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The crystal structure of wallisite[1], $PbTlCuAs_2S_5$, the Cu analogue of hatchite, $PbTlAgAs_2S_5$

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(With electron microprobe analyses by C. Bahezre, Bureau de Recherches Géologiques et Minières, Paris, and G. Burri, Laboratory of X-Ray Microanalysis, University of Bern)

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Auszug

Wallisit kristallisiert in der Raumgruppe $P\bar{1}$ mit $a'' = 9{,}21_5 \pm 0{,}01$, $b'' = 8{,}52_4 \pm 0{,}01$, $c'' = 7{,}98_0 \pm 0{,}01$ Å, $\alpha'' = 55°59' \pm 6'$, $\beta'' = 62°30' \pm 6'$, $\gamma'' = 69°24' \pm 6'$ und einem Zellinhalt von $2[PbTlCuAs_2S_5]$; $d_x = 5{,}71$ g cm^{-3}. Die reduzierte Zelle hat die Abmessungen $a = 8{,}98_3 \pm 0{,}01$, $b = 7{,}76_1 \pm 0{,}01$, $c = 7{,}98_0 \pm 0{,}01$ Å, $\alpha = 65°33' \pm 6'$, $\beta = 65°30' \pm 6'$, $\gamma = 73°55' \pm 6'$. Die Struktur wurde mittels [001]- und [010]-Patterson-Projektionen unter Verwendung der y-Parameter der isomorphen Hatchit-Struktur ermittelt. Sie besteht aus $Cu_2As_4S_{10}$-Doppelketten $\parallel b''$, welche durch die Pb,Tl-Atome zusammengehalten werden. Die Einzelkette hat die Zusammensetzung $CuAs_2S_7$. Jede Doppelkette ist aus Doppeltetraedergruppen Cu_2S_6 und Pyramidengruppen As_2S_5 aufgebaut. Die Pb,Tl(1)-Position weist eine Achter-Koordination von S auf und ist hauptsächlich von Pb-Atomen besetzt, während die Tl,Pb(2)-Position nur zwei nächste S-Nachbarn hat und wohl zur Hauptsache von Tl-Atomen besetzt ist. Die vollkommene Spaltbarkeit $\parallel (001)$ wird durch die gefundene Struktur ($R = 16.4\%$), welche mit Hatchit $PbTlAgAs_2S_5$ isomorph ist, gut erklärt.

Abstract

Wallisite crystallizes in the space group $P\bar{1}$ with $a'' = 9.21_5 \pm 0.01$, $b'' = 8.52_4 \pm 0.01$, $c'' = 7.98_0 \pm 0.01$ Å, $\alpha'' = 55°59' \pm 6'$, $\beta'' = 62°30' \pm 6'$, $\gamma'' = 69°24' \pm 6'$ and a cell content of $2[PbTlCuAs_2S_5]$; $d_x = 5.71$ g cm^{-3}.

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[1] Contribution No. 179. — Part 36 on sulfides and sulfosalts.

The reduced cell is $a = 8.98_3 \pm 0.01$, $b = 7.76_1 \pm 0.01$, $c = 7.98_0 \pm 0.01$ Å, $\alpha = 65°33' \pm 6'$, $\beta = 65°30' \pm 6'$, $\gamma = 73°55' \pm 6'$. The structure was determined from [001] and [010] Patterson projections by assuming the y parameters of the isomorphous hatchite structure. It consists of $Cu_2As_4S_{10}$ double chains $\parallel b''$, which are joined by the Pb,Tl atoms. Each constituent single chain corresponds to $CuAs_2S_7$. Each double chain is composed by Cu_2S_6 double tetrahedra and As_2S_5 pyramid groups. The Pb,Tl(1) position has an eightfold coordination of S and consists mainly of Pb atoms, whereas the Tl,Pb(2) position has only two nearest S neighbours and consists mainly of Tl atoms. The complete (001) cleavage is well explained by the structure ($R = 16.4\%$) which is isomorphous with hatchite $PbTlAgAs_2S_5$.

Introduction

Wallisite (Fig. 1) was discovered in 1963 as a new mineral in the Lengenbach quarry (Binnatal, Switzerland) on specimen L2533 together with scleroclase, rathite I (twinned), pyrite and a still unknown sulfosalt[2].

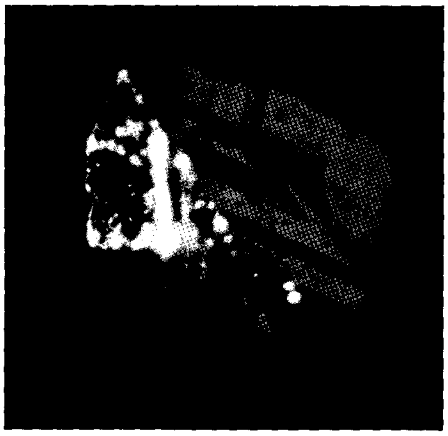

Fig. 1. Wallisite crystal (L2533—1963)

Morphology, lattice constants and space group

A cell, chosen in accordance with the morphological characteristics (Fig. 2), has: $a'' = 9.21_5 \pm 0.01$, $b'' = 8.52_4 \pm 0.01$, $c'' = 7.98_9 \pm 0.01$ Å, $\alpha'' = 55°59' \pm 6'$, $\beta'' = 62°30' \pm 6'$, $\gamma'' = 69°24' \pm 6'$, as determined by precession photographs using Cu$K\alpha$ radiation. The description of wallisite in this paper is based upon this "working" cell designated

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[2] W. Nowacki, Über einige Mineralfunde aus dem Lengenbach (Binnatal, Kt. Wallis). Ecl. Geol. Helv. 58 (1965) 403—406.

by double-primed characters. The very pronounced cleavage plane is (001) (see also Figs. 1 and 2).

Figure 2*a* gives a stereographic projection of the crystal of Fig. 1 and Figs. 2*b* and 2*c* are drawings made by the method of PARKER[3]. The observed face angles are given in Table 1.

