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The crystal structure of hatchite, $PbTlAgAs_2S_5$*

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Dedicated to Professor Dr. G. Menzer on occasion of his 70th birthday

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Auszug

Die Kristallstruktur von Hatchit, $PbTlAgAs_2S_5$, wurde bestimmt: C_i^1—$P\bar{1}$, reduzierte Zelle $a = 9{,}22 \pm 0{,}01$, $b = 7{,}84 \pm 0{,}01$, $c = 8{,}06 \pm 0{,}01$ Å, $\alpha = 66°25' \pm 15'$, $\beta = 65°17' \pm 15'$, $\gamma = 74°54' \pm 15'$, $Z = 2$, $d_x = 5{,}8\,\mathrm{g\,cm^{-3}}$. Die direkte Interpretation der dreidimensionalen Pattersonsynthese ergab die Orte von drei der vier Schweratomlagen. Die vollständige Struktur wurde durch sukzessive dreidimensionale Fourier- und Differenz-Fouriersynthesen gefunden und zu $R = 0{,}09$ (für alle Reflexe) bzw. 0,08 (für die beobachteten Reflexe) verfeinert. Es war nicht möglich, zwischen Pb und Tl zu unterscheiden.

Das (Pb,Tl)(1)-Atom ist von 8 S in Abständen, wie sie für (Pb—S)-Bindungen normal sind (2,81–3,31 Å) umgeben, während das (Tl,Pb)(2)-Atom eine sehr ungewöhnliche Koordination von 8 S, 2 As und ein Ag hat. Zwei der ein (Tl,Pb)-(2) umgebenden S-Atome sind so gelegen, daß normale (Pb—S)-oder (Tl—S)-Abstände resultieren (3,05, 3,12 Å). Die Struktur besteht wesentlich aus unendlichen Doppelketten // [$01\bar{1}$] (bezogen auf die gestrichene Zelle, vgl. Text) von trigonalen Pyramiden AsS_3 und AgS_3, wobei die As,S eine As_2S_5-Gruppe bilden. Die Ag-Atome weisen ein viertes S-Atom in relativ kurzem Abstand von 2,93 Å auf, eine tetraedrische Koordination ergebend. Diese Doppelketten können auch als aus AgS_4-Doppeltetraedern (mit einer gemeinsamen Kante) der Zusammensetzung Ag_2S_6, welche durch As_2S_5-Gruppen vereint sind, bestehend beschrieben werden, wodurch sich die Gesamtzusammensetzung $Ag_2As_4S_{10}$ ergibt. Die Doppelketten werden seitlich durch die Pb- und Tl-Atome zusammengehalten. Durch diese Struktur wird die // (011) (bezogen auf die gestrichene Zelle) beobachtete Spaltbarkeit gut erklärt.

Abstract

The crystal structure of hatchite, $PbTlAgAs_2S_5$, has been determined. The crystal is triclinic with the space group C_i^1—$P\bar{1}$. The cell constants of the reduced

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cell are $a = 9.22 \pm 0.01$ Å, $b = 7.84 \pm 0.01$ Å, $c = 8.06 \pm 0.01$ Å, $\alpha = 66°25' \pm 15'$, $\beta = 65°17' \pm 15'$, $\gamma = 74°54' \pm 15'$ and $Z = 2$; $d_x = 5.8$ g cm^{-3}. The direct interpretation of the three-dimensional Patterson function gave three out of four heavy-atom locations. The complete structure was obtained by successive three-dimensional Fourier and difference-Fourier syntheses, and refined to $R = 0.09$ for all reflections, and to 0.08 for observed reflections only. It was impossible to distinguish Tl atoms from Pb atoms.

The (Pb,Tl)(1) atom is surrounded by eight S atoms at distances normal for Pb—S bonds, while the (Tl,Pb)(2) atom has quite an unusual coordination, being surrounded by eight S, two As and one Ag atoms. Two of the S atoms around the (Tl,Pb)(2) atom are situated at positions with reasonable interatomic distances for Pb—S or Tl—S bonds (3.05, 3.12 Å). The structure consists essentially of infinite double chains of As—S_3 and Ag—S_3 trigonal pyramids running along the $[01\bar{1}]$ direction, (referred to the primed cell, see text) the As,S forming an As_2S_5 group. The Ag atoms have a fourth S atom at relatively short distance of 2.93 Å, yielding a tetrahedral coordination. These double chains may also be described as consisting of AgS_4 double tetrahedra (having a common edge) of the composition Ag_2S_6, joined together by As_2S_5 groups, yielding the total composition $Ag_2As_4S_{10}$. The double chains are combined laterally with the Pb and Tl atoms. The existence of cleavage parallel to (011), referred to the primed cell, is well explained by the proposed structure.

1. Introduction

Hatchite is a rather rare sulfosalt mineral having the chemical composition $PbTlAgAs_2S_5$ as will be shown in this paper. Up to the present it was found only in the dolomite of the Lengenbach quarry (Binnatal, Ct. Wallis, Switzerland). The mineral was described first by Solly and Smith (1912), but not enough data were available then to establish the existence of a new mineral species, only a few small crystals having been found. Recently some triclinic crystals were found which could be identified by x-ray methods (determination of the lattice constants and axial ratio) as hatchite (Nowacki and Kunz, 1961; Nowacki *et al.*, 1961). The first chemical analysis was made by Bahezre, Paris (Nowacki, 1965, and Table 1), and hatchite turned out to be a distinct crystal species. It seems to be not as rare as was first thought, since several specimens with small hatchite crystals on them have been found during the last years in the Lengenbach quarry (Nowacki, 1967).

