color; it is mainly brownish orange−red at the Gal-Khaya and brighter orange−red or almost red, at the Chauvay. The color of the compound appears to be controlled by variable concentrations of the same components. In particular, the mineral from the Gal-Khaya deposit is depleted in Zn and Sb by an order of magnitude, contains less Cs, but is markedly enriched in Tl and slightly in Hg and As (Table 1).

According to optical and electron microprobe study, single crystals of galkhaite from both deposits are unzoned in contrast to some crystals from the Getchel Mine (Chen and Szymański, 1981).

We have the examined chemical composition of 12 galkhaite crystals from Gal-Khaya and 19 crystals from Chauvay on a JXA-5 electron microprobe operating at 20 kV. The following synthetic standards were used: S_{K_α} and Hg_{M_α} (HgS), Sb_{L_α} (Sb$_2$S$_3$), Zn_{K_α} (ZnS), Cu_{K_α} (CuFeS$_2$), Cs_{L_α} (CsI), and Tl_{M_β} (TlGaSe$_2$). Table 1 gives the composition of galkhaite and average empirical formulas of the mineral: (Hg$_{4.89}$Cu$_{0.92}$Zn$_{0.07}$)$_{5.88}$(Cs$_{0.71}$Tl$_{0.17}$)$_{0.88}$(As$_{3.98}$Sb$_{0.17}$)$_{4.15}$S$_{12.10}$ (Gal-Khaya) and (Hg$_{4.64}$Cu$_{0.98}$Zn$_{0.34}$)$_{5.96}$(Cs$_{0.85}$Tl$_{0.04}$)$_{0.89}$ (As$_{3.68}$Sb$_{0.42}$)$_{4.10}$S$_{12.05}$ (Chauvay). Their comparison indicates that the composition of galkhaite from the Chauvay deposit is more stable; the difference between the maximum and minimum contents of components is significantly less than that in the mineral from Gal-Khaya. In addition, the mineral from the Chauvay deposit is distinguished by a more uniform distribution of elements and a slight decrease in the Hg and As concentrations; the Tl content is very low (0.*n* wt %), but the Zn, Sb, and Cs contents are elevated. It is evi-

dent that Cs is constantly contained in the described samples, whereas Tl can be lacking altogether (Chen and Szymański, 1981, Table. 1, analysis 17). This conclusion follows from comparison of mineral compositions from all four deposits (Table 2). It cannot be ruled out that a Tl variety of this sulfosalt with the formula (Hg,Cu,Zn,□)$_6$TlAs$_4$S$_{12}$ and a set of elements similar to christite, routhierite, simonite, and stalderite does exist in nature.

The mineral from Gal-Khaya, Khaydarkan, and Chauvay has been examined by semiquantitative emission spectroscopy. Cs was not detected and trace element contents were nearly identical (Gruzdev et al., 1972; Volgin et al., 1981).

EXPERIMENTAL

The unit-cell dimensions were refined and a three-dimensional set of intensities of galkhaite from the Chauvay deposit was recorded on a Bruker Nonius X8Apex diffractometer with a 4K CCD detector (*Apex2* ..., 2004). The X-ray diffraction data were obtained according to the standard procedure at 293 K (Mo$_{K_\alpha}$, graphite monochromator). The extinctions were counted semiempirically on the basis of the intensities of equivalent reflections. The structure of the compound was solved with the SIR2004 software package (Burla et al., 2005). The atomic coordinates were refined by the matrix least squares procedure in an anisotropic approximation using SHELX-97 (Sheldrick, 1998). The formula of galkhaite inferred as a result of refinement of the structure is [Hg$_{4.83}$(Cu,Zn)$_{0.98}$□$_{0.18}$](Cs$_{0.71}$Tl$_{0.14}$□$_{0.15}$)(As$_{3.44}$Sb$_{0.56}$) S$_{12}$. The experimental data on galkhaite are listed in Table 3; the final atomic coordinates and displacement parameters are given in Tables 4, 5; bond lengths, in Table 6.