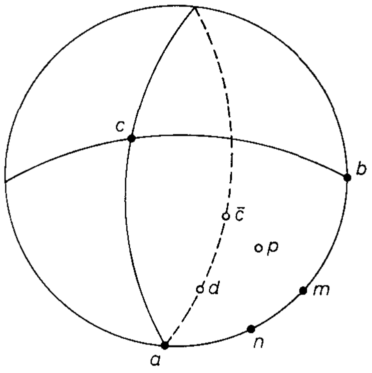

Fig. 2*a*. Stereographic projection of the crystal. $a = (100)$, $d = (20\bar{1})$, $\bar{c} = (00\bar{1})$, $c = (001)$, $b = (010)$, $m = (110)$, $n = (210)$, $p = (11\bar{1})$

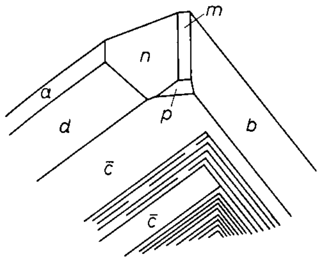

Fig. 2*b*

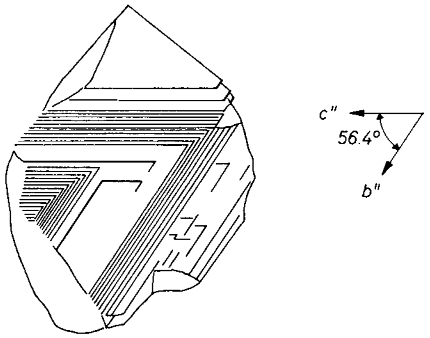

Fig. 2*c*

Fig. 2*b*. Crystal drawing, based on Fig. 2*a*, obtained by the method of PARKER[3]

Fig. 2*c*. Drawing of the wallisite crystal with measured angle $\alpha'' = \sphericalangle\,(b'', c'') = 56°24'$ (55°59' by x-ray methods)

The reduced cell has the constants

$$a = 8.98_3 \pm 0.01, \quad b = 7.76_1 \pm 0.01, \quad c = 7.98_0 \pm 0.01\ \text{Å},$$
$$\alpha = 65°33' \pm 6', \quad \beta = 65°30' \pm 6', \quad \gamma = 73°55' \pm 6'.$$

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[3] R. L. PARKER, Kristallzeichnen. Gebr. Borntraeger, Berlin, 1929.

Table 1. *Observed face angles of wallisite*

	Optical methods	x-ray methods	
	Angle with c = (001)		
a = (100)*	109°48′ ± 30′	109°12′	± 15′ from Weissenberg photographs
d = (20$\bar{1}$)	136°20′ ± 10′	136° 5′	
c = (00$\bar{1}$)	180°02′ ± 10′	180°	
	Angle with a = (100)*		
m = (110)	52°10′ ± 30′	52° 7′	± 5′ from precession photographs
n = (210)	32°00′ ± 30′	31°54′	
b = (010)**	97°30′ ± 30′	97°57′	
	Angle with b = (010)		
c = (001)	118°05′ ± 10′	118° 1′	
p = (11$\bar{1}$)	47°48′ ± 10′	—	

The faces indicated by * and ** gave respectively smeared and double images in the optical measurements.

The transformation formulae are the following

$$\begin{array}{llll@{\qquad\qquad}llll} \mathbf{a} = & -\mathbf{a}'' & & +\mathbf{c}'' & \mathbf{a}'' = & -\mathbf{a} & & +\mathbf{c} \\ \mathbf{b} = & & -\mathbf{b}'' & +\mathbf{c}'' & \mathbf{b}'' = & & -\mathbf{b} & +\mathbf{c} \\ \mathbf{c} = & & & \mathbf{c}'' & \mathbf{c}'' = & & & \mathbf{c} \end{array}$$

NOWACKI[2] erroneously gave as "reduced" cell another cell: $a''' = 9.21_5$ $b''' = 8.52_4$, $c''' = 7.76_1$, $\alpha''' = 121°32'$, $\beta''' = 100°54'$, $\gamma''' = 110°36$, The transformation is:

$$\begin{array}{llll} \mathbf{a}''' = & \mathbf{a}'' & & \\ \mathbf{b}''' = & & \mathbf{b}'' & \\ \mathbf{c}''' = & -\mathbf{a}'' & & +\mathbf{c}''. \end{array}$$

The space group is either $P1$ or $P\bar{1}$. The d values are listed by NOWACKI[4].

Wallisite was found a second time (L3447—1964) as an overcrust on scleroclase[4]. It seems to be rarer than hatchite (see below).

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[4] W. NOWACKI, Über neue Mineralien aus dem Lengenbach. Jb. Naturhist. Museum Bern 1963—65, publ. 1967, S. 293—299.

Chemical composition

The first chemical analysis of wallisite by an electron microprobe (C. Bahezre, Bureau de Recherches Géologiques et Minières, Paris, Anal. No. M. 0866, 20. 3. 1964) gave the following result:

Pb	23.4 + 1%
Tl	32.7 ± 1.5
As	22.4 ± 1
Cu	8.1 ± 0.5
S	14.4 ± 1
Σ	101.0 %

Since the total amount of material was exceedingly small, it was not possible to determine the density accurately. However, it has been known that the densities of most of the Pb(Tl)-As sulfosalts are in the range 4.5 to 6.0 g cm^{-3}. An attempt was made to evaluate the numbers of atoms in the cell by assuming various densities in the above range. On the assumption that the space group of wallisite is $P\bar{1}$ and that the number of atoms in the cell is even, we derived a possible chemical formula, $2[(\mathrm{Pb,Tl})_2\mathrm{CuAs}_2\mathrm{S}_3]$, which gives an approximate density of 5.1 g cm^{-3}. This chemical formula was found to be unusual because of the small content of sulfur. Further chemical analysis (Table 2), however, showed an indication of higher sulfur content. By assuming the total number of Pb and Tl to be two as given in the above formula, the following formulae are derived respectively from I and II (Table 2):

$$\mathrm{Pb}_{0.98}\mathrm{Tl}_{1.02}\mathrm{Cu}_{0.96}\mathrm{Ag}_{0.20}\mathrm{As}_{2.25}\mathrm{S}_{4.69}$$

and

$$\mathrm{Pb}_{0.98}\mathrm{Tl}_{1.02}\mathrm{Cu}_{0.87}\mathrm{Ag}_{0.20}\mathrm{As}_{2.20}\mathrm{S}_{4.76}\,.$$

These show a very good agreement with each other and may be idealized in a specific form $\mathrm{PbTlCuAs}_2\mathrm{S}_5$.

If there are two such formula units in the cell, the density becomes 5.71 g · cm^{-3} which is in the ordinary range of densities for sulfosalts as stated above. Since as in most of the sulfosalts, the new formula is consistent with the normal valencies of the elements involved, it is very likely that the formula represents the chemical composition of wallisite. The Cu sites in the structure are presumably replaced by Ag to some extent as indicated by the chemical analyses.