The structure determination of hatchite was undertaken as a part of a systematic study of arsenosulfosalt crystals for the purpose of obtaining knowledge on the structural principle of arsenosulfosalts minerals containing Ag or Tl atoms.

Table 1. *Chemical composition of hatchite*

	Pb	Tl	Ag	Cu	As	S	Total
I	24.6	24.5	10.9	0.95	20.7	19.0	100.65%
II	25.5	26.5	10.5	0.7	18.1	19.1	100.4
III	25.0	24.6	13.0	—	18.1	19.3	100.0

I = Bahezre in NOWACKI, 1965; II = BURRI, Anal. Nr. 46 [The analysis given in NOWACKI and BAHEZRE (1963) for hatchite is not reliable, the specimen analyzed not being real hatchite]; III = theoretical values for $PbTlAgAs_2S_5$.

2. Experimental

Two specimens, I (L. 1268 in NOWACKI and KUNZ, 1961) and II (Stufe S in NOWACKI, BURRI *et al.*, 1967), were used for the x-ray work. The constants of a small unit cell (the "primed" cell), obtained from specimen II with back-reflection Weissenberg photographs, are:

$$a' = 9.37 \pm 0.01\,\text{Å},\quad b' = 7.84 \pm 0.01\,\text{Å},\quad c' = 8.06 \pm 0.01\,\text{Å}$$

$$\alpha' = 66°25' \pm 15',\quad \beta' = 63°20' \pm 15',\quad \text{and}\quad \gamma' = 84°58' \pm 15'.$$

These are in accordance with the values determined by NOWACKI and KUNZ (1961). The true reduced cell* has the constants

$$a = 9.22 \pm 0.01\,\text{Å},\quad b = 7.84 \pm 0.01\,\text{Å},\quad c = 8.06 \pm 0.01\,\text{Å},$$

$$\alpha = 66°25' \pm 15',\quad \beta = 65°17' \pm 15',\quad \gamma = 74°54' \pm 15',$$

the transformation formulae being

$$a = a' - c',\ b = b',\ c = c'$$

$$a' = a + c,\ b' = b,\ c' = c.$$

The structure determination and description is given in terms of the primed cell. — The space group is $C_1^1\text{—}P1$ or $C_i^1\text{—}P\bar{1}$.

An x-ray microprobe analysis of specimens I and II was carried out by C. BAHEZRE, Paris, and by G. BURRI, Bern, respectively (Table 1). Both specimens have identical chemical composition within the experimental errors. The unit-cell content, calculated with a den-

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sity 5.5 g cm^{-3}, which is assumed to be not far from the true density of the crystal, is $Pb_{1.84}Tl_{1.88}Ag_{1.58}Cu_{0.23}As_{4.33}S_{9.29}$ and $Pb_{1.93}Tl_{2.03}Ag_{1.53}Cu_{0.17}As_{3.79}S_{9.33}$ for I and II respectively. The idealized chemical formula of the crystal is, therefore, $PbTlAgAs_2S_5$ and two formula units are contained in the cell, giving a calculated density 5.8 g cm^{-3}.

Intensity measurements were carried out twice, utilizing both specimens. The photographic method was employed for the measurements with I, while a Supper-Pace automated diffractometer was used for II. The data of I were collected by V. KUNZ, Bern; these were used only in the earlier stage of the structure determination since the data contained fairly large errors caused by absorption. Integrating Weissenberg photographs of I were taken up to the sixth layer around the a' axis, and up to the second layer around the b' axis with Cu$K\alpha$ radiation. Intensities were measured with a Joyce-Loebl double-beam densitometer, and corrected for the Lorentz-polarization factor. No absorption correction was applied since the crystal used had a irregular form. For the diffractometer measurements an attempt was made to form a sphere by Bond's method, but it was unsuccessful because of the cleavage of the crystal. Therefore a small piece was cut off from specimen II. In order to remove the damaged part of the crystal, the piece was dipped in concentrated HNO_3 for thirty minutes and then washed in a saturated solution of CH_3NH_4 with a small amount of NH_4OH. Since the crystal has a large absorption coefficient (1011 cm^{-1} for Cu$K\alpha$ radiation), the crushed surface layer causes a large diminution of the intensity. The size of the crystal used was about $0.066 \times 0.056 \times 0.070$ mm^3. Rotating the crystal around the $[01\bar{1}]$ (primed cell) and the a' axis, 1749 reflections were measured with Cu$K\alpha$ radiation, among which 139 reflections were not observed. The corrections of the measured intensities for absorption were carried out assuming a sphere with a diameter of 0.064 mm, for which μr is 3.24.

3. Determination of the structure and refinements

A three-dimensional Patterson function was calculated by V. KUNZ from the photographic data to get information about the metal-atom positions. Since the unit cell is rather small, no severe overlapping of peaks is expected. Only the positions of the peaks were, therefore, plotted on a square unit cell, as shown in Fig. 1, instead of preparing the exact Patterson map. The image-seeking procedure was employed to interpret the map as follows.

