Canadian Mineralogist
Vol. 19, pp. 571-581 (1981)

THE STRUCTURE AND CHEMISTRY OF GALKHAITE, A MERCURY SULFOSALT CONTAINING Cs AND Tl

T.T. CHEN AND J.T. SZYMAŃSKI

Mineral Sciences Laboratories, CANMET, Department of Energy, Mines and Resources
555 Booth Street, Ottawa, Ontario K1A 0G1

ABSTRACT

The electron-microprobe analysis of forty-seven crystals of galkhaite $(Hg,Cu,Zn,Tl,Fe,\square)_6(Cs,Tl,\square)(As,Sb)_4S_{12}$ from the Getchell mine, Humboldt County, Nevada, shows that Cs exceeds Tl in nearly all the crystals. The crystal structure of galkhaite (*a* 10.365(3) Å, space group $I\bar{4}3m$) has been refined to $R = 2.64\%$ from 680 unique reflections obtained by averaging the whole Mo$K\alpha$ sphere to $2\theta = 80°$. The refinement indicates that Cs occupies the *2a* sites whereas Tl is distributed between the *2a* sites with Cs and the *12d* sites with (Hg,Cu,Zn,Fe) in a ratio of about 2.67:1. Neither position is fully occupied in the structure. There is a linear antipathetic relationship between the Cs and Tl contents of this sulfosalt; the slope of the relative proportion Cs:Tl is about 3:2.

Keywords: galkhaite, microprobe analyses, cesium, thallium, sulfosalt, crystal-structure redetermination.

SOMMAIRE

L'analyse à la microsonde électronique de 47 cristaux d'une galkhaite $[Hg,Cu,Zn,Tl,Fe,\square)_6(Cs,Tl,\square](As,Sb)_4S_{12}$ de la mine Getchell (comté de Humboldt, Nevada) fournit Cs > Tl pour presque tous les cristaux. La structure cristalline de la galkhaïte [*a* 10.365(3) Å, groupe spatial $I\bar{4}3m$] a été affinée jusqu'à $R = 2.64\%$ sur 680 réflexions uniques, moyennes de toutes les réflexions mesurées au Mo $K\alpha$ jusqu'à $2\theta = 80°$. L'affinement indique que Cs n'occupe que les sites *2a* alors que Tl est partagé entre les sites *2a* avec Cs et les sites *12d* avec (Hg,Cu,Zn,Fe) dans un rapport d'environ 2.67:1. Ces deux positions sont incomplètement occupées. Le contenu en Cs et celui en Tl de ce sulfosel sont en relation linéaire inverse de rapport 3:2.

(Traduit par la Rédaction)

Mots-clés: galkhaïte, analyses à la microsonde, césium, thallium, sulfosel, redétermination de la structure cristalline.

INTRODUCTION

Gruzdev *et al.* (1972) first reported the occurrence of the sulfosalt galkhaite [cubic, *a* 10.41(1) Å, space group $I\bar{4}3m$] from the Gal Khaya deposit, Yakutia, and the Khaydarkan deposit, Kirgizia. Their chemical analyses showed the following compositions: $(Hg_{0.74}Cu_{0.17}Zn_{0.14}Tl_{0.01})_{1.06}(As_{0.98}Sb_{0.02})_{1.00}S_{2.01}$ (Gal Khaya) and $(Hg_{0.80}Cu_{0.15}Zn_{0.03}Tl_{0.05})_{1.03}(As_{0.85}Sb_{0.15})_{1.00}S_{1.97}$ (Khaydarkan). Botinelly *et al.* (1973) reported galkhaite from the Getchell mine, Humboldt County, Nevada and gave the results of two analyses of the composition. The microprobe analysis, carried out by Gerald Czamanske and normalized to S = 12, gave $(Hg_{4.26}Cu_{0.91}Zn_{0.31}Tl_{0.29})_{\Sigma 5.77}As_{3.60}S_{12}$. The spectrographic analysis (N. M. Conklin), again normalized to S = 12, gave $(Hg_{3.21}Cu_{1.46}Tl_{0.51}Zn_{0.23}Fe_{0.11})_{\Sigma 5.52}(As_{4.96}Sb_{0.06})_{\Sigma 5.02}S_{12}$. The principal difference between these analytical results lies in the ratio of (As,Sb) to S, but the important feature is that neither ratio is as high as that claimed by Gruzdev *et al.* (1972), namely, 1:2. Conklin's analysis included additional trace amounts of Ag, Cd, Al, Ca, Mg and Mn. Jungles (1974) published a review of these two mineral descriptions and his own comments on galkhaite from the point of view of a mineral collector.

Divjaković & Nowacki (1975) published a single-crystal X-ray structure determination of galkhaite using a crystal from the Getchell mine but based their starting premises for the composition of galkhaite on the spectrographic analysis of Botinelly *et al.* (1973). Their X-ray study showed a heavy element at the origin (*2a* site) of a body-centred cubic cell, space group $I\bar{4}3m$; they concluded that this was Tl. Refinement of the population parameter of this atom gave a surprisingly low value of 0.48, giving a chemical formula $[Hg_{0.76}(Cu,Zn)_{0.24}]_{12}Tl_{0.96}(AsS_3)_8$ or, rewritten based on S = 12, $[Hg_{0.76}(Cu,Zn)_{0.24}]_6(Tl_{0.48}\square_{0.52})As_4S_{12}$.

Another structure determination of galkhaite, reported at about the same time by Kaplunnik *et al.* (1975), was done on crystals from Gal Khaya. It was based on the chemical formula for the Gal Khaya material quoted above. The space group was found to be $I\bar{4}3m$, with a 10.422(3) Å. The refinement was apparently based on 122 observed reflections (out of a possible 347 within the $\sin\theta/\lambda$ = 0.87 Å^{-1} limit quoted). No mention was made of absorption corrections being applied to the data, which were collected from a very large crystal (0.3–0.5 mm across). The structure proposed by Kaplunnik *et al.* (1975) is analogous to the Divjaković & Nowacki (1975) model so far as the (Hg, Cu, Zn), As and S of the latter are concerned, but differs from the latter model in the atoms claimed to be at, or near, the origin. Kaplunnik *et al.* proposed that two thirds of the origin sites were occupied by As^{3-} ions and that one third of the origin sites had an As atom at a distance of 1.25 Å from the origin, along the body diagonal of the cell. Thus, with the $\bar{4}3m$ symmetry around the origin, discrete As_4 tetrahedral molecules were suggested, with As–As distances of 2.1 Å. The combination of two-thirds occupancy for As^{3-} and one-third occupancy for the As_4 tetrahedron, added to the As in the 8c sites, yields an As:S ratio of 1:2. We strongly suspect that this very unusual combination was designed to make the compositional formula, derived from the X-ray analysis, fit the results of the chemical analysis of galkhaite at their disposal. The agreement factors quoted are R = 9.8% for all 122 reflections, and R = 5.2% if only 98 reflections are considered (?). These values are significantly worse than the agreement obtained by Divjaković & Nowacki (4.5% for all 132 data, 4.3% for observed data). This proposed structure will therefore not be considered further, except to state that if the observed density of electrons at or near the origin (combination of As^{3-} and As_4 tetrahedra) is reinterpreted in terms of a single heavy metal, the Divjaković & Nowacki structure is obtained, and the As:S ratio becomes 1:3.