Table 2. *Electron microprobe analyses of wallisite*

	I	II	III
Pb	25 ± 1%	25.2	26.3
Tl	25.8 ± 1	26	26.1
Cu	7.5 ± 0.2	6.9	8.1
Ag	2.7 ± 0.5	2.7	—
As	20.8 ± 0.5	20.5	19.1
S	18.6 ± 1	19	20.4
Σ	100.4	100.3	100.0

I = C. BAHEZRE, Bureau de Recherches Géologiques et Minières, Paris, Anal. No. M. 1220, 10. 4. 1964.

II = G. BURRI, Bern, Anal. No. 103, 23. 5. 1966 (same crystal as I).

III = theoretical values for $PbTlCuAs_2S_5$.

In any case, it is very likely that the unit cell contains four Pb,Tl atoms and therefore it was expected that the structure could be solved based upon these heavy atoms as in the case of the structure of hutchinsonite[5].

Structure determination

Intensities were recorded with an integrating Weissenberg camera and measured by a Joyce-Loebl microdensitometer. The x-ray specimens were irregularly shaped but, as an approximation, the transmission factor for a spherical specimen was employed to correct for absorption.

The structure analysis was carried out in the projections along the b'' and the c'' axes. The b''-axis Patterson projection revealed fairly well-defined peaks which suggested the (Pb,Tl)—(Pb,Tl) vectors. Among several possible combinations of the Pb,Tl locations deduced from Patterson diagram, one gave a well-defined Fourier map. The structure based upon this map was successfully refined by Fourier methods until the R value was reduced to about 26%.

The c''-axis Patterson projection shows only arrays of highly multiple peaks and therefore a straightforward analysis was not possible. At this stage the relations between wallisite and hatchite[6,7]

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[5] Y. TAKÉUCHI, S. GHOSE and W. NOWACKI, The crystal structure of hutchinsonite, $(Tl,Pb)_2As_5S_9$. Z. Kristallogr. **121** (1965) 321—348.

[6] W. NOWACKI and V. KUNZ, Gitterkonstanten und Raumgruppe von Hatchit und Trechmannit N. Jahrb. Min., Mh. **1961**, 94—95.

[7] F. MARUMO and W. NOWACKI, The crystal structure of hatchite, $PbTlAgAs_2S_5$. Z. Kristallogr. **125** (1967) 249—265.

were examined. Both are triclinic and have a similar chemical compositions and similar lattice constants. To make clear the relationship between these two minerals, the reduced cell of hatchite was first derived:

$$\begin{array}{ll} a = 9.22\,\text{Å} & \alpha = 66°25' \\ b = 7.84 & \beta = 65°17' \\ c = 8.06 & \gamma = 74°54'. \end{array}$$

The reduced cell is related to that described by NOWACKI and KUNZ[6] ($\mathbf{a}'$, $\mathbf{b}'$, $\mathbf{c}'$) by the transformation:

$$\begin{array}{llllllll} \mathbf{a} = & \mathbf{a}' & & -\,\mathbf{c}' & \qquad \mathbf{a}' = & \mathbf{a} & & +\,\mathbf{c} \\ \mathbf{b} = & & \mathbf{b}' & & \qquad \mathbf{b}' = & & \mathbf{b} & \\ \mathbf{c} = & & & \mathbf{c}' & \qquad \mathbf{c}' = & & & \mathbf{c}. \end{array}$$

Table 3. *Comparison of the reduced cells of hatchite and of wallisite*

	Hatchite	Wallisite
a	9.22 Å	8.98 Å
b	7.84	7.76
c	8.06	7.98
α	66°25′	65°33′
β	65°17′	65°30′
γ	74°54′	73°55′

It was found that the two reduced cells are strikingly similar (Table 3). The transformation formulae between the hatchite (′) and wallisite cells (″) are:

$$\begin{array}{llllllll} \mathbf{a}' = & -\,\mathbf{a}'' & & +\,2\mathbf{c}'' & \qquad \mathbf{a}'' = & -\,\mathbf{a}' & & +\,2\mathbf{c}' \\ \mathbf{b}' = & & -\,\mathbf{b}'' & +\,2\mathbf{c}'' & \qquad \mathbf{b}'' = & & -\,\mathbf{b}' & +\,\mathbf{c}' \\ \mathbf{c}' = & & & -\,\mathbf{c}'' & \qquad \mathbf{c}'' = & & & -\,\mathbf{c}'. \end{array}$$

The Weissenberg equator $hk0$ of the two minerals show a great resemblance. Dr. F. MARUMO kindly put at our disposal his data of a complete three-dimensional structure determination of hatchite. It turned out that the c''-axis Patterson projection of wallisite is similar to that of hatchite. Thus it was very likely that wallisite, $PbTlCuAs_2S_5$, is the copper analogue of hatchite, $PbTlAgAs_2S_5$. A trial was then made of computing $F(hk0)$ by using x coordinates of wallisite as found above and by adopting the y coordinates of