DISCUSSION

Galkhaite is close to a type of fahlores whose crystal chemistry was discussed in detail by Kaplunnik et al. (1975), Divjaković and Nowacki (1975), Chen and Szymański (1981, 1982), and Pobedimskaya et al. (1991). The structure of the mineral can be represented as a lattice consisting of identically oriented vertex-shared [(Hg,Cu)S$_4$] tetrahedrons (Hg,Cu)−S 2.5068(3) Å with large cavities formed in the primary structural type of sphalerite (ZnS) as a result of 8 anion vacancies—2 tetrahedrons [S$_4$]—at the point of origin and the center of the *I*-cell and 12 cation vacancies as 2 cation octahedrons around sites 000 and ½½½. Thus, instead of 32 cations and 32 anions within 8 cells of sphalerite equivalent of the galkhaite cell, it contains 12(Hg,Cu) + 8As + 12□ and 24S + 8□ (□ is a vacancy). The partial absence of sulfur atoms results in umbellate coordination of AsSb [(As,Sb)−S 2.2804(4) Å rather than tetrahedral as characteristic of sphalerite; a large cation (Cs,Tl) occupies a site unusual of sphaler-

Table 2. Comparison of chemical compositions of galkhaite, wt %

Element	Chemical analysis					Electron microprobe analysis			
	1	2	3	4	5	6	7	8	9
S	21.00	19.31	?	?	?	21.14	19.71	19.71–21.37	20.80
Hg	47.60	49.02	50.87	51.09	50.35	53.38	51.05	50.87–53.82	50.29
Zn	3.00	0.60	N.d.	N.d.	0.45	0.00	0.00	0.00–0.58	1.17
Cu	3.49	2.85	3.20	4.88	3.50	3.29	3.32	2.67–3.36	3.42
Sb	0.59	5.51	?	?	?	0.41	1.90	0.33–2.62	2.04
As	23.60	19.49	?	?	?	16.78	15.26	15.19–16.84	14.92
Cs						5.68	4.70	3.96–6.08	6.57
Tl	0.46	2.90	0.32–0.66	0.51	3.00	0.00	3.98	0.00–3.98	0.24
Total	99.74	99.68				100.68	99.92	99.38–101.46	99.45

Element	Electron microprobe analysis							
	10	11	12	13	14	15	16	17
S	20.92	20.67–21.31	20.9	22.3	20.9–22.7	22.1	22.3	22.4
Hg	50.47	49.73–51.24	51.6	48.7	48.3–53.0	52.2	51.7	51.9
Zn	0.89	0.89–1.51	0.3	2.3	0.3–2.5	1.6	1.6	1.7
Cu	3.46	3.14–3.56	1.6	3.4	1.6–3.6	3.3	3.4	3.3
Sb	3.07	2.04–3.32	3.1	n.d.	n.d.–3.1	3.3	3.0	3.1
As	14.59	14.55–15.64	14.5	15.3	14.5–15.9	14.0	14.5	14.6
Cs	5.86	5.86–6.64	7.1	3.7	3.7–7.1	3.4	3.3	3.2
Tl	0.61	0.24–0.61	N.d.	4.2	n.d.–4.2	0.8	0.8	0.9
Total	99.87	99.23–101.09	100.7	99.9	99.9–101.8	100.7	100.6	101.1

Note: (1) Gal-Khaya; (2) Khaydarkan (Gruzdev et al., 1972); (3, 4) Chauvay; (5) Khaydarkan (Volgin et al., 1981); (6–8) Gal-Khaya: (6) Tl not detected, (7) the highest Tl content; (9–11) Chauvay: (9, 10) the lowest and highest Tl contents, respectively; (12–14) Getchell Mine: (12) Tl not detected, (13) the highest Tl content (Chen and Szymański, 1981); (15–17) Khaydarkan (Chen and Szymański, 1982). The mineral from the Getchell Mine contains 0.1–0.5 wt % Fe in five analyses, 0.5 and 1.6 wt % Ag in two analyses, and 0.4–3.1 wt % Sb in three analyses (Chen and Szymański, 1981; Table. 1). Range of content is given in columns 8, 11, and 14; n.d., not determined.

Table 3. Crystallographic data and refinement parameters of the crystal structure of galkhaite

Characteristic	Value	Characteristic	Value
a, Å	10.4144(1)	Range of θ (degree)	4.79–36.23
V, Å^3	1129.54(2)	Total reflections	6753
Space group	$I\bar{4}3m$	Unique reflections	528 ($R_{int} = 0.0335$)
Z	2	Reflections with $|F_0| \geq 4\sigma_F$	510
D_{calc}, g/cm^3	5.483	R_1	0.0203
μ, mm^{-1}	45.483	wR_2	0.0520
Crystal size, mm	$0.17 \times 0.10 \times 0.08$	$GOOF$ for F_{hkl}^2	1.278
λ, Å	0.71073	Absolute structure parameter	0.176(4)

ite in the centers of vacant cation octahedrons being coordinated by 12 S as Laves polyhedron (Cs,Tl)–S 3.8837(4) Å.