In a study of mercury minerals, one of us (T.T.C.) noted that a substantial concentration of cesium was present in galkhaite. Owing to the rare occurrence of cesium and thallium in nature and to the association of these two elements with mercury in this mineral, an extensive study of the chemical variations in galkhaite (T.T.C.) and a re-examination of the crystal structure (J.T.S.) were undertaken.

SAMPLE

Only galkhaite from the Getchell mine was examined in this study; attempts to obtain material from the Gal Khaya and Khaydarkan deposits were unsuccessful. The samples examined in this study include (1) 26 detached cubic crystals, which include two from the Royal Ontario Museum (ROM *M*35441), 23 from the U.S. National Museum of Natural History – Smithsonian Institution (USNM 127441) and one from the Ecole Nationale Supérieure des Mines de Paris (ENSM 36280), and (2) one hand specimen containing dozens of galkhaite crystals from the National Mineral Collection of the Geological Survey of Canada (GSC 13949), (3) one microcrystal mount (4 crystals) purchased from Ward's Scientific Establishment and (4) several hand specimens (11 galkhaite grains in polished sections) obtained from Dr. R.I. Thorpe of the Geological Survey of Canada (TQ 78–149, 78–151).

Galkhaite crystals are usually brownish to reddish black and show an adamantine lustre, except for the GSC 13949 crystals, which are relatively reddish and vitreous. The crystals are cubes or clusters of cubes, approximately 1 mm in edge, and commonly show striations normal to [111] on {100} (Fig. 1). On one crystal (Ward's specimen), minor {110} faces also are developed. The same striations were noted on the Khaydarkan crystals, and the minor faces on the Gal Khaya crystals (Gruzdev *et al.* 1972). In GSC 13949 and Ward's specimens, galkhaite occurs as striated cubes in vugs, associated with getchellite, realgar, orpiment, pyrite (arsenian), stibnite (arsenian), fluorite and quartz. However, in specimens TQ 78–149 and 78–151 (dark grey "rock"), galkhaite occurs as irregular grains with the same mineral association in a fine grained quartz matrix. Pyrite and

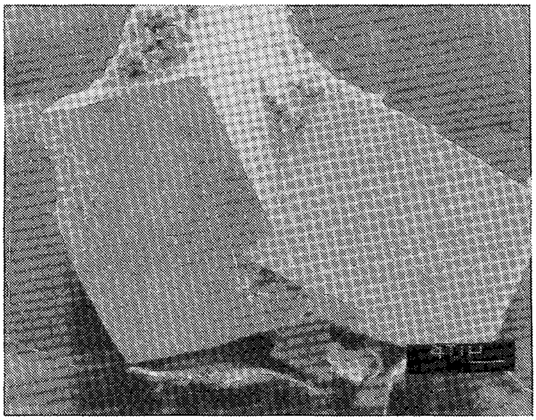

FIG. 1. SEM photograph of galkhaite crystals showing striations diagonal to the cube faces (GSC 13949).

quartz are common inclusions in galkhaite, whereas some galkhaite occurs as inclusions in realgar. The optical properties of galkhaite were found to be identical to those reported by Botinelly *et al.* (1973).

MICROPROBE ANALYSES OF GALKHAITE

Forty-seven crystals were analyzed for composition. Each crystal was first examined using an SEM equipped with an energy-dispersion analyzer, and subsequently analyzed using an electron microprobe. In all crystals, the presence of S, Hg, As, Cu, Zn and Cs was confirmed, and in some crystals minor amounts of Sb and Fe also are present. With the use of the wavelength-dispersion spectrometer, Tl was detected in all crystals but one. The presence of Cs in galkhaite was obvious, as the energy-dispersion spectra clearly showed the Cs*Lα*, *Lβ*₁ *Lβ*₂ and *Lγ*₁ emission lines.

Electron-microprobe analyses were performed using an accelerating voltage of 20 kV and the following emission lines and standards: S*Kα* enargite, Hg*Mα* cinnabar, Cu*Kα* enargite, Fe *Kα* argentopyrite, Cs*Lα* CsCl, Tl*Lα* lorandite, As*Lα* lorandite, Zn*Kα* ZnS and Sb*Lα* chalcostibite. The data were processed using a modified EMPADR VII computer program of Rucklidge & Gasparrini (1969). Because of peak overlapping and the lack of suitable standards that would closely duplicate the galkhaite matrix, the totals of the analyses were usually found to be greater than 102% if emission lines and standards other than those quoted above were used for the analyses. The main discrepancies were found in Hg, S and As contents. For example, using the As*Kα* line rather than As*Lα* tended to result in a higher As content for galkhaite; using a Pd_3HgTe_3 (Hg *Mα*) standard instead of cinnabar (Hg*Mα*) gave a higher Hg content for galkhaite; a lorandite standard rather than an energite standard resulted in a higher S content. Table 1 lists results of 21 analyses that were obtained using the standards and emission lines indicated above. In general, the variations in analyses resulting from the use of various standards and emission lines are (in wt. %) Hg ±1.2, S ±0.6 and As ±0.5. Zn and Cu are accurate to 0.1 wt. %; because of the possible interferences by the lines Hg*Lα* and As*Kα*, the reported values for Tl (*Lα*) are considered to be within 0.5 wt. % of the true values. Only one Cs standard was available for this study; consequently, the accuracy of the Cs analysis is not known. However, the reported Cs values are far short, in all cases but one, of the S:Cs ratio of 12:1 required for stoichiometry in the subsequent crystal-structure analysis.