Table 4

h k l	$\vert F_o \vert$	F_c	h k l	$\vert F_o \vert$	F_c	h k l	$\vert F_o \vert$	F_c	h k l	$\vert F_o \vert$	F_c
0 0 1	90.8	-58.5	7 0 6	45.6	-40.2	-9 0 2	12.0	16.1	5 7 0	0.0	7.0
2	146.0	-100.3	7	50.9	57.6	0 1 0	0.0	-17.9	6	0.0	3.3
3	112.9	85.8	8 0 0	28.3	16.3	2	187.3	-204.1	7	51.7	51.1
4	10.9	-11.7	1	122.0	-149.9	3	157.9	166.6	0 8 0	34.3	22.1
5	57.0	-68.2	2	30.6	21.6	4	151.6	-137.8	1	78.1	-88.7
6	52.3	-50.8	3	43.8	56.1	5	0.0	11.1	2	42.3	37.5
7	56.7	46.9	4	31.5	-18.0	6	114.4	88.5	3	23.0	27.9
1 0 0	0.0	- 1.3	5	49.7	59.4	7	26.9	-18.6	4	0.0	16.9
1	75.6	-43.7	6	26.0	21.8	8	61.7	54.1	5	54.0	59.7
2	333.1	350.8	7	13.1	7.3	9	81.1	-55.5	-1 1 0	74.4	-61.6
3	157.4	-139.1	9 0 0	13.8	-13.3	10	46.3	-36.8	-2	304.2	322.7
4	97.8	-85.2	1	21.8	25.6	0 2 0	203.0	-204.4	-3	60.8	54.3
5	77.2	64.0	2	25.5	24.5	1	91.0	110.3	-4	56.7	50.2
6	30.5	-28.4	3	76.4	-91.6	2	40.9	-35.7	-5	45.3	-35.8
7	43.6	-52.9	4	33.7	44.8	3	37.1	32.4	-6	154.8	-127.4
8	26.9	-22.2	5	50.6	67.6	4	150.9	173.9	-7	43.6	-31.4
2 0 0	62.3	36.6	6	24.0	-29.6	5	105.1	-100.7	-8	35.8	-39.3
1	0.0	-11.2	10 0 0	20.5	24.4	6	85.2	77.5	-9	33.8	22.2
2	25.0	-11.2	1	21.9	-33.6	7	133.5	-112.5	-10	28.4	22.9
3	58.9	-56.9	2	14.3	21.5	8	59.7	-35.0	-1 2 0	46.1	-49.0
4	198.6	176.7	3	11.8	19.4	9	79.0	63.0	-2	98.4	-105.5
5	129.9	-126.3	4	0.0	- 2.1	10	21.2	-18.5	-3	0.0	7.5
6	58.2	-49.6	5	32.3	-33.9	0 3 0	0.0	10.1	-4	99.4	97.9
7	70.4	64.6	-1 0 1	40.2	30.2	1	0.0	14.8	-5	62.3	54.5
8	24.5	-22.1	2	100.7	88.3	2	91.7	97.5	-6	94.4	76.1
3 0 0	110.8	-95.1	3	70.0	46.3	3	138.4	-125.2	-7	29.2	-24.5
1	180.4	-152.2	4	75.5	-63.8	4	0.0	6.2	-8	34.3	-31.4
2	46.1	-33.3	5	75.7	59.4	5	139.8	-133.0	-9	28.5	-20.5
3	43.0	-47.0	6	59.9	-45.1	6	37.1	-30.5	-1 3 0	32.1	28.1
4	36.4	30.6	7	32.8	16.8	7	138.4	107.8	-2	82.9	-92.6
5	24.0	-15.6	-2 0 1	75.8	-58.7	8	29.6	- 4.1	-3	44.8	42.8
6	116.7	106.0	2	38.5	-36.0	9	109.6	83.4	-4	47.8	-50.0
7	60.7	-50.6	3	152.9	148.7	10	9.4	-24.8	-5	13.4	10.5
8	40.3	-43.3	4	115.6	-95.9	0 4 0	0.0	18.2	-6	30.5	19.9
4 0 0	200.8	-235.9	5	101.9	85.3	1	130.8	-156.3	-7	19.9	-17.5
1	172.8	152.1	6	91.6	84.1	2	191.4	-159.1	-8	107.1	95.7
2	69.5	-69.0	7	29.7	-32.2	3	52.2	-55.3	-9	12.3	-12.6
3	107.2	-119.4	-3 0 1	141.2	157.5	4	0.0	-11.8	-1 4 0	41.9	46.8
4	50.1	42.0	2	133.1	-141.3	5	121.4	110.2	-2	124.8	144.2
5	41.3	-42.7	3	82.2	90.0	6	31.5	25.1	-3	28.4	32.4
6	0.0	- 0.1	4	98.3	101.4	7	57.9	44.6	-4	65.4	-68.2
7	7.7	9.1	5	17.7	6.4	8	0.0	- 4.7	-5	43.6	47.4
8	28.8	34.8	6	0.0	- 9.3	9	26.7	-19.6	-6	42.4	-38.8
5 0 0	70.4	71.2	-4 0 1	24.7	22.8	0 5 0	77.4	-87.4	-7	49.7	29.6
1	71.5	57.4	2	66.5	79.7	1	72.1	68.7	-8	0.0	5.2
2	197.7	-213.0	3	10.6	6.1	2	52.3	-46.3	-1 5 0	116.9	-132.9
3	75.2	75.2	4	16.6	-15.2	3	73.2	74.1	-2	37.4	35.7
4	26.6	-19.7	5	21.2	23.1	4	0.0	15.9	-3	59.1	-54.4
5	88.0	-101.7	6	26.5	23.0	5	26.5	21.6	-4	116.4	127.6
6	13.3	15.1	-5 0 1	21.8	24.4	6	46.4	42.7	-5	28.6	27.1
7	0.0	7.6	2	31.9	-40.2	7	53.6	-47.8	-6	45.2	-31.8
8	17.5	15.2	3	19.8	-12.7	8	0.0	3.2	-7	40.9	39.4
6 0 0	71.6	-83.5	4	11.7	6.4	9	48.2	-44.6	-1 6 0	70.7	76.7
1	63.5	66.3	5	64.1	-67.6	0 6 0	53.7	-45.2	-2	35.8	-48.2
2	56.6	52.3	-6 0 1	0.0	- 3.4	1	96.5	111.0	-3	106.6	-112.2
3	10.8	- 8.1	2	35.8	40.3	2	0.0	16.1	-4	34.5	26.6
4	112.3	-113.3	3	88.5	-104.0	3	20.2	24.4	-5	64.4	-57.3
5	71.1	77.7	4	26.5	23.7	4	50.4	43.7	-6	56.2	60.0
6	27.1	-28.5	5	0.0	10.6	5	62.0	-72.6	-1 7 0	45.7	50.1
7	66.4	-72.3	-7 0 1	86.3	-109.5	6	24.3	-23.3	-2	67.2	-54.8
8	27.7	31.6	2	30.6	39.1	7	20.8	-12.2	-3	41.5	43.6
7 0 0	32.4	16.4	3	16.3	- 6.3	8	0.0	0.5	-4	26.5	-25.3
1	34.8	28.1	4	25.8	-30.5	0 7 0	0.0	3.0	-5	21.6	-25.5
2	40.8	-39.4	-8 0 1	22.5	24.3	1	0.0	4.6	-1 8 0	33.4	-39.5
3	43.0	39.2	2	23.8	-25.5	2	85.1	74.6	-2	15.5	15.5
4	0.0	2.7	3	21.2	-20.7	3	75.6	-82.4	-3	25.5	28.3
5	0.0	1.7	-9 0 1	29.7	-44.1	4	0.0	3.1			

hatchite. The results turned out to give a very good agreement between F_o and F_c, the R value being 30%. Since serious overlapping of atoms is not observed in either projection, a series of least-squares refinements was carried out using both *hk*0 and *h*0*l* reflections together. In Table 4 the values of $|F_o|$ and F_c are listed.