Having adverted to the crystal-forming factors (Borisov et al., 2002), recall that the structural type of sphalerite has a face-centered cell for both cations and anions. In other words, the structure results from ordering of atoms by the major crystallographic planes of {111} type with a trigonal atom net and derived planes, including {200}, with square nets. No vacant nodes occur in sphalerite itself. In galkhaite with a doubled cubic cell parameter in comparison with

Table 4. Atomic coordinates (x, y, z, Å) and displacement parameters (U_{eq}, Å^2) of galkhaite

Atom	x	y	z	FSO	U_{eq}
Hg	0.7500	0.5000	0.0000	0.8055(5)	0.03614(2)
Cu	0.7500	0.5000	0.0000	0.1625(5)	0.03614(2)
Cs	0.0000	0.0000	0.0000	0.704(2)	0.04355(8)
Tl	0.0000	0.0000	0.0000	0.146(2)	0.04355(8)
As	0.75534(1)	0.75534(1)	0.75534(1)	0.864(1)	0.01970(3)
Sb	0.75534(1)	0.75534(1)	0.75534(1)	0.137(1)	0.01970(3)
S	0.61188(2)	0.83768(4)	0.61188(2)	1.000	0.02487(7)

Note: $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$. FSO is factor of site occupancy.

Table 5. Anisotropic displacement parameters (Å^2) of the galkhaite structure

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	0.06164(6)	0.02339(2)	0.02339(2)	0.000	0.000	0.000
Cu	0.06164(6)	0.02339(2)	0.02339(2)	0.000	0.000	0.000
Cs	0.04355(6)	0.04355(6)	0.04355(6)	0.000	0.000	0.000
Tl	0.04355(6)	0.04355(6)	0.04355(6)	0.000	0.000	0.000
As	0.01970(3)	0.01970(3)	0.01970(3)	−0.00152(3)	−0.00152(3)	−0.00152(3)
Sb	0.01970(3)	0.01970(3)	0.01970(3)	−0.00152(3)	−0.00152(3)	−0.00152(3)
S	0.02741(8)	0.0198(1)	0.02741(8)	0.00103(7)	−0.0103(1)	0.00103(7)

$T = \exp(-2\pi^2(h^2 a^{*2} U_{11} + ... + 2hkl^* b^* U_{12}))$

sphalerite, the corresponding planes are {222} and {400}, which are extremely close-packed for both cations and anions. Cation and anion atom nets calculated with the CAS-PAN software package (Bliznyuk and Borisov, 1992) are presented in Figs. 1a and 1b. In fact, the sites of (Hg,Cu) and (As,Sb) cations are close to the nodes of the sublattice formed by intersection of crystallographic planes (222), (22$\bar{2}$), and (2$\bar{2}$2); deviations do not exceed 0.1 Å. Similar atomic nets of anions have greater deviations (up to 0.4 Å), indicating the leading role of heavy cations in this structure.

Table 6. Interatomic distances (Å) in the structure of galkhaite

Hg–S	2.5068(3) 4x
As–S	2.2804(4) 3x
Cs–S	3.8837(4) 12x

The structure of galkhaite may be represented the most graphically with help of two sorts of face-shared cubic subcells with (As,Sb) atoms at vertices ($a_{As} \approx a/2$). One of them is body-centered by large cation (Cs,Tl) and does not contain other atoms. Face-