TABLE 1. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF GALKHAITE[†]

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.
S	22.3	22.3	22.2	22.4	22.0	22.0	21.8	21.7	21.8	21.9	21.8	21.4	21.7	22.1	21.9	22.6	20.9	21.4	22.5	22.7	22.3
Hg	48.7	50.8	49.0	49.3	51.7	52.4	53.0	51.4	51.7	51.2	52.0	52.6	52.0	50.0	50.0	48.3	51.6	49.8	49.1	48.9	49.7
Zn	2.3	1.7	2.4	2.0	1.8	1.3	1.4	1.7	1.5	1.6	1.4	1.5	1.6	2.4	2.2	1.9	0.3	1.2	2.5	2.2	2.5
Cu	3.4	3.4	3.3	3.2	3.5	3.6	3.4	3.5	3.5	3.6	3.6	3.6	3.3	3.4	3.3	3.2	1.6	3.0	2.6	2.7	2.6
Fe	nd	nd	0.1	0.1	nd	nd	nd	nd	-	-	-	-	-	nd	nd	nd	nd	nd	0.5	0.5	0.5
Tl	4.2	2.2	3.7	3.6	1.7	1.1	1.4	2.3	2.5	2.3	2.5	0.8	3.9	2.2	4.1	2.7	nd	1.6	2.5	2.9	2.4
Cs	3.7	5.3	4.5	4.6	5.4	5.7	5.5	5.1	5.1	5.6	5.0	5.8	3.9	5.1	4.0	5.5	7.1	5.9	5.1	4.6	5.2
As	15.3	15.6	15.2	14.9	15.4	15.0	15.3	15.0	14.8	14.9	14.7	14.7	14.8	15.5	15.8	15.9	14.5	15.1	15.6	15.7	15.7
Sb	nd	nd	nd	0.4	nd	nd	nd	nd	-	-	-	-	-	nd	nd	nd	3.1	2.4	nd	nd	nd
Total	99.9	101.3	100.4	100.5	101.5	101.1	101.8	100.7	100.9	101.1	101.0	100.4	101.2	100.7	101.3	100.1	100.7*	100.9**	100.4	100.2	100.9

Nos. 1-4 GSC-13949; No. 4 X-ray single crystal. † in wt. %
Nos. 5-13 USNM-127441. No. 14 Ward's. No. 15 ROM-M35441.
No. 16 ENSM-36280. Nos. 17-18 TQ 78-151. Nos. 19-21 TQ 78-149.
* Including Ag 1.6, ** Including Ag 0.5. nd not detectable.

Table 1 shows that the composition of galkhaite varies from crystal to crystal. The most significant variations (in wt. %) are in cesium (3.6–7.1) and thallium (not detectable–6.7). The observed compositional ranges do not agree with previously reported data (Gruzdev *et al.* 1972, Botinelly *et al.* 1973). The average composition is S 22.0, Hg 50.7, Zn 1.8, Cu 3.2, Tl 2.4, Cs 5.1, As 15.2 and Sb 0.3, total 100.7 wt. %, corresponding to $(Hg_{4.42}Cu_{0.88}Zn_{0.48})_{\Sigma 5.78}Tl_{0.21}Cs_{0.67}(As_{3.55}Sb_{0.04})_{\Sigma 3.59}S_{12}$. The analysis of galkhaite with highest Cs (no. 17) gives $(Hg_{4.74}Cu_{0.46}Ag_{0.27}Zn_{0.08})_{\Sigma 5.55}Cs_{0.98}(As_{3.56}Sb_{0.47})_{\Sigma 4.03}S_{12}$, whereas the analysis with the lowest Cs (central portion, Fig. 2) gives $(Hg_{4.23}Cu_{0.95}Zn_{0.61})_{\Sigma 5.79}Tl_{0.57}Cs_{0.33}(As_{3.56}Sb_{0.04})_{\Sigma 3.60}S_{12}$. The average composition, in general, agrees with that reported by G. Czamanske (Botinelly *et al.* 1973), with the exception of cesium, which he did not determine.

The composition of each crystal is fairly uniform, although some crystals show slight variations in Hg, As, Tl and Cs content. An in-

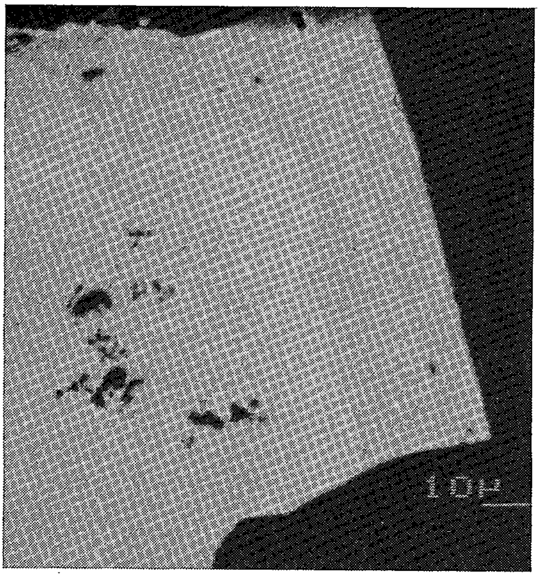

FIG. 2. SEM back-scattered electron image showing compositional zoning along the periphery of a galkhaite crystal. The outermost zone (grey) gave Hg 49.1, Cu 3.4, Zn 2.1, Tl 2.2, Fe 0.1, As 15.5, Sb 0.2, Cs 5.0 and S 22.1 wt. %. The central portion (light) of the crystal gave Hg 48.9, Cu 3.5, Zn 2.3, Tl 6.7, As 15.4, Sb 0.3, Cs 2.5 and S 22.2% (GSC 13949).

crease in Cs content is accompanied by a decrease of Tl. This relationship is found not only within individual crystals, but also among different crystals. Only two crystals were found, using SEM back-scattered electron images, to show distinct compositional zoning. The major differences are in Cs and Tl content. Figure 2 shows one of these crystals, in which the outermost zone is Cs-rich (Cs 5.0%, Tl 2.2%) and the central portion of the crystal, Cs-poor (Cs 2.5%, Tl 6.7%). The zoning is not related to the striations on the crystals, as the zoning occurs along the crystal periphery roughly parallel to {100}, whereas the striations occur parallel to the cube-face diagonals (Fig. 1). The SEM back-scattered electron images did not show any apparent compositional change associated with crystal striations.

X-RAY-DIFFRACTION STUDIES

Several crystals of galkhaite from the Getchell mine, Nevada, were examined by X-ray diffraction. The Debye-Scherrer powder patterns are in excellent agreement with that of Botinelly *et al.* (1973). The cell dimension was found to be 10.365(3) Å, a value significantly smaller than that reported by Divjaković & Nowacki (1975), 10.379(4) Å, though in close agreement with that of Botinelly *et al.* (1973), 10.36 Å. One cubic crystal was ground to a sphere 0.282 mm in diameter using the Bond method (1951). Detailed examination of this single crystal on a 4-circle diffractometer with Mo$K\alpha$ radiation revealed a variation of some 20% between the intensities of equivalent reflections. The only possible explanation of this phenomenon is that most of the diffracted intensity emanates from the unpolished surface of the ground sphere of this highly absorbing material, and that the surface texture may not have been uniform. A second single crystal was therefore tested; it was a corner broken from a cube, with one long cubic edge (0.2 mm) and two shorter cubic edges (0.08, 0.05 mm). Parts of three planar cubic faces were described, as well as numerous irregular "faces" on the cleaved side of the fragment. Absorption corrections were evaluated for this crystal, using a Gaussian integration procedure and a grid of 12x12x10 points (Gabe & O'Byrne 1970). The agreement between absorption-corrected equivalent intensities was much better than in the case of the spherical specimen. The cell dimension was refined by least squares (Busing 1970) from the optimized observed 2θ, χ and ω values for 48 reflections ($53° < 2\theta < 60°$) using $\lambda(\text{Mo}K\alpha_1) = 0.70930$ Å.