From the chemical composition four heavy atoms (Pb and Tl) are expected in the primed cell. Both centrosymmetric and noncentrosymmetric cases were considered, since it was not known which was the real one until the structure was solved. In the centrosymmetric case there must be four independent vectors between heavy atoms, among which two peaks are cross-vector peaks, having double weights. The remainders are inversion peaks with single weights. In the noncentrosymmetric case there must be six cross-vector peaks. In Fig. 1 there are two salient peaks, *A* and *B*. If we assume these peaks as the cross-vector peaks in the centrosymmetric case, we can choose peaks *C* and *D* as inversion peaks. Based upon this configuration of the heavy atoms, probable positions of other metallic atoms were obtained as shown in Fig. 1 by shaded circles, which explain the Patterson map fairly well except for peak heights. There are twelve independent peaks which are higher than peak *D*, besides peaks *A*, *B*, *C* and the one at the origin. The (Pb,Tl)—(Pb,Tl) peaks should be several times higher than the (Pb, Tl)—Ag and the (Pb,Tl)—As

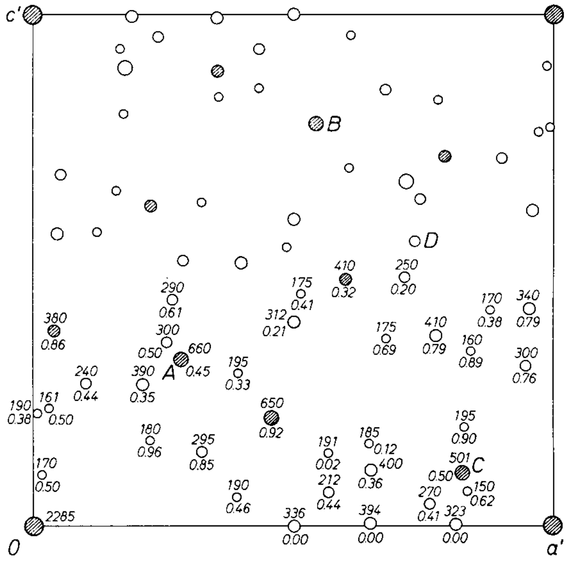

Fig. 1. Arrangement of the three-dimensional Patterson peaks of hatchite. The relative peak heights and y' coordinates in fractions of b' are indicated with numbers above and below the circles respectively. The shaded circles indicate the metallic-atom positions obtained by assuming C_i^1—$P\bar{1}$ as space group of hatchite

peaks, since we can expect temperature factors of the same order for all the metallic atoms. It is impossible to explain the heights of these twelve peaks by considering overlappings if the height of a (Pb,Tl)—(Pb,Tl) peak is equal to the height of D, because we need more peaks than the number expected from the cell content. The situation is the same even if we assume a noncentrosymmetric structure. However, the highest peaks A, B and C are undoubtedly (Pb,Tl)—(Pb,Tl) peaks. We can explain these three peaks by putting Pb (Tl) atoms at A, B and the origin, since vector AC is equal to vector OB. Therefore the first trial was started with this arrangement of the heavy atoms to find the remaining atoms with successive two-dimensional refinements by the Fourier and the difference-Fourier methods. After four cycles of calculations all metallic atom positions were found, although an ambiguity remained in the assignment of atom kinds, yielding an R value of 0.26 for the $0kl$, and 0.34 for the $h0l$ reflections. The arrangement of the metallic atoms thus obtained is essentially the same as obtained in the first stage of the interpretation of the Patterson map with the assumption of centers of symmetry. Sulfur-atom positions were found from the three-dimensional difference Fourier function synthesized with the phases determined by metallic atoms only. The R value dropped down to 0.27 for all the observed reflections after one cycle of refinement with the difference Fourier method, suggesting that the model is fundamentally correct. However it turned out at this stage that the experimental errors were so large that the Ag atoms could not be distinguished from the As atoms, and it is not certain if one of the atoms is Ag or (Pb,Tl). Therefore the new intensity data collected with the diffractometer were used for the refinement of the model. Assignment of all atom

Table 2. *The final positional parameters of hatchite* (referred to the primed cell)

Atom	x'	y'	z'	$\sigma(x')$	$\sigma(y')$	$\sigma(z')$
(Pb,Tl)(1)	0.4064	0.2473	0.0574	0.0003	0.0004	0.0004
(Tl,Pb)(2)	0.1322	0.6968	0.7249	0.0005	0.0006	0.0006
Ag	0.0853	0.8910	0.1553	0.0008	0.0009	0.0010
As(1)	0.1928	0.4550	0.4228	0.0009	0.0010	0.0011
As(2)	0.3670	0.1068	0.6698	0.0009	0.0010	0.0011
S(1)	0.452	0.371	0.371	0.002	0.002	0.002
S(2)	0.246	0.624	0.099	0.002	0.002	0.003
S(3)	0.414	0.869	0.286	0.002	0.002	0.003
S(4)	0.091	0.182	0.474	0.002	0.002	0.003
S(5)	0.183	0.215	0.891	0.002	0.002	0.003

Table 3. *The final temperature factors of hatchite*

The values are the coefficients in the expression exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{23}kl + \beta_{13}lh)]$