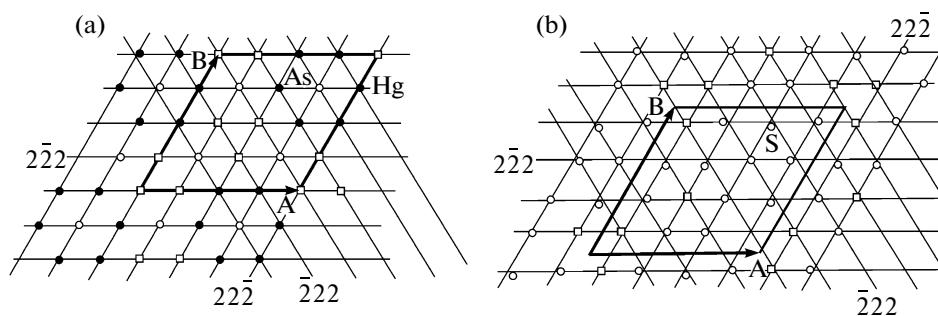**Fig. 1.** Structure of galkhaite: (a) net of nodes in plane 222 formed by its intersection with planes 2$\bar{2}$2, 22$\bar{2}$, $\bar{2}$22 and actual position of Hg and As cations; □, vacant points; A and B, translations in this plane (and angle between them); $A = -a + c = 14.658$; $B = -a + b = 14.658$; $\gamma = 60°$; (b) a similar net of nodes displaced relative to the aforementioned net with actual positions of S atoms in plane 222.
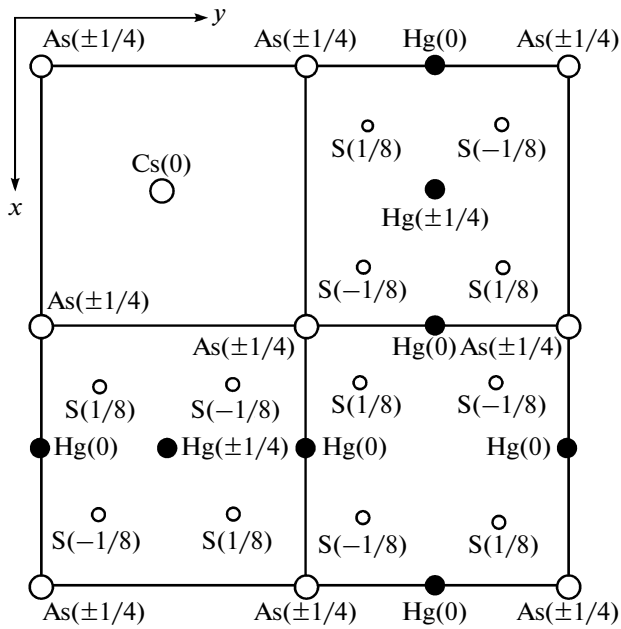
Fig. 2. Fragment of the idealized structure of galkhaite: four adjacent face-shared cubic cation subcells make up the half-thickness layer ($-\frac{1}{4} < z < \frac{1}{4}$); the next layer is formed by I translation.

shared subcells of the second sort adjacent along all faces except for apical (As,Sb) have two atoms (Hg,Cu) and 4S per cell. Cations (Hg,Cu) center four faces sharing neighboring subcells of the same type. S anions occur at the centers of tetrahedral cavities of the cation framework looking toward two opposite faces sharing with the first-type subcells. Thus, alternating cells of two types or columns of the second-type cells are established along coordinate axes in any coor-

dinate plane. The next layer is superimposed with a shift along diagonal in order to ensure similar alternation in the third direction (Fig. 2). Note that three subcells of the second type account for each subcell of the first type.

Covalent bonds (As,Sb)–S and (Hg,Cu)–S make up specific cocoons around large univalent cations (Cs,Tl) filling the entire space to form a cellular structure. The following geometric aspect of the galkhaite structure resembles Bergman phases of intermetallic compounds (Hoch and Simon, 2008). The large univalent cation (Cs,Tl) is a probable template, i.e., a crystallization nucleus, surrounded by 12 S atoms making up four umbels [(As,Sb)S_3] to form a Laves polyhedron. A hauberk consisting of metallic atoms (Hg,Cu) forms around this polyhedron as a Fedorov heptaparallelohedron, a 24-fold polyhedron, i.e., an octahedron, whose vertices are cut off by a cube (Fig. 3a). Inasmuch as these polyhedrons fill the entire space, the sequence of polyhedrons enclosed to one another is completed. We can mention the intermediate shell, a cube (As,Sb)$_8$ surrounding (Cs,Tl). Since S anions are not incorporated into this cube and (As,Sb) vertices center the hexagonal faces of the 24-fold polyhedron, then it is as if the S- and (As,Sb)-shells mutually intersect.