Intensity data were collected with graphite-monochromated Mo$K\alpha$ radiation to a limit of $2\theta = 80°$, using a θ–2θ scan technique at 2°/min in 2θ, with a scan width of 2° plus the α_1–α_2 dispersion. Background counts were obtained for 40 seconds on either side of the peak position. Three standards were measured every 50 reflections to maintain a check on crystal alignment and instrument stability. A uniform systematic decrease of about 5% in the intensity of the standards was noted over the period of data collection (about six weeks). As the crystal alignment was found to be unchanged at the end, a linear scaling procedure was applied to the data to account for this decrease. All data within the above sphere were collected and corrected for absorption. The data were averaged, keeping the Bijvoet pairs separate. This resulted in a data set of 300 *hkl* reflections, 300 $hk\bar{l}$ reflections, and 80 *hk*0 and *h*00 reflections (total 680). Up to 24 individual intensities were averaged for a single I_{hkl}. The agreement factor $[\Sigma(I-\bar{I})/\Sigma I]$ for the averaged data set was 0.045. Standard deviations were obtained in the averaging process from the standard deviations of the individual measurements. Of the 680 unique reflections, only 23 could be considered as unobserved at the 10% significance level [$I < 1.65\sigma(I)$]. However, all data were included in the subsequent refinement of the structure at their actual averaged values, (no data were considered as unobserved and rejected), with the weights obtained in the usual way: $w = 1/\sigma^2(F)$, where $\sigma(F)$ is obtained from $\sigma(I)$ as follows: $\sigma(F) = \frac{1}{2}\,\sigma(I)\,(I.\ Lp)^{-\frac{1}{2}}$. After data collection was complete, the crystal was removed from the diffractometer and analyzed with the microprobe a number of times. The average of these analyses (Table 1, no. 4) was then used to give the compositional ratios shown in Table 5.

All calculations (other than intensity-data averaging) were done using the X-RAY–76 system of crystallographic programs (Stewart *et al.* 1976). The data averaging was carried out by Dr. Y. LePage at the Division of Chemistry, National Research Council of Canada, using their in-house set of crystallographic programs. Structure-factor tables are available at a nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa K1A 0S2.

THE ROLE OF TL

Before possible models for refinement are discussed, a brief consideration of the role of thallium is required. Thallium appears to play a dual role in its occurrence and distribution in minerals. As Tl^+, it commonly occurs in silicates (especially in micas), substituting for K^+. Its properties are similar to those of the heavier alkali metals, and its ionic radius ($^{XII}Tl^+ = 1.70$ Å) can be compared with those of potassium ($^{XII}K^+ = 1.64$ Å), rubidium ($^{XII}Rb^+ = 1.72$ Å) and cesium ($^{XII}Cs^+ = 1.88$ Å) (Shannon 1976). However, it has been identified in sulfosalts, especially those containing As and Sb, as a replacement of other metals, commonly Pb and Fe (Ivanov *et al.* 1960). When replacing K^+ in micas, Tl^+ is twelve-coordinated. In sulfosalts, it is usually four- and, rarely, six-coordinated. It is commonly held that Tl^{3+} is unstable in minerals (Ivanov *et al.* 1960) and could only occur under extremely oxidizing conditions; yet it is quite stable in the laboratory. In fact, the double sulfate $Cs^+_3Tl^{3+}(SO_4)_3$ (Perret *et al.* 1974) has been prepared in which Cs^+ and Tl^{3+} occupy totally distinct sites in quite a stable structure. Whereas it is a fact that in nearly all minerals in which thallium occurs as a primary constituent it does so as Tl^+, the possibility of minor replacement in minerals in the form of Tl^{3+} should not be ruled out.

TABLE 2. ASSIGNMENT OF ATOMIC TYPES IN SPACE GROUP $I\bar{4}3m$ BY DIVJAKOVIĆ & NOWACKI (1975)

Atom type	Population parameter	Site	Position	Parameter
S	1.0	24*g*	x,x,z	$x = 0.3884(4)$ $z = 0.1629(5)$
Hg,(Cu,Zn)	0.76, 0.24	12*d*	$\frac{1}{4},\frac{1}{2},0$	
As	1.0	8*c*	x,x,x	$x = 0.2456(4)$
Tℓ	0.48	2*a*	0,0,0	

REFINEMENT

In the structure determination by Divjaković & Nowacki (1975), it was shown that the atoms of galkhaite occupy four possible positions in space group $I\bar{4}3m$ (Table 2). No indication was found of other possible sites where additional atoms could be located. Further refinement of the galkhaite structure presents an unusual crystallographic problem: there are only three positional parameters to refine (x, z for S, x for As), and the values of these are not seriously in doubt. The metals are all in special positions; the crystallographic problem concerns the determination of the combination of scattering curves that best fits the observed data.

Four possible models were considered for the distribution of Cs and Tl between the 2*a* and 12*d* sites in this structure: (1) (Cs + Tl) are located at the 2*a* sites; with the 12*d* sites occupied by (Hg,Cu,Zn,Fe). (2) Tl occupies the 2*a* sites, and Cs is with (Hg,Cu,Zn,Fe) at the 12*d* sites. (3) Cs occupies the 2*a* sites, and Tl is with (Hg,Cu,Zn,Fe) at the 12*d* sites. (4) Cs occupies the 2*a* sites, whereas Tl is distributed between the 2*a* and 12*d* sites.

Microprobe results are not sufficiently accurate simply to add up the atomic percentages to see which combination would fill the sites correctly. Besides, the measured sum of the atomic fractions of the metals invariably is less than 7 (based on S = 12); incomplete filling of the sites appears highly probable.

We now consider these four models in turn. The first is based on the premise that Tl^+ behaves like an alkali element, and *all* the thallium occurs with cesium in the 2*a* sites. The 12*d* sites then contain mercury and the other minor elements. The second model is rather unlikely, both chemically, because Cs is totally dissimilar to Hg, and compositionally, because one of the analyses (#17) shows Tl = 0, (Hg. *etc.*) = 5.56, Cs = 0.98 (based on S = 12). To have to put Cs in with Hg and overfill the position, leaving a void at 2*a*, seems very improbable. The third model is a distinct possibility if we accept that Tl has a dual role and that it can replace heavy metals in sulfosalts containing As. The fourth model makes no assumptions concerning the role of Tl and allows the least-squares refinement process to settle the issue of whether *all* Tl is with Cs at the 2*a* sites (model 1) or *all* Tl is with Hg at the 12*d* sites (model 3), or whether there is some distribution between the two extremes.