Atom	β_{11}	$\sigma(\beta_{11})$	β_{22}	$\sigma(\beta_{22})$	β_{33}	$\sigma(\beta_{33})$	β_{12}	$\sigma(\beta_{12})$	β_{23}	$\sigma(\beta_{23})$	β_{13}	$\sigma(\beta_{13})$	B_i
(Pb,Tl)(1)	.012	.001	.010	.001	.014	.001	.003	.001	—.011	.001	—.014	.001	2.6Å^2
(Tl,Pb)(2)	16	1	26	1	18	1	9	1	—.022	2	—.018	1	4.2
Ag	.16	1	15	1	16	2	4	2	—.008	2	—.009	2	4.0
As(1)	11	1	10	2	10	2	4	2	—.011	3	—.010	2	2.3
As(2)	13	1	9	2	12	2	2	2	—.010	3	—.014	2	2.5
S(1)	11	2	13	3	13	4	0	4	—.007	6	—.013	5	2.8
S(2)	10	2	14	3	16	4	4	4	—.014	6	—.013	5	2.8
S(3)	11	2	12	3	13	4	2	4	—.011	6	—.011	5	2.8
S(4)	13	3	11	3	18	4	2	4	—.013	6	—.017	5	2.9
S(5)	9	2	16	3	12	4	4	4	—.015	6	—.009	5	2.6

B_i = equivalent isotropic temperature factor.

Table 4. *Comparison of observed and calculated structure amplitudes*

h	k l	$\|F_o\|$	F_c	h	k l	$\|F_o\|$	F_c	h	k l	$\|F_o\|$	F_c	h	k l	$\|F_o\|$	F_c	h	k l	$\|F_o\|$	F_c
1	0 0	29	17	-5	5 0	41	39	2	2 1	106	-97	6	-4 1	63	-60	4	8 1	8	5
2		45	32	-6		37	35	3		46	41	7		89	89	-1		17	15
3		131	-112	-7		34	-33	4		20	11	8		0	3	-2		18	19
4		240	-223	-8		9	13	5		114	-112	9		14	-17	-3		31	28
5		75	66	0	6 0	69	-77	6		68	61	-1		89	-101	-4		17	-16
6		85	-81	1		43	50	7		61	-54	-2		64	-66	-5		43	42
7		24	24	2		55	-60	8		19	21	-3		15	-13	1	-8 1	9	-7
8		0	11	3		78	-89	9		13	13	-4		71	-69	2		10	11
9		12	-8	4		26	30	10		17	-34	-5		18	17	3		29	-27
10		9	23	5		49	-53	-1		218	232	-6		10	13	-1		0	6
0	1 0	11	10	6		58	60	-2		194	174	-7		40	38	0	0 2	31	-38
1		20	-24	-1		74	78	-3		118	-106	0	5 1	39	-45	1		175	-209
2		343	331	-2		30	27	-4		149	-141	1		80	-88	2		56	56
3		64	52	-3		43	45	-5		160	-156	2		41	49	3		110	-100
4		42	37	-4		44	48	-6		17	-12	3		96	-110	4		19	13
5		67	-60	-5		57	-58	-7		19	21	4		49	52	5		138	123
6		131	-123	-6		13	-10	-8		22	26	5		12	18	6		66	-64
7		29	-29	-7		15	-14	-9		27	36	6		50	52	7		88	85
8		15	-17	-8		13	12	0	-2 1	308	-335	7		52	55	8		78	-74
9		29	32	0	7 0	9	8	1		8	4	8		12	-15	9		37	-37
10		8	19	1		32	33	2		244	-228	-1		79	80	10		28	26
-1		0	-2	2		77	-83	3		24	-24	-2		107	-114	-1		31	-26
-2		225	-184	3		34	38	4		109	96	-3		90	96	-2		56	-40
-3		175	145	4		42	-43	5		39	-34	-4		20	-20	-3		163	155
-4		172	-151	5		23	-19	6		100	91	-5		24	-24	-4		97	98
-5		0	12	-1		14	-1	7		20	-8	-6		23	21	-5		73	71
-6		59	58	-2		89	88	8		31	32	-7		51	-50	-6		31	-28
-7		27	-25	-3		68	-68	9		0	3	-8		35	43	-7		77	-76
-8		25	29	-4		21	17	10		19	-31	0	-5 1	50	62	-8		14	-15
-9		52	-55	-5		18	18	-1		126	122	1		43	-50	0	1 2	0	0
-10		0	-10	-6		0	4	-2		141	132	2		93	-97	1		33	-28