A very high symmetry and relatively small cubic cell parameter ensure the existence of geometric analogues of galkhaite. For example, a significant part of the cation framework of the typical structure of REE$_3$Sb$_5$O$_{12}$ [space group $I\bar{4}3m$, $a = 10.743$ Å for REE = Y (Glyakin et al., 1988)] is identical to galkhaite. Only the Sb octahedron occurs here instead of a large cation (Cs,Tl), so that all vacant cation sites in galkhaite are completely occupied by cations. Having the same symmetry and almost identical unit-cell dimensions,
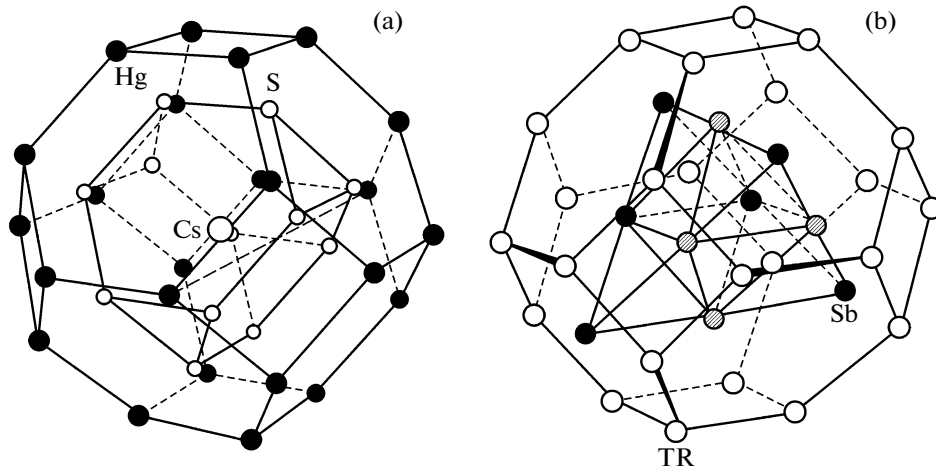

Fig. 3. (a) Fedorov heptaparallelohedron consisting of 24 Hg atoms surrounding a Laves polyhedron [CsS$_{12}$]$^{23-}$ in the structure of galkhaite; (b) similar cation polyhedron [REE$_{24}$] in the structure of REE$_3$Sb$_5$O$_{12}$ (REE = Y) around the complex anion [Sb$_4$(SbO$_4$)$_6$]$^{18-}$.

Table 7. Comparison of the cation framework in the structure of galkhaite and $REE_3Sb_5O_{12}$ (REE = Y)

Compound	Site occupancy			
	2a (000)	8c (xxx)	12e (00x)	12d (¼ ¼ 0)
$(Hg,Cu)_6(Cs,Tl)(As,Sb)_4S_{12}$	(Cs,Tl)	(As,Sb) x = 0.7553	Vacancy	(Hg,Cu)
$Y_6Sb_{10}O_{24}$	Vacancy	Sb(2) x = 0.745	Sb(1) x = 0.280	Y

the cation frameworks of both structures closely correlate (Table 7). The coincidence of the parameter-free sites 12d forming the body of the repeating part of the unit cell, that is, the aforementioned 24-fold polyhedron, is the most important (Fig. 3b).

CONCLUSIONS

Summarizing all available information concerning the composition, properties, and structure of galkhaite, it can be considered that in the presence of Cs and Tl, the former is commonly predominant and only rarely occurs as a sole component. The maximum Cs content in Tl-free galkhaite is 7.1 wt % (Chen and Szymański, 1981). A thallium analogue of galkhaite or a variety with Tl prevaling over Cs have not not yet found in nature. It can be suggested that [(As,Sb)S₃] is the most stable constituent, i.e., that blanks in the sites of these atoms are the least probable and, therefore, calculation of the unit cell on the basis of 8(As,Sb) and 24S is warranted. Defects at the sites of other cations are less critical because of high symmetry, and the structure sustains a significant number of vacancies and isomorphic substitutions therein. The structure of galkhaite demonstrates once again the high stability of the cation framework with the geometrically closest three-layer packing even in the presence of more than 35% of vacancies and framework-forming atoms differing in size and chemical nature. Such a cation framework is characteristic of other Hg-bearing minerals (laffittite, aktashite, stalderite, Hg-bearing tetrahedrite, α- and β-HgS). Commensurable cation frameworks are a probable cause of close association of these minerals in nature.

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