All four possibilities were tried in the least-squares refinement. In the first three cases, the sum of the atomic fractions for each position was normalized to unity, and the mean scattering curves were prepared from coefficients given by Cromer & Mann (1968) for the neutral atomic species. The anomalous scattering factors of Cromer & Liberman (1970) were averaged according to the atomic composition at the particular site. The As real and anomalous scattering factors were also adjusted to take into account the minor replacement of As by Sb.

In the fourth case, the composition was taken exactly as obtained from the microprobe analysis for the 2*a* and 12*d* metal sites (no normalization to unity). A constrained refinement was carried out of the Tl population parameter between the 2*a* and 12*d* sites, such that the sum total for Tl was as that found in the microprobe analysis. [Such a procedure has been described and implemented by Finger & Prince (1975) in the least-squares-refinement program RFINE, but it can also be carried out using CRYLSQ of the X-RAY system (Stewart *et al.* 1976). Both programs were used and gave substantially the same results. The X-RAY results are given here.]

The starting parameters in the refinements were taken from the published structure of Divjaković & Nowacki (1975). In the latter stages, an isotropic extinction parameter (Larson 1970) was included in the refinement done in the anisotropic thermal mode. The population parameters of the metals at the 12*d* and 2*a* sites were refined in cases 1, 2 and 3 (see above). The chirality of the models (absolute configuration) was also checked by comparing the residuals of the refined inverse models. Model 4 gave residuals of 2.64 and 6.52% for the coordinates as presented in Table 4 and for the inverse case, respectively. It should be borne in mind that both the 12*d* and 2*a* sites, where heavy metals with large values for Δf'' are located, are centrosymmetric and that the noncentrosymmetric part of the structure consists of (As,Sb) in the 8*c* sites and S in the 24*g* sites.

TABLE 3. COMPARISON OF FOUR REFINED STRUCTURAL MODELS FOR GALKHAITE

	Model # 1	Model # 2	Model # 3	Model # 4
2*a* Site	$\mathrm{Cs}_{0.663}$+ $\mathrm{T\ell}_{0.337}$	$\mathrm{T\ell}_{1.000}$	$\mathrm{Cs}_{1.000}$	$\mathrm{Cs}_{0.595}$+ $\mathrm{T\ell}_{0.220(5)}$ Σ=0.815
Refined Pop. par.	0.663(13)	0.507(10)	0.787(15)	–
12*d* Site	Hg = 0.748 Cu = 0.153 Zn = 0.093 Fe = 0.005 Σ = 1.000	Hg = 0.677 Cu = 0.139 Zn = 0.084 Fe = 0.005 Cs = 0.095 Σ = 1.000	Hg = 0.710 Cu = 0.145 Zn = 0.088 Fe = 0.005 Tℓ = 0.051 Σ = 1.000	Hg = 0.704 Cu = 0.144 Zn = 0.088 Fe = 0.005 Tℓ = 0.014 Σ = 0.955
Refined Pop. par.	0.994(6)	1.014(7)	0.986(6)	–
R	0.0281	0.0304	0.0271	0.0264

TABLE 4. RESULTS OF REFINEMENT OF MODEL # 4. OCCUPANCIES, POSITIONAL AND THERMAL PARAMETERS (x100), WITH STANDARD DEVIATIONS

Site	Atom	Ratio	Vacancy	Position	Positional parameters	Anisotropic Thermal Parameters*						$\overline{B}$ Equiv.
						U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	
24*g*	S	1.000	–	*x,x,z*	*x*=0.38826(10) *z*=0.16249(15)	2.87(4)	U_{11}	2.32(6)	-1.00(5)	0.11(3)	U_{13}	2.12
12*d*	Hg Cu Zn Tℓ Fe Σ =	0.704 0.144 0.088 0.014 0.005 0.955	0.045	½,½,0		6.01(3)	2.29(1)	U_{22}	0.0	0.0	0.0	2.79
8*c*	As Sb Σ =	0.983 0.017 1.000	–	*x,x,x*	*x*=0.24525(7)	1.95(2)	U_{11}	U_{11}	-0.26(2)	U_{12}	U_{12}	1.54
2*a*	Cs Tℓ Σ =	0.595 0.220(5) 0.815	0.185	0,0,0		4.82(10)	U_{11}	U_{11}	0.0	0.0	0.0	3.81

*The anisotropic thermal parameters are expressed in the form:- $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + \ldots 2U_{12}a^*b^*hk + \ldots)]$

A comparison of the refinement of the four models outlined above is given in Table 3, and the refined parameters for the best model (No. 4) are given in Table 4. This is for the weighted least-squares analysis, using weights obtained as described above.

Model 4 refined to a significantly lower value of *R* than the other three. Model 4 indicates that about 73% of the thallium is located with cesium in the 2*a* sites. The remainder is distributed over the 12*d* sites, which are six times more numerous. The structural formula derived from this model is $(Hg,Cu,Zn,Tl,Fe,\square)_6(Cs,Tl,\square)[(As,Sb)S_3]_4$. Neither type of metal site is fully occupied: the 2*a* sites contain $(Cs_{0.595}Tl_{0.220}\square_{0.185})$, whereas the 12*d* sites contain $(Hg_{0.704},Cu_{0.144},Zn_{0.088},Tl_{0.014},Fe_{0.005},\square_{0.045})$. The (As,Sb) 8*c* sites showed no anomaly in the final ΔF synthesis when the atom was refined at full occupancy. We have no explanation for the systematically low (As,Sb) content found in the microprobe analysis. It should be noted that Czamanske (Botinelly *et al.* 1973) found the same low proportion of As in his microprobe analysis of galkhaite.

DESCRIPTION OF THE STRUCTURE

The bond lengths and angles for the present refinement are given in Table 6. (Cs,Tl) is twelvefold-coordinated by S [3.863(2) Å], these atoms being arranged in four groups of three S; each group is part of an AsS_2 flattened trigonal pyramid, located along a body diagonal of the cell. The As–S distances are 2.265(1) Å, and the S–As–S angles are 93.85(5)°. In the positive [111] directions, the As is 4.403(1) Å from, and points towards, the (Cs,Tl) at the origin, whereas the three S atoms bond to (Cs,Ti) at ½,½,½ (see above). The nonbonded distance, As...Cs (½,½,½), is 4.574(1) Å. The Hg atoms are all located in the (100) planes of the unit cell. Hg is coordinated to 4 S atoms at 2.496(1) Å in a virtually regular tetrahedron [angles: 3x 109.24(3), 3x 109.93(3)°]. The geometry of the structure in terms of polyhedra is well described by Divjaković & Nowacki

TABLE 5. CRYSTAL DATA FOR GALKHAITE

Source: Getchell Mine, Humboldt County, Nevada.