0	2 0	169	-200	0	8 0	54	51	-3		91	89	3		77	77	2		104	-113
1		26	-10	1		31	-32	-4		181	175	4		26	-29	3		360	-388
2		61	-53	2		10	12	-5		142	-136	5		142	143	4		103	102
3		52	53	-1		93	-91	-6		0	-1	6		16	16	5		100	-95
4		124	113	-2		47	42	-7		18	-17	7		24	-27	6		50	51
5		45	41	-3		34	33	-8		0	-4	8		28	29	7		68	62
6		54	54	-4		13	10	0	3 1	164	187	9		23	-64	8		18	-19
7		36	-35	0	0 1	90	72	1		187	231	-1		40	-42	9		73	68
8		30	-30	1		46	-48	2		52	54	-2		19	25	10		27	-32
9		22	-26	2		162	146	3		196	196	-3		43	-49	-1		348	391
-1		99	101	3		32	27	4		179	-177	-4		16	-13	-2		54	48
-2		69	-60	4		33	-22	5		19	-16	-5		10	6	-3		103	92
-3		32	14	5		106	-95	6		40	-42	-6		15	-14	-4		27	-30
-4		164	138	6		145	-137	7		62	-61	0	6 1	85	-82	-5		121	-117
-5		124	-111	7		33	36	8		65	67	1		65	68	-6		29	21
-6		57	47	8		0	12	9		34	36	2		59	-64	-7		26	-23
-7		110	-105	9		40	35	-1		185	-205	3		18	-23	-8		18	12
-8		18	-15	10		19	26	-2		51	-51	4		49	52	0	-1 2	75	-67
-9		45	56	-1		119	-98	-3		159	-146	5		11	-4	1		34	-33
-10		0	-7	-2		49	-39	-4		21	-11	6		32	32	2		101	98
0	3 0	15	-20	-3		74	61	-5		30	29	7		21	-23	3		217	199
1		41	40	-4		44	-38	-6		47	-46	-1		87	85	4		140	-124
2		73	-74	-5		165	155	-7		39	42	-2		93	-90	5		34	21
3		53	53	-6		37	-37	-8		0	-2	-3		86	-83	6		108	-98
4		0	-10	-7		18	19	-9		18	24	-4		45	39	7		30	-32
5		31	32	-8		0	-1	0	-3 1	123	-131	-5		58	-53	8		107	104
6		33	32	-9		54	-61	1		69	75	-6		127	115	9		28	-23
7		17	-9	0	1 1	26	-24	2		99	98	-7		25	28	10		48	57
8		58	57	1		28	-18	3		56	-52	0	-6 1	56	-62	-1		206	-187
9		23	-29	2		25	10	4		205	190	1		32	34	-2		16	5
-1		12	-7	3		137	-119	5		25	-18	2		34	35	-3		33	-28
-2		66	69	4		148	135	6		37	-38	3		78	75	-4		14	15
-3		156	-145	5		29	33	7		15	-15	4		16	15	-5		47	43
-4		0	3	6		29	26	8		53	-51	5		39	-39	-6		30	25
-5		140	-132	7		19	-19	9		32	33	6		41	40	-7		71	69
-6		20	-8	8		133	-128	10		7	19	7		42	-41	-8		21	-22
-7		111	111	9		29	28	-1		66	67	8		9	4	0	2 2	71	-75
-8		0	5	10		15	-15	-2		183	-187	-1		39	-42	1		268	350
-9		56	66	-1		62	51	-3		23	19	-2		16	-19	2		31	-29
0	4 0	11	11	-2		37	-29	-4		20	26	-3		8	6	3		39	-39
1		46	50	-3		189	166	-5		46	45	-4		31	31	4		95	-95
2		108	122	-4		0	12	-6		81	83	-5		16	-12	5		215	-211
3		0	12	-5		15	13	-7		27	-23	0	7 1	80	-77	6		57	54
4		44	-48	-6		25	-24	-8		0	-8	1		0	-3	7		30	-26
5		43	44	-7		110	-106	0	4 1	44	44	2		16	10	8		42	36
6		20	-17	-8		18	13	1		154	-184	3		50	53	9		28	27
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Table 4. *(Continued)*