The computations were performed on HITAC 5020E using the Busing-Martin-Levy program[8]. The R value was then reduced to 16.4% for all reflections and 14.5% if nonobserved reflections were excluded. In spite of the very high absorption of the specimen, the

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[8] W. R. Busing, K. O. Martin and H. A. Levy, ORFLS, a FORTRAN crystallographic least-squares program ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, 1962.

Table 5. *Atomic parameters for wallisite and hatchite* (in parentheses)

	x''	$\sigma(x'')$	y''	$\sigma(y'')$	z''	$\sigma(z'')$	B	$\sigma(B)$
Pb,Tl(1)	0.4034	0.0007	0.7518	0.0010	0.3053	0.0012	2.61 Å^2	0.15 Å^2
	(0.4064		0.7527		0.3047)			
Tl,Pb(2)	0.1248	0.0009	0.3088	0.0013	0.4189	0.0015	4.15	0.19
	(0.1322		0.3032		0.4217)			
Cu	0.0846	0.0025	0.1168	0.0037	0.0508	0.0043	3.35	0.45
(Ag)	(0.0853		0.1090		0.0463)			
As(1)	0.1910	0.0017	0.5436	0.0026	0.8876	0.0030	2.25	0.30
	(0.1928		0.5450		0.8778)			
As(2)	0.3632	0.0018	0.9058	0.0027	0.7645	0.0031	2.34	0.29
	(0.3670		0.8932		0.7766)			
S(1)	0.4538	0.0038	0.6253	0.0059	0.7363	0.0064	1.68	0.58
	(0.4517		0.6290		0.7417)			
S(2)	0.2406	0.0040	0.3672	0.0062	0.7337	0.0070	2.09	0.65
	(0.2464		0.3764		0.7229)			
S(3)	0.4206	0.0041	0.1260	0.0064	0.1485	0.0074	2.26	0.67
	(0.4136		0.1312		0.1548)			
S(4)	0.0745	0.0040	0.8267	0.0062	0.6736	0.0069	2.05	0.64
	(0.0911		0.8177		0.6560)			
S(5)	0.1686	0.0038	0.8057	0.0058	0.0965	0.0066	1.70	0.59
	(0.1831		0.7847		0.1058)			

transmission correction for the specimen of irregular shape was approximated by that for a spherical shape as stated above. If this fact is taken into account, the above *R* values appear to be low enough to conclude that the atomic locations obtained are essentially correct. The atomic parameters and their standard deviations are listed in Table 5, the values for hatchite being given in parentheses.

Description and discussion of the structure

The bond lengths and bond angles calculated using the Busing-Martin-Levy program[9] are listed in Table 6. The structure of wallisite is characterized by $Cu_2As_4S_{10}$ double chains consisting of CuS_4 tetrahedra and AsS_3 pyramids (Fig. 3). Two Cu tetrahedra in the double chain are related by a center of symmetry and share an edge, thus forming a group Cu_2S_6. These pairs are joined together by As and S atoms to form a double chain running along the b'' axis. Each constituent single chain corresponds to $CuAs_2S_7$. The AsS_3 pyramids

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[9] W. R. Busing, K. O. Martin and H. A. Levy, ORFFE, a FORTRAN crystallographic function and error program ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, 1964.

have a configuration similar to that which has been found in other sulfosalts like rathite[10], binnite[11], hutchinsonite[5], hatchite[7] etc.

Copper is surrounded by three nearest S atoms (2.22—2.41 Å) in an almost planar trigonal arrangement (the sum of the bond angles is 356.8°); in addition there is a fourth S atom almost perpendicular to this (Cu,S) plane at a distance of 2.80 Å, yielding a deformed tetrahedral (3 + 1) coordination for Cu. [The S—S distances in this tetrahedron are: S′(2)—S′(5) = 4.09, S′(2)—S′(4) = 3.94, S′(2)—S″(5) = 3.90, S′(4)—S′(5) = 3.99, S′(4)—S″(5) = 3.75, S′(5)—S″(5) = 3.80Å]. Up to the present this seems to be the only example of this kind of

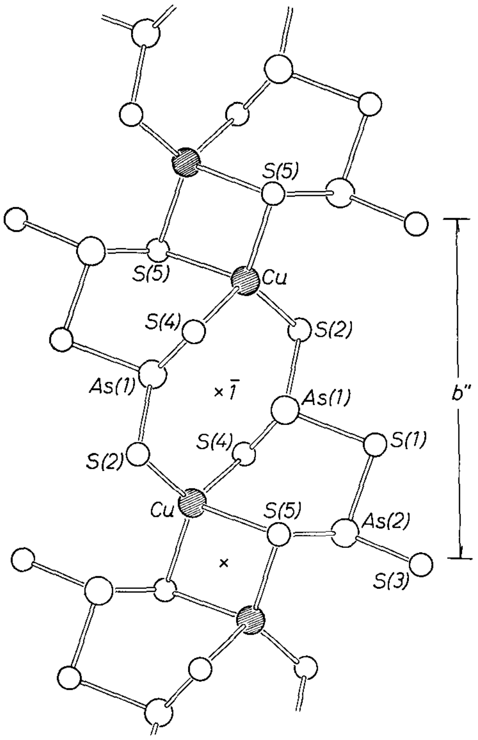

Fig. 3. The double chain of composition $Cu_2As_4S_{10}$, as projected on approximately (102)

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[10] F. Marumo and W. Nowacki, The crystal structure of rathite-I. Z. Kristallogr. **122** (1965) 433—456.

[11] B. J. Wuensch, Y. Takéuchi and W. Nowacki, Refinement of the crystal structure of binnite, $Cu_{12}As_4S_{13}$. Z. Kristallogr. **123** (1966) 1—20.