Composition:

a) Microprobe Analysis, (No.4, Table 1):

$(Hg_{4.22}Cu_{0.87}Zn_{0.53}Fe_{0.03})_{\Sigma 5.65}T\ell_{0.30}Cs_{0.59}(As_{3.42}Sb_{0.06})_{\Sigma 3.48}S_{12}$

b) X-ray refinement results:

$(Hg_{4.22}Cu_{0.87}Zn_{0.53}Fe_{0.03}T\ell_{0.08}\square_{0.27})_{\Sigma 6.00}\ (Cs_{0.595}T\ell_{0.220}\square_{0.185})\ [(As_{0.983}Sb_{0.017})S_3]_4$

Formula: $(Hg,Cu,Zn,Fe,T\ell,\square)_6(Cs,T\ell,\square)[(As,Sb)S_3]_4$, Z = 2.

Crystal System: Cubic

Cell Dimension: *a* = 10.365(3)Å

Systematic Absences: h + k + ℓ = 2*n* + 1

Space Group: $I\bar{4}3m$, (No. 217).

Absorption: μ(Mo*K*α) = 411cm^{-1}

Density: d(calc.) = 5.34 Mg m^{-3}
d(obs.) not measured, but Gruzdev *et al.* (1972) report 5.4 Mg m^{-3}.

Intensity Data: whole Mo*K*α sphere collected to 2θ = 80°, (13834 reflections), averaged to give:-
300 hkℓ reflections
300 hk$\bar{\ell}$ reflections
80 hk0 reflections. Total = 680.

TABLE 6. BOND LENGTHS (Å) AND ANGLES (°) WITH STANDARD DEVIATIONS

Polyhedron	Number and Bond Lengths and Angles.		
HgS_4 tetrahedron	Bond lengths:		
	4	Hg - S	2.496(1)
	Non-bonded tetrahedral edges:		
	2	S...S	4.071(2)
	2	S...S	4.088(2)
	Additional non-bonded distances:		
	4	Hg...As	3.666(1)
	4	Hg...Hg	3.665(1)
	Angles:		
	3	S–Hg–S	109.93(4)
	3	S–Hg–S	109.24(4)
AsS_3 trigonal pyramid	Bond lengths:		
	3	As - S	2.265(1)
	Non-bonded distances:		
	3	S...S	3.309(2)
	1	Cs...As	4.403(1)
	Angles:		
	3	S–As–S	93.85(5)
	3	Cs...As–S	122.49(4)
CsS_{12} Laves Polyhedron	Bond lengths:		
	12	Cs - S	3.863(2)
	Angles:		
	24	S^1-Cs-S^2	95.16(2)
	12	S^1-Cs-S^3	145.10(3)
	12	S^1-Cs-S^4	116.95(2)
	12	S^1-Cs-S^5	50.73(2)
	6	S^1-Cs-S^6	50.18(3)
	Equivalent positions for above:		
	1. $-\frac{1}{2}+x, -\frac{1}{2}+x, -\frac{1}{2}+z$	4. $\frac{1}{2}-z, -\frac{1}{2}+x, \frac{1}{2}-x$	
	2. $-\frac{1}{2}+z, \frac{1}{2}-x, \frac{1}{2}-x$	5. $-\frac{1}{2}+z, -\frac{1}{2}+x, -\frac{1}{2}+x$	
	3. $-\frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2}-z$	6. $\frac{1}{2}-x, \frac{1}{2}-x, -\frac{1}{2}+z$	
	Cs is at (0,0,0)		
SMe_4 Tetrahedron	Bond lengths:		
	1	Cs - S	3.863(2)
	2	Hg - S	2.496(1)
	1	As - S	2.265(1)
	Angles:		
	2	Hg-S-As	100.57(5)
	2	Hg-S-Cs	130.09(3)
	1	Hg-S-Hg	94.44(6)
	1	As-S-Cs	92.85(5)

TABLE 7. X-RAY POWDER PATTERN OF GALKHAITE, CALCULATED FOR CuKα RADIATION FROM SINGLE-CRYSTAL DIFFRACTOMETER INTENSITIES

#	Index	d(A)	I_{cal}	I_{obs}*	#	Index	d(A)	I_{cal}	I_{obs}
1	110	7.329	58	60	22	444	1.496	9	10
2	200	5.183	3	2	23	543, 710	1.466	3	-
3	211	4.232	85	90	24	633, 552, 721	1.411	10	10
4	220	3.665	3	5	25	732, 651	1.316	6	5
5	310	3.278	4	5	26	800	1.296	6	5
6	222	2.992	100	100	27	554, 741, 811	1.276	3	5
7	321	2.770	82	80	28	653	1.239	4	5
8	400	2.591	38	40	29	743, 831, 750	1.205	2	-
9	411, 330	2.443	9	10	30	662	1.189	10	10
10	420	2.318	1	5	31	752	1.174	3	-
11	332	2.210	14	20	32	840	1.159	9	10
12	422	2.116	1	-	33	833, 910	1.145	1	-
13	431, 510	2.033	18	20	34	655, 761, 921	1.118	5	5
14	521	1.892	23	20	35	754, 851, 930	1.093	2	-
15	440	1.832	54	70	36	763, 932	1.069	3	-
16	433, 530	1.778	4	5	37	844	1.058	8	5
17	532, 611	1.681	18	20	38	853, 941, 770	1.047	2	-
18	620	1.639	1	-	39	772	1.026	1	-
19	541	1.599	2	-	40	943, 950	1.007	2	-
20	622	1.563	32	40	41	666, 10.2.2	0.997	6	-
21	631	1.528	3	-	42	765, 952, 10.3.1	0.988	4	-

*I_{obs} values taken from Botinelly *et al.* (1973).

(1975). However, care must be taken in their paper to read (Cs,Tl) for Tl in the discussion of polyhedra.

POWDER PATTERN OF GALKHAITE

A calculated powder pattern was obtained using the program POWGEN (Hall & Szymański 1975). This program calculates the equivalent Debye-Scherrer intensities from the observed single-crystal intensities measured on the 4-circle diffractometer. In the present case, the multiplicities of the reflections had to be adjusted to take into account the fact that $I_{hkl} \neq I_{hkl}$ for the single-crystal intensities. The results are given in Table 7. Only positive indices are given, but the intensities are summed for the whole form. It can be seen that there is excellent agreement with the observed intensities and spacings of Botinelly *et al.* (1973), and that our material is identical to theirs. Table 7 also provides more precise intensity values for the purpose of future identification of galkhaite.

DISCUSSION

In view of the conflicting compositional analyses of galkhaite [this paper, Gruzdev *et al.* (1972), Botinelly *et al.* (1973)], the question of the identity of the mineral in this study must be adequately answered. In the absence of Gal Khaya or Khaydarkan material for a re-examination and comparison, the problem resolves itself into two questions: (1) Is the present material identical to the Getchell mine material of Botinelly *et al.* (1973) and Divjaković & Nowacki (1975)? (2) Is the present material identical to the Russian material [Gruzdev *et al.* (1972), Kaplunnik *et al.* (1975)]?