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5			50	46
6			99	-100
7			65	-65
8			0	-10
9			0	-1
10			14	24
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-5			51	53
-6			64	-67
-7			29	25
-8			35	-42
0	-3	2	147	-144
1			132	-144
2			6	-8
3			43	41
4			132	126
5			48	46
6			60	57
7			18	15
8			39	-41
9			9	-10
10			19	-43
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-2			28	-28
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6			57	-54
7			17	-21
8			56	-56
9			16	17
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8			22	8
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5			115	-112
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8			67	62
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4			86	-90
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6			38	-35
7			37	36
8			32	34
9			71	-64
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3			124	-114
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5			86	-78
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7			14	19
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4			63	68
5			17	22
6			72	76
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5			49	50
6			16	-15
7			8	2
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3			50	-53
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1			37	-32
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3			10	7
4	8	3	10	3
5			13	11
6			20	-19
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5			122	-126
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2			53	-61
3			74	82
4			166	170
5			49	-52
6			29	26
7			82	-79
8			40	-38
9			73	67
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3			15	-16
4			67	76
5			127	131
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6			172	177
7			33	-34
8			73	66
9			61	-62
10			15	-16
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7			68	-66
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9			67	-64
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Table 4. *(Continued)*

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7			54	45
8			74	72
9			24	-22
10			46	46
-1			0	5
-2			56	54
-3			46	-47
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-5			66	64
-6			15	9
-7			20	22
0	-3	4	63	-64
1			117	113
2			59	53
3			18	-18
4			37	40
5			129	-131
6			0	-3
7			46	-43
8			21	19
9			38	41
10			6	4
-1			94	96
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-3			25	-26
-4			8	2
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1			78	-87
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3			0	4
4			22	23
5			45	-46
6			121	-124
7			27	17
8			0	1
9			51	50
10			0	-6
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2			46	47
3			136	-149
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5			0	-4
6			11	-14
7			66	67
8			23	-21
9			12	12
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-2			27	-30
-3			38	38
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2			0	-6
3			68	-70
4			65	71
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6			67	68
7			58	-56
8			34	-36
9			13	-12
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4			17	-22
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8			22	-22
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7			70	-70
8			14	-11
9			14	-13
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3			90	-93
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10			14	-8
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3			24	-22
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2			125	-136
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4			53	-56
5			79	-79
6			84	87
7			0	-9
8			62	62
9			38	38
10			31	-38
-1			77	83
-2			98	102
-3			16	16
-4			0	4
-5			66	-66
1	-5	5	60	-55
2			10	-9
3			34	-37
0	6	5	71	73
1			77	80
2			28	-26
3			68	70
4			132	-135
5			30	-26
6			22	26
7			36	-36
8			64	66
9			24	-33
-1			75	-76
-2			12	10
-3			59	-55
-4			40	40
-5			29	32
0	7	5	44	45
1			78	-79
2	7	5	30	28
3			44	48
4			0	-1
5			75	76
6			63	-66
7			29	-29
8			11	1
-1			33	-29
-2			0	3
-3			44	42
-4			30	-29
0	8	5	19	18
1			15	-16
2			72	76
3			71	-72
4			12	13
5			0	7
6			16	-7
7			28	32
-1			60	57
-2			45	-44
-3			38	40
0	9	5	19	-17
1			34	32
2			16	11
3			11	-13
4			47	48
-1			67	68
0	0	6	42	-44
1			35	-41
2			50	52
3			0	0
4			71	77
5			20	-22
6			29	27
7			38	-39
8			50	-50
9			9	-3
10			43	-43
-1			45	43
-2			0	11
-3			68	66
-4			34	-28
0	1	6	43	42
1			111	122
2			59	-64
3			0	2
4			59	-70
5			42	-46
6			68	73
7			40	-39
8			65	66
9			33	-30
10			21	-25
-1			81	86
-2			21	-23
-3			63	-64
-4			12	-7
0	-1	6	94	95
1			39	-38
2			42	43
3			37	41
4			0	-1
5			50	56
6			111	-117
7			35	-39
8			46	-47
9			27	27
10			38	43
-1			42	-42
-2			11	-12
-3			7	-3
0	2	6	0	10
1			35	33
2			89	95
3			118	125
4			60	-65
5			0	5
6			96	-101
7			29	-34
8			82	79
9			15	-14
10			34	32
-1			101	-104
-2			20	-23
-3			39	-37
-4			15	14
0	-2	6	56	56
1			39	43
2			37	-33
3			31	32
4			136	-148
5			24	-28
6			17	16
7			26	29
8			71	72
9			32	-31
-1			33	-32
-2			47	45
0	3	6	26	-31
1	3	6	134	-129
2			60	66
3			57	-61
4			76	77
5			144	152
6			0	-1
7			54	50
8			97	-96
9			56	-54
10			39	38
-1			33	-35
-2			56	-57
-3			56	52
-4			0	0
1	-3	6	10	5
2			95	-98
3			38	-36
-1			21	24
0	4	6	56	-58
1			67	-77
2			25	-28
3			104	-120
4			117	125
5			0	-2
6			17	14
7			101	101
8			33	-34
9			43	42
10			45	-50
-1			112	120
-2			25	-22
-3			20	17
-4			24	-26
1	-4	6	0	-1
2			11	14
3			30	-30
0	5	6	51	-53
1			118	129
2			0	4
3			15	-25
4			16	2
5			86	-93
6			47	49
7			16	-16
8			20	13
9			38	34
10			10	-11
-1			32	-27
-2			27	-29
-3			49	-47
-4			50	47
0	6	6	33	-33
1			26	-25
2			63	-64
3			107	117
4			17	-17
5			12	8
6			30	-30
7			47	-45
8			24	23
9			16	-22
-1			51	-52
-2			84	86
-3			19	-15
-4			25	27
0	7	6	77	78
1			29	-28
2			20	-22
3			51	-49
4			69	-69
5			33	33
6			9	-10
7			59	57
8			16	-14
-1			23	-25
-2			46	45
-3			37	37
0	8	6	27	30
1			16	14
2			9	-1
3			56	-56
4			14	15
5			48	-44
6			18	19
7			9	-10
-1			56	56
-2			15	-16
0	9	6	46	-46
1			43	41
2			14	-15
3			57	58
4			8	3
0	0	7	22	24
1			61	61
2			55	-60
3			109	-117
4			0	-5
5			45	-47
6			61	67
7			24	26