Table 6. *Bond lengths and bond angles of wallisite and hatchite* (in parentheses)

	S(1)	S(2)	S(3)	S(4)	S(5)	Mean	As(1)	As(2)	Cu(Ag)
Pb,Tl(1)	3.16 Å ± 0.06 (3.24)	2.99 Å ± 0.03 (3.01)	2.73 Å ± 0.05 (2.81)	3.28 Å ± 0.05 (3.20)	3.07 Å ± 0.05 (3.02)	3.08 Å (3.10)			
	3.19 ± 0.05 (3.31)	3.30 ± 0.04 (3.26)	2.89 ± 0.05 (2.98)						
Tl,Pb(2)	3.64 ± 0.04 (3.65)	3.46 ± 0.06 (3.46)	3.14 ± 0.05 (3.12)	2.99 ± 0.06 (3.05)	3.35 ± 0.04 (3.46)	3.38 (3.41)	3.37 Å ± 0.02 (3.48)	3.73 Å ± 0.02 (3.82)	3.87 Å ± 0.02 (3.89)
		[3.73 ± 0.03] [(3.89)]		3.51 ± 0.05 (3.61)	3.57 ± 0.04 (3.53)	[3.42] — [(3.47)]			
Cu,(Ag)		2.41 ± 0.04 (2.54)		2.22 ± 0.06 (2.52)	2.35 ± 0.06 (2.48)	2.33 — (2.51)	3.22 (3.38)	3.46 (3.32)	3.49 ± 0.08 (3.38)
					[2.80 ± 0.06] [(2.93)]	$[2.44_5]$ — [(2.62)]			

Remark: Numbers in square brackets indicate a more distant neighbour. The number in square brackets in the column "Mean" gives the mean value, the distance in square brackets included.

Table 6. *(Continued)*

	S(1)	S(2)	S(3)	S(4)	S(5)	Mean
As(1)	2.31 ± 0.04 (2.35)	2.25 ± 0.07 (2.23)		2.27 ± 0.04 (2.23)		2.28 — (2.27)
As(2)	2.34 ± 0.06 (2.30)		2.28 ± 0.05 (2.27)		2.26 ± 0.04 (2.25)	2.29 — (2.27)

Pb,Tl(1)—Pb,Tl′(1) = 4.01 ± 0.01 (4.06) Å
Tl,Pb(2)—Tl,Pb′(2) = 3.78 ± 0.02 (3.98)

S′(2)—Pb,Tl(1)—S′(1)	64.0° ± 1.3°	S(3)—Tl,Pb(2)—S′(1)	59.7° ± 1.4°
S(1)—Pb,Tl(1)—S(2)	67.9 ± 1.4	S′(1)—Tl,Pb(2)—As′(1)	85.6 ± 0.8
S′(2)—Pb,Tl(1)—S(1)	65.2 ± 1.2	S′(1)—Tl,Pb(2)—S(5)	70.2 ± 0.8
S′(1)—Pb,Tl(1)—S(2)	68.4 ± 1.2	S(5)—Tl,Pb(2)—As′(1)	57.9 ± 1.0
S(5)—Pb,Tl(1)—S″(3)	99.3 ± 1.3	S(5)—Tl,Pb(2)—S′(5)	113.9 ± 0.7
S(1)—Pb,Tl(1)—S(5)	83.4 ± 1.3	S′(5)—Tl,Pb(2)—As′(1)	143.8 ± 0.7
S(2)—Pb,Tl(1)—S″(3)	93.3 ± 1.2	S′(5)—Tl,Pb(2)—S′(4)	87.1 ± 1.3
S′(2)—Pb,Tl(1)—S(5)	90.2 ± 1.1	S′(5)—Tl,Pb(2)—S″(4)	71.0 ± 1.2
S′(1)—Pb,Tl(1)—S″(3)	92.2 ± 1.5	S′(4)—Tl,Pb(2)—S″(4)	56.8 ± 1.2
S(1)—Pb,Tl(1)—S′(3)	74.1 ± 1.3	S′(4)—Tl,Pb(2)—As′(1)	69.9 ± 0.9
S(2)—Pb,Tl(1)—S′(3)	75.5 ± 1.2		
S(5)—Pb,Tl(1)—S′(3)	70.7 ± 1.2	S(1)—As(1)—S(4)	97.3 ± 1.4
S″(3)—Pb,Tl(1)—S′(3)	78.4 ± 2.1	S(1)—As(1)—S(2)	97.9 ± 1.9
S(5)—Pb,Tl(1)—S(4)	86.9 ± 1.3	S(4)—As(1)—S(2)	101.7 ± 2.1
S″(3)—Pb,Tl(1)—S(4)	81.8 ± 1.3		
S(2)—Pb,Tl(1)—S(4)	64.4 ± 1.2		
S(1)—Pb,Tl(1)—S(4)	64.3 ± 1.0	S(3)—As(2)—S(1)	94.7 ± 1.8
		S(3)—As(2)—S′(5)	98.9 ± 1.9
S(2)—Tl,Pb(2)—S″(4)	108.2 ± 1.1	S(1)—As(2)—S′(5)	101.1 ± 1.7
S(2)—Tl,Pb(2)—S(3)	112.1 ± 1.2		
S(2)—Tl,Pb(2)—S(5)	79.9 ± 1.2	S′(2)—Cu—S′(4)	116.5 ± 2.4
S(2)—Tl,Pb(2)—S′(1)	58.7 ± 1.1	S′(2)—Cu—S″(5)	96.7 ± 1.5
S(2)—Tl,Pb(2)—S′(5)	69.9 ± 1.1	S′(2)—Cu—S′(5)	118.6 ± 1.9
S(3)—Tl,Pb(2)—S″(4)	72.7 ± 1.1	S′(4)—Cu—S′(5)	121.7 ± 1.7
S(3)—Tl,Pb(2)—S′(4)	82.5 ± 1.4	S″(5)—Cu—S′(5)	94.9 ± 1.5
S(3)—Tl,Pb(2)—As′(1)	64.1 ± 0.8	S″(5)—Cu—S′(4)	96.1 ± 1.7

Cu coordination. In binnite[11] and tetrahedrite[12] half of the Cu atoms also have a planar trigonal coordination (2.204 to 2.258, 2.234 to

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[12] B. J. Wuensch, The crystal structure of tetrahedrite. Z. Kristallogr. **119** (1964) 437—453.