It is felt that the answer to both questions is affirmative, based on the physical properties and X-ray-diffraction evidence: (1) All the material examined has the same space group and reasonably close cell dimensions. The variation in the latter is: 10.36 (Botinelly *et al.* 1973), 10.365(3) (this paper), 10.379(4) (Divjaković & Nowacki 1975), 10.422(2) (Kaplunnik *et al.* 1975). It is not known to what extent this difference is due to differences in composition of individual galkhaite crystals, and how much the experimental error has been underestimated. (2) The powder patterns of the Russian material (Gruzdev *et al.* 1972) are in good agreement with that obtained by Botinelly *et al.* (1973), and the latter is in excellent agreement with ours (Table 7). (3) The variations in crystal habit and the striations observed in this work are identical to those described by Gruzdev *et al.* (1972) for the Russian material. (4) The physical properties of the Getchell mine galkhaite have been closely compared with the published data (Gruzdev *et al.* 1972) by Jungles (1974) and by Botinelly *et al.* (1973), and the agreement is good. (5) If the combination of As atoms at or near the origin of the cell, as proposed by Kaplunnik *et al.* (1975) is re-interpreted as a single heavy metal, the resultant structure is that reported by Divjaković & Nowacki (1975), and the latter is the same as ours, except for a reassignment of metal types.

In conclusion, we suggest that the present material *is* galkhaite, that apart from the compositional differences that occur even within the same batch of crystals, our material is identical to the Getchell mine material examined by Botinelly *et al.* (1973) and by Divjaković & Nowacki (1975), and that the Getchell mine material is the same as the Russian material.

There remains the problem of reconciling the various analytical data on galkhaite previously reported. Botinelly *et al.* (1973) gave results of two analyses: the spectrographic analysis (done by N.M. Conklin) showed $(Hg, etc.)_{0.98}(As,Sb)_{0.89}S_{2.13}$ (sulfur by difference), and rounded off to 1:1:2. The microprobe results (analysis done by Gerald Czamanske) gave $(Hg, etc.)_{1.44}As_{0.90}S_{3.00}$. The theoretical ratio for galkhaite is 1.5:1:3. If the spectrographic results of Conklin are renormalized to S=3, the ratio is 1.55:1.25:3. It can be seen that Conklin's wt. % As is too high and Czamanske's is too low. Botinelly *et al.* (1973) chose to quote the ratio as 1:1:2, probably following the ratio given by Gruzdev *et al.* (1972). The structural analysis of Divjaković & Nowacki (1975) was based on Czamanske's microprobe results; these were obtained without the use of energy-dispersion spectrometry, which explains the failure to note the presence of cesium. The results of 23 analyses given in Table 1 are consistent with Czamanske's result, even to the point of showing a systematic low wt. % As. As already pointed out, our ratios can be made to closely approximate the theoretical, but the wt. % totals become significantly too large (up to 105%); it is felt that quoting these is the less satisfactory of the poor alternatives.

We have no adequate explanation for the very precise (but inaccurate) 1:1:2 ratios given by Gruzdev *et al.* (1972) [later in Kaplunnik *et al.* (1975) these results were attributed to "analyst N.G. Shumkova"].

The present refinement gives a total population parameter for the 2*a* sites of (Cs + Tl) = 0.815(5) which, although still far from unity, is much larger than the value of 0.48 for Tl found by Divjaković & Nowacki (1975).

These authors rationalized the very long Tl–S distance of 3.863 Å, longer than the expected distance of 3.56 Å, in terms of the inability of the Laves polyhedra to compress to give shorter S–S contacts. Although this may be part of the reason for the long metal–sulfur distance, the presence of Cs at this site, with its larger ionic radius ($^{XII}\text{Cs}^{+}$ = 1.88, $^{XII}\text{Tl}^{+}$ = 1.70 Å), would account for a lengthening up to 3.72 Å. Alternatively, we can arrive at an estimated ^{XII}Cs–S bond length from a knowledge of ^{VIII}Cs–S distances; *e.g.*, in $Cs_2Zn_3S_4$ (Bronger & Hendricks 1980) the Cs–S bonds are 2x 3.535(7), 2x 3.568(6), 2x 3.597(7) and 2x 3.701(6) Å. Now $^{VIII}\text{Cs}^{+}$ is 1.74 Å, and on the basis of the difference between $^{XII}\text{Cs}^{+}$ and $^{VIII}\text{Cs}^{+}$ (0.14 Å), we would expect a Cs–S distance in galkhaite in the range 3.68–3.84 Å, and most likely in the lower end of the range, as all Cs–S distances are equal. The figure of 3.72 Å deduced above would seem reasonable if the 2*a* sites were competely filled with Cs. Possibly, some of the increase from 3.72 to 3.863 Å may be accounted for by the phenomenon of lengthening of interatomic distances in the event of partial occupancy of metal sites (Shannon 1976).

The Hg–S bonds, 2.496(1) Å, are fairly short, though individual shorter Hg–S bonds are known; *e.g.*, christite (Brown & Dickson 1976) has four Hg–S bonds of 2.460(9), 2.471(8), 2.646(11) and 2.661(11) Å in a distorted tetrahedron. The average of these four, 2.560 Å, is about what is expected for an Hg–S bond. In galkhaite, the presence of four equal short bonds and the regularity of the tetrahedron [angles 3x 109.24(4), 3x 109.93(4)°] are worthy of comment.

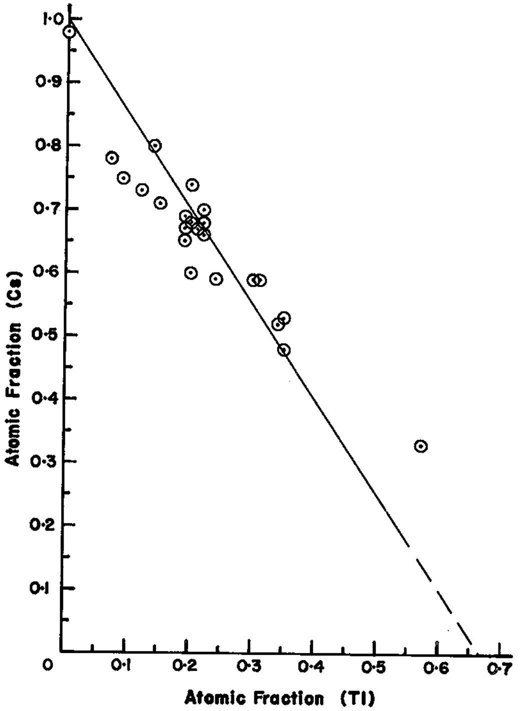

FIG. 3. Plot of atomic fraction of thallium against that of cesium, based on a formula of S = 12. The 23 points are the values in Table 1 and the two sets of analytical data quoted in Figure 2.