Table 4. *(Continued)*

h	k	l	$\lvert F_o \rvert$	F_c
8	0	7	33	- 27
9			59	56
10			20	- 24
-1			77	77
-2			7	5
0	1	7	19	- 17
1			74	72
2			0	3
3			127	135
4			27	- 29
5			114	-118
6			21	- 21
7			68	- 70
8			68	64
9			31	34
10			16	- 7
-1			30	- 30
-2			41	39
0	-1	7	14	- 1
1			74	- 74
2			11	13
3			62	- 61
4			47	49
5			12	1
6			35	- 33
7			59	57
8			53	- 50
9			6	11
0	2	7	36	35
1			0	1
2			0	- 15
3			102	116
4			21	- 24
5			84	94
6			17	- 1
7			81	- 82
8			11	- 5
9			91	- 86
10			22	22
-1			89	- 97
-2			10	12
-3			0	1
1	-2	7	8	- 5
2			9	9
3			12	7
0	3	7	59	62
1			58	- 60
2			20	23
3			19	- 22
4			28	- 26
5	3	7	71	75
6			16	- 12
7			44	44
8			29	- 29
9			19	- 16
10			15	- 18
-1			27	27
-2			9	7
-3			17	14
2	-3	7	19	- 18
3			7	- 2
0	4	7	12	13
1			61	61
2			78	84
3			52	- 56
4			0	11
5			83	- 87
6			31	23
7			14	11
8			0	1
9			37	33
10			27	- 31
-1			33	28
-2			106	-102
-3			17	- 18
0	5	7	92	- 93
1			16	- 16
2			46	- 49
3			65	70
4			74	76
5			23	21
6			0	3
7			99	- 98
8			36	38
9			0	4
10			14	19
-1			0	2
-2			11	- 9
-3			9	1
0	6	7	13	- 14
1			70	- 70
2			0	- 15
3			0	- 5
4			66	- 65
5			81	82
6			10	10
7			72	70
8			18	16
9			49	- 55
-1			39	- 35
-2	6	7	50	50
0	7	7	53	53
1			45	- 45
2			37	40
3			83	- 86
4			15	14
5			19	16
6			51	- 51
7			71	72
8			12	- 16
-1			23	22
-2			32	- 33
0	8	7	59	- 58
1			37	42
2			40	43
3			26	- 26
4			39	39
5			48	- 54
6			0	- 2
1	0	8	27	25
2			30	32
3			38	- 36
4			38	41
5			75	- 78
6			27	- 32
7			14	- 11
8			0	5
0	1	8	36	- 37
1			21	23
2			22	- 22
3			26	27
4			0	10
5			10	- 11
6			13	14
7			58	- 59
8			15	- 15
9			36	- 35
1	-1	8	9	- 25
2			0	1
3			80	- 91
0	2	8	57	52
1			39	- 38
2			50	- 49
3			14	- 5
4			40	- 38
5			44	44
6			60	- 55
7			53	52
8			11	14
9			20	- 16
-1	2	8	20	21
0	3	8	51	52
1			53	57
2			89	94
3			68	- 70
4			41	- 45
5			55	- 63
6			18	- 18
7			72	74
8			37	- 31
9			49	46
10			10	- 9
-1			19	- 22
0	4	8	60	- 57
1			31	28
2			19	- 16
3			65	67
4			98	105
5			49	- 44
6			28	31
7			83	- 82
8			39	- 38
9			27	24
-1			12	10
0	5	8	19	- 19
1			21	22
2			81	- 85
3			75	74
4			0	- 10
5			40	41
6			77	79
7			51	- 53
8			28	25
9			45	- 50
-1			37	- 31
0	6	8	65	68
1			17	- 19
2			0	- 1
3			20	20
4			59	- 61
5			39	43
6			14	- 12
7			13	- 14
8			36	35
-1			19	- 19
0	7	8	15	- 17
1			36	- 40
2			83	86
3			0	6
4			0	1
5	7	8	17	- 21
6			55	- 57
7			35	38
2	8	8	15	- 18
3			65	- 67
4			40	43
5			15	15
4	1	9	35	- 32
5			52	57
6			31	33
2	2	9	55	57
3			31	- 30
4			64	- 67
5			10	- 7
6			57	- 58
7			67	66
8			35	35
1	3	9	9	- 11
2			70	70
3			33	- 28
4			65	66
5			14	- 12
6			80	- 78
7			17	- 11
8			61	- 57
1	4	9	25	25
2			0	- 3
3			22	- 25
4			26	24
5			33	- 32
6			42	42
7			19	18
8			42	- 42
1	5	9	48	49
2			56	- 60
3			8	- 9
4			24	- 29
5			0	- 2
6			13	16
7			21	- 20
8			32	35
2	6	9	39	38
3			61	62
4			18	- 20
5			8	7
6			53	- 54
4	7	9	56	59
5			18	19

kinds was easily made with the help of the Fourier map calculated with the new data. The atomic configuration thus obtained is almost centrosymmetric, suggesting the existence of centers of symmetry in the structure, so space group C_i^1—$P\overline{1}$ was adopted in the following calculations.

Three cycles of least-squares refinements were carried out with isotropic temperature factors, using equal weights for all reflections. The R value was reduced to 0.13. Further refinements were carried out with using a different weighting scheme. The final R value was 0.090 for all 1749 reflections, and 0.082 for the 1710 observed reflections. In the calculations the atomic scattering factors were used with the corrections for the real components of the anomalous dispersions, utilizing the values published by CROMER (1965). The weighting scheme employed was $w = |\overline{F_o}|/(|\overline{F_o}| + |F_o| + |F_o|^2/|\overline{F_o}|)$, where $|\overline{F_o}|$ is the mean value of the observed structure amplitudes. For nonobserved reflections $|F_o|$ was assumed as $2 \cdot |F_{\min}|$ in the calculation of w. The final atomic parameters are given in Table 2 and the final temperature factors in Table 3. The observed and the final calculated structure factors are given in Table 4

Table 5. *Interatomic distances in hatchite*

	S(1)	S(2)	S(3)	S(4)	S(5)	Mean	σ	(Tl,Pb)(2)	(Pb,Tl)(1)	Ag
(Pb,Tl)(1)	3.24 Å 3.31	3.01 Å 3.26	2.81 Å 2.98	3.20 Å	3.02 Å	3.10Å	0.02_2		(4.06 Å)	
(Tl,Pb)(2)	3.65	3.46 (3.89)	3.12	3.05 3.61	3.46 3.53	3.41 (3.47)		(3.98 Å)		
Ag		2.54		2.52	2.48 (2.93)	2.51 (2.62)	0.02_3	(3.89)		(3.38 Å)
As(1)	2.35	2.23		2.23		2.27	0.02_3	3.48		
As(2)	2.30		2.27		2.25	2.27		(3.82)		

for comparison. All calculations were performed on the University of Bern IBM 1620 computer.