2.272 Å); but there is no fourth S atom. Instead we have two As atoms at distances of 3.47 Å. The same situation as for Cu in wallisite occurs for Ag in the isotypic hatchite structure[7], and similarly in smithite ($AgAsS_2$)[13], trechmannite ($AgAsS_2$)[14], marrite ($PbAgAsS_3$)[15] and miargyrite ($AgSbS_2$)[16]. The Cu atoms show a high temperature coefficient. Though the thermal parameters obtained in this structure are not highly reliable, the high value for Cu is in conformity with the Fourier peaks. Specifically, in spite of the partial replacement of Cu by Ag, the peaks corresponding to Cu are lower than the peak heights theoretically expected for Cu. The Cu—S(4) distance of 2.22 Å

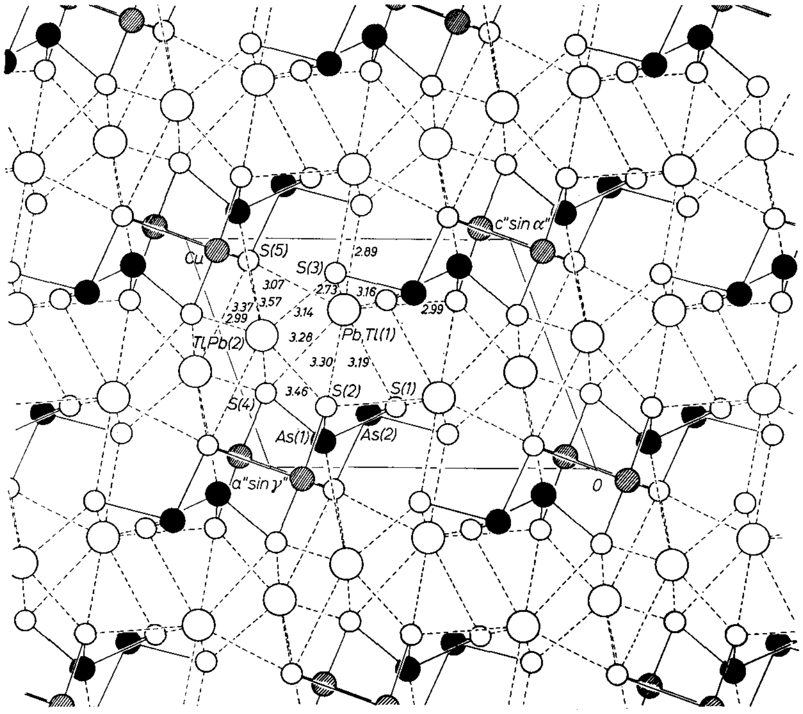

Fig. 4. The projection of the wallisite structure ‖ b''

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[13] E. Hellner und H. Burzlaff, Die Struktur des Smithits $AgAsS_2$. Naturwiss. **51** (1964) 35—36.

[14] T. Matsumoto and W. Nowacki, The crystal structure of trechmannite, $AgAsS_2$. Z. Kristallogr. **128** (1968) [in press].

[15] B. J. Wuensch and W. Nowacki, The crystal structure of marrite, $PbAgAsS_3$. Z. Kristallogr. **125** (1967) 459—488 (Menzer-Festschrift).

[16] Ch. R. Knowles, A redetermination of the structure of miargyrite, $AgSbS_2$. Acta Crystallogr. **17** (1964) 847—851.

is shorter than the normal value of 2.34 Å. But similar short distances are observed in binnit[11] (2.204, 2.258 Å), tetrahedrite[12] (2.234, 2.272 Å), and seligmannite[17] (2.25, 2.27 and 2.28 Å).

If, in the structures of sulfosalts of the system Pb—As—S, the As:Pb ratio is higher than 1.00, the As—S bonds form a complex, finite or infinite group. In the structure of wallisite, an As-S pyramid shares one sulfur atom with another As-S pyramid and forms a finite complex As_2S_5. Therefore an alternate expression of the configuration of the chain in wallisite is that it is consisted of As_2S_5 groups and Cu-S tetrahedra.

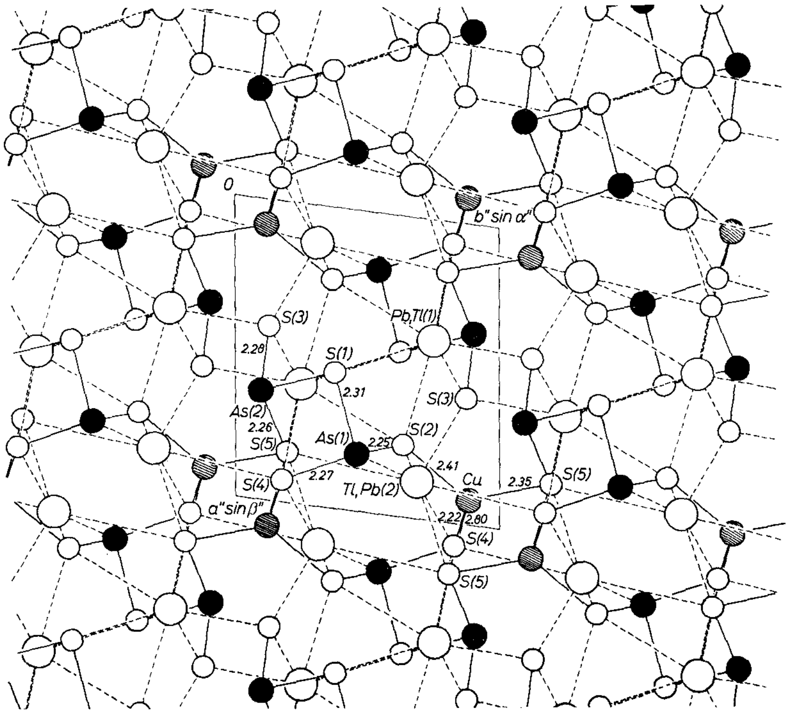

Fig 5. The projection of the wallisite structure ‖c″

Between these chains the Pb and Tl atoms are located and thus the formula $(Pb,Tl)_2(Cu,Ag)As_2S_5$ was confirmed. This composition correponds to that of dufrenoysite with an excess of Cu(Ag). The perfect cleavage of wallisite ‖ (001), which is also a well developed

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[17] G. Leineweber, Strukturanalyse des Bournonits und Seligmannits mit Hilfe der Superpositionsmethoden. Z. Kristallogr. **108** (1956) 161—184.

face (Figs. 1 and 2) is well explained in the b''-axis projection of the structure (Fig. 4). Figure 5 shows the c'' projection of the structure.