There remains the problem of the role of thallium and its apparent antipathetic relationship with Cs in galkhaite. The atomic fraction of thallium is plotted against the atomic fraction of Cs in Figure 3 for the 21 sets of analytical data in Table 1 and the two in Figure 2. A number of features are apparent from this plot. Firstly, the graph can be extrapolated to atomic fraction (Tl) = 0 and intercepts near atomic fraction (Cs) = 1.0. Secondly, there are very few compositions with (Cs) < 0.5, and only one with (Tl) > (Cs), this being the Cs-poor part of the zoned crystal in Figure 2. One composition is close to full Cs occupancy with zero Tl occupancy. This is in agreement with our premise that galkhaite is a *cesium* sulfosalt, with thallium being a secondary element. It appears that the ratio of substitution is 2 Tl for 3 Cs; the reason for this is not understood. The one possible explanation is that Tl occurs in both valence states, *e.g.*, as Tl^+ in the $2a$ sites and as Tl^{3+} in the $12d$ sites. Certainly the higher oxidation state would be preferable in the $12d$ sites from the standpoint of ionic size (${}^{IV}Tl^{3+}$ = 0.75 Å, midway between ${}^{IV}Hg^{2+}$ = 0.96 and ${}^{IV}Cu^{2+}$ = 0.57 Å). Considerations of electroneutrality would indicate a substitution ratio other than 1:1. However, it is felt that the presently available results of microprobe analyses are not sufficiently accurate to pursue this matter further.

ACKNOWLEDGEMENTS

The scanning electron microscopy study was performed by Dr. D.C. Harris and D.R. Owens of CANMET. The material for this study was provided by Drs. C. Guillemin of the Ecole National Supérieure des Mines de Paris, R.I. Gait and J.A. Mandarino of the Royal Ontario Museum, H.R. Steacy and R.I. Thorpe of the Geological Survey of Canada and J.S. White of the U.S. National Museum of Natural History – Smithsonian Institution. We are grateful for the discussions with and the assistance of Dr. J.D. Scott of Eldorado Nuclear Ltd. We acknowledge gratefully the work done by Dr. Yvon LePage, Division of Chemistry, National Research Council of Canada, in carrying out the X-ray intensity-averaging process. Several valuable suggestions made by Dr. A. Kato of the National Science Museum, Tokyo, Japan, were incorporated.

REFERENCES

BOND W.L. (1951): Making small spheres. *Rev. Sci. Instr.* **22**, 344-345.

BOTINELLY, T., NEUERBURG, G.J. & CONKLIN, N.M. (1973): Galkhaite, $(Hg,Cu,Tl,Zn)(As,Sb)S_2$ from the Getchell mine, Humboldt County, Nevada. *J. Res. U.S. Geol. Surv.* **1**, 515-517.

BRONGER, W. & HENDRIKS, U. (1980): Darstellung und Kristallstruktur von $Cs_2Zn_3S_4$ und $Rb_2Zn_3S_4$. *Rev. Chimie Minérale* **17**, 555-560.

BROWN, K.L. & DICKSON, F.W. (1976): The crystal structure of synthetic christite, $HgTlAsS_3$. *Z. Krist.* **144**, 367-376.

BUSING, W.R. (1970): Least-squares refinement of lattice and orientation parameters for use in automatic diffractometry. *In* Crystallographic Computing (F.R. Ahmed, ed.). Munksgaard, Copenhagen.

CROMER, D.T. & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for X-rays. *J. Chem. Phys.* **53**, 1891-1898.

——— & MANN, J.B. (1968): X-ray scattering factors computed from numerical Hartree–Fock wave functions. *Acta Cryst.* **A24**, 321-325.

DIVJAKOVIĆ, V. & NOWACKI, W. (1975): Die Kristallstruktur von Galchait $[Hg_{0.76}(Cu,Zn)_{0.24}]_{12}Tl_{0.96}(AsS_3)_8$. *Z. Krist.* **142**, 262-270.

FINGER, L.W. & PRINCE, E. (1975): A system of FORTRAN IV computer programs for crystal structure computations. *Nat. Bur. Stand. Tech. Note* **854**.

GABE, E.J. & O'BYRNE, T. (1970): An absorption correction program for the PDP–8. *Amer. Cryst. Assoc. Summer Meet. Abstr.* A4. (translated into FORTRAN and adapted to CDC computers by Gabe & Szymański.)

GRUZDEV, V.S., STEPANOV, V.I., SHUMKOVA, N.G., CHERNISTOVA, N.M., YUDIN, R.N. & BRYZGALOV, I.A. (1972): Galkhaite $(HgAsS_2)$, a new mineral from arsenic–antimony–mercury deposits of the U.S.S.R. *Dokl. Akad. Nauk S.S.S.R.* **205**, 1194-1197 (in Russ; translation: **205**, 150-153).

HALL, S.R. & SZYMAŃSKI, J.T. (1975): Powder pattern generation from single crystal data. *Amer. Cryst. Assoc. Winter Meet. Abstr.* F13. Now incorporated in the X-RAY–76 system of programs [see Stewart *et al.* (1976)].

IVANOV, V.V., VOLGIN, V. YU., KRASNOV, A.A. & LIZUNOV, N.V. (1960): Thallium. *In* Geochemistry of Rare Elements (K.A. Vlasov, ed.). Academy of Science Press, Moscow (translation published by Amer. Geol. Inst. in cooperation with the Geochemical Society).

JUNGLES, G. (1974): Galkhaite, a newly described mineral from Siberia, found at the Getchell mine, Nevada. *Mineral. Rec.* **5**, 290.

KAPLUNNIK, L.N., POBEDIMSKAYA, E.A. & BELOV, N.V. (1975): The crystal structure of galkhaite $HgAsS_2$. *Dokl. Akad. Nauk S.S.S.R.* **225**, 561-563 [in Russ.; translation (1976) in *Sov. Phys. Dokl.* **20**(11), 723-724].

LARSON, A.C. (1970): The inclusion of secondary extinction in least-squares refinement of crystal structures. *In* Crystallographic Computing (F.R. Ahmed, ed.). Munksgaard, Copenhagen.

PERRET, R., TUDO, J., JOLIBOS, B. & COUCHOT, P. (1974): Préparation et caractérisation cristallographique de quelques sulfates doubles d'indium (III) et de thallium(III), $M^I_3M^{III}(SO_4)_3$ (M^I=Na, K, Rb et Cs). *J. Less-Common Metals* **37**, 9-12.

RUCKLIDGE, J.C. & GASPARRINI, E. (1969): EMPADR VII. Specifications of a computer program for processing electron microprobe analytical data. *Dep. Geol. Univ. Toronto.*

SHANNON, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.* **A32**, 751-767.

STEWART, J.M., MACHIN, P.A., DICKINSON, C.W.. AMMON, H.L., HECK, H. & FLACK, H. (1976). The X-RAY system of crystallographic programs, version of 1976. *Univ. Maryland Comp. Sci. Ctr. Tech. Rep.* TR–446.

Received May 1981, revised manuscript accepted October 1981.