4. Description of the structure and discussion

The interatomic distances and bond angles are given in Table 5 and Table 6 respectively. The (Pb,Tl)(1) atom is surrounded by eight S atoms forming an irregular coordination polyhedron. The distances are normal for Pb—S or for Tl—S bonds, ranging between 2.81 and 3.31 Å. The (Tl,Pb)(2) atom has quite an unusual coordination, as seen in Figs. 2 and 3. Namely this atom is surrounded by 2 S atoms at distances of about 3.05 and 3.12 Å, 5 S + 1 As atoms at distances between 3.46 and 3.65 Å, and 1 As + 1 S + 1 Ag atoms at distances between 3.82 and 3.89 Å.

Configurations of S atoms around Pb differ from case to case. However we can recognize four typical modes as shown in Fig. 4. They are (*a*) the octahedral coordination, (*b*) seven-fold coordination, (*c*) eight-fold coordination and (*d*) nine-fold coordination. The first type is observed in galena, cosalite (Weitz and Hellner, 1960) and freieslebenite (Hellner, 1957). In the galena structure, if we shift a layer ∥ (100) along the [011] direction by the amount of $\sqrt{2}\, a_{\text{PbS}}/4$,

Table 6. *Bond angles in hatchite* ($\sigma \approx 1.5°$)

S(2)—Ag—S(5)	119.6°	S(1)—As(1)—S(2)	98.5°
S(2)—Ag—S(4)	112.5	S(1)—As(1)—S(4)	96.6
S(5)—Ag—S(4)	123.2	S(2)—As(1)—S(4)	100.7
S(5)—Ag—S(5′)	103.3	S(1)—As(2)—S(3)	94.7
S(2)—Ag—S(5′)	96.2	S(1)—As(2)—S(5)	101.1
S(4)—Ag—S(5′)	91.8	S(3)—As(2)—S(5)	101.3

the coordination around the Pb atoms at the boundary of the layer becomes the second type. This was found in the structures of rathite-I (Marumo and Nowacki, 1965), rathite-II (LeBihan, 1962), du-

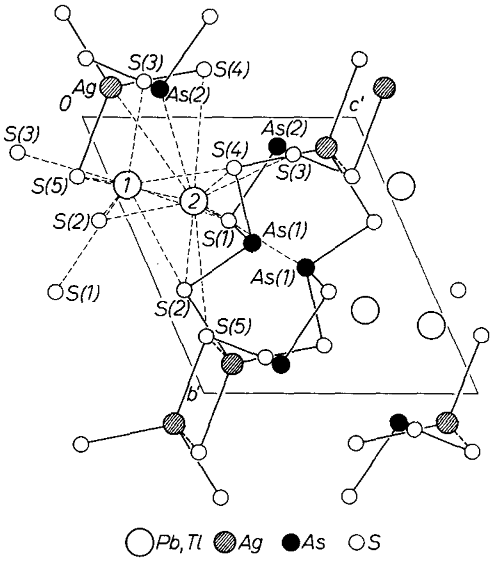

Fig. 2. The projection of the structure of hatchite along the *a*′ axis

frenoysite (Marumo and Nowacki, 1967), jamesonite (Niizeki and Buerger, 1957), hutchinsonite (Takéuchi, Ghose and Nowacki, 1965) and galenobismutite (Iitaka and Nowacki, 1962). The last type is composed of a trigonal prismatic and a trigonal-planar coordination, and observed in rathite-group minerals. The third type coordination is obtained by removing one of the S atom of the trigonal-planar coordination in the nine-fold type. This is observed in cosalite, seligmannite (Leineweber, 1956), jamesonite and bournonite (Leineweber, 1956). Irregular configurations of S atoms around Pb are observed sometimes, for example in gratonite (Rösch, 1963). Only a few examples are known concerning the coordination of S atoms around Tl atoms. In lorandite, Tl atoms have two-fold coordinations of sulfur, with the distances of 2.96 and 3.09 Å (Knowles, 1964). In hutchinsonite the Tl atoms have a coordination of type (*b*). Which

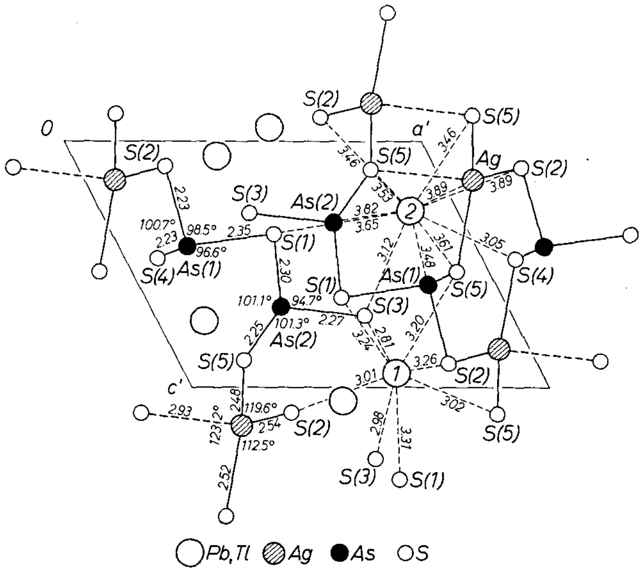

Fig. 3. The projection of the structure of hatchite along the b' axis