There are two nonequivalent Pb,Tl atoms in the cell. One of them, Pb,Tl(1) (Fig. 6), has eight neighbours of sulfur atoms and an average Pb—S distance is 3.08 Å (hatchite 3.10 Å). However the coordination of the other one, Tl,Pb(2) (Fig. 7), is very irregular and it has only two nearest neighbours if the Pb—S distances longer than 3.3 Å are excluded. Such a coordination is quite unusual for Pb atoms in other sulfosalts and it is supposed that this location is mainly occupied by Tl atoms. This feature is quite similar with that of hutchinsonite where two nonequivalent Pb,Tl locations exist and one of them has an irregular coordination of sulfur atoms with two nearest neighbours. As suggested by the chemical analyses of wallisite, there is approximately an equal number of Pb and Tl atoms in the cell. For such a case, at least, it appears that Pb and Tl tend to have an ordered arrangement. It should be mentioned that there is a close approach of 3.78 Å between the Tl,Pb(2) atoms. Usually the closest approach between Pb atoms in sulfosalts is around 4.1 ≈ 4.2 Å, but in lorandite, $TlAsS_2$, the Tl—Tl distances are as close as 3.5 Å.

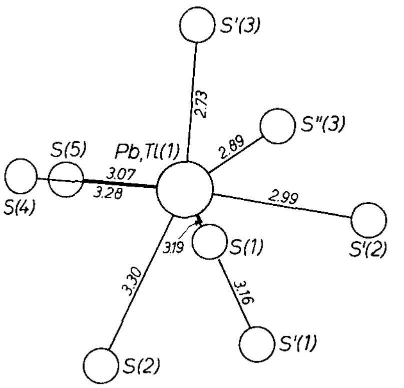

Fig. 6. Coordination around the Pb,Tl(1) atom

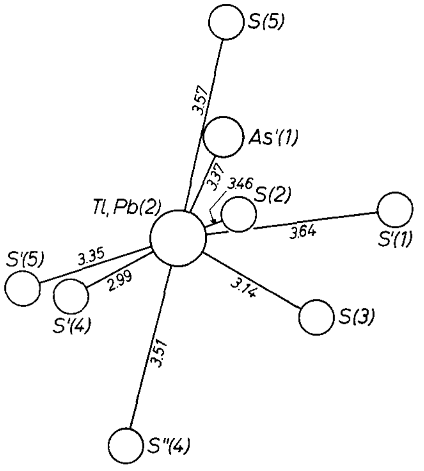

Fig. 7. Coordination around the Tl,Pb(2) atom

There is a certain relation of the structure of wallisite to that of galena (Fig. 8). The axes of wallisite — a'', b'', c'' — are related to those of galena — a_1, a_2, a_3 — by the equations

$$\begin{aligned}\mathfrak{a}'' &= \tfrac{3}{2}\,\mathfrak{a}_1 \qquad\quad - \tfrac{1}{2}\,\mathfrak{a}_3\\ \mathfrak{b}'' &= \tfrac{1}{2}\,\mathfrak{a}_1 + \mathfrak{a}_2 + \tfrac{1}{2}\,\mathfrak{a}_3\\ \mathfrak{c}'' &= \mathfrak{a}_1 \qquad\qquad + \mathfrak{a}_3 .\end{aligned}$$

If we adopt[18] $a_1 = a_2 = a_3 = 5.9362$ Å, we obtain by these results: $a'' = 9.386$ Å, $b'' = 7.270$ Å, $c'' = 8.395$ Å, $\alpha'' = 54°44'$, $\beta'' = 63°26'$, $\gamma'' = 75°01'$, as compared with the experimental values $a'' = 9.21_5$ Å, $b'' = 8.52_4$ Å, $c'' = 7.98_0$ Å, $\alpha'' = 55°59'$, $\beta'' = 62°30'$, $\gamma'' = 69°24'$. In Fig. 8 is shown a projection of the galena structure along $b'' = [121]_{\mathrm{PbS}}$. The directions of the axes a'', b'' and c'' are respectively equivalent to $[30\bar{1}]$, $[121]$ and $[101]$ of galena. The coordinates of the atoms in galena can thus be expressed in terms of the wallisite axes as follows:

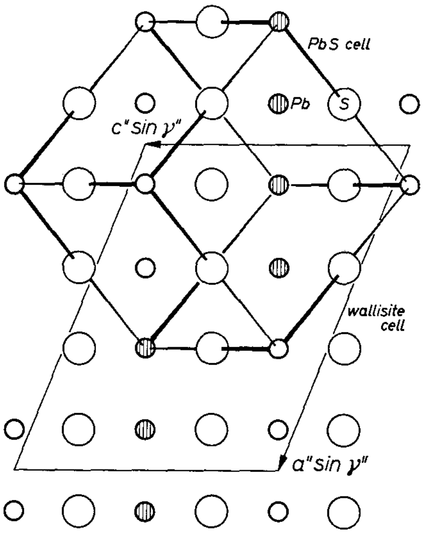

Fig. 8. The PbS structure projected along [121]. Shaded small circles correspond to Pb,Tl of wallisite

$$\begin{aligned}x_1 &= \tfrac{3}{2}\,x'' + \tfrac{1}{2}\,y'' + z''\\ x_2 &= y''\\ x_3 &= -\tfrac{1}{2}\,x'' + \tfrac{1}{2}\,y'' + z'' .\end{aligned}$$

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[18] H. E. Swanson and R. R. Fuyat, NBS Circular 539, II, 18 (1953).

If the origin in wallisite is taken on Tl,Pb(2), the coordinates of Pb,Tl(1) become $x_1 = 0.5258$, $x_2 = 0.4430$, $x_3 = 0.0314$, which should be compared with the coordinates 0.5, 0.5, 0, as expected from the galena structure. Similarly the Cu coordinates become 0.5244, 0.1920, 0.4440, which are far from the tetrahedral site 0.25, 0.25, 0.25 in the galena structure. Thus at least the Pb,Tl sites of wallisite are similar to that of galena. As a matter of fact, the ratio of the total number of Pb,Tl, Cu and As and that of S in the cell of wallisite is unity. According to HELLNER[19] the sulfosalts which have such a ratio are expected to have a close resemblance with the PbS-type structure. But in the bulk of the structure it is very difficult to trace the PbS-type structure because of the high deformation due to the As—S bonding.

The above characteristics of the structure of wallisite are completely parallel[7] with those of hatchite and thus the isomorphism between wallisite and hatchite has been established.

Acknowledgments

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[19] E. HELLNER, A structural scheme for sulfide minerals. J. Geol. **66** (1958) 503—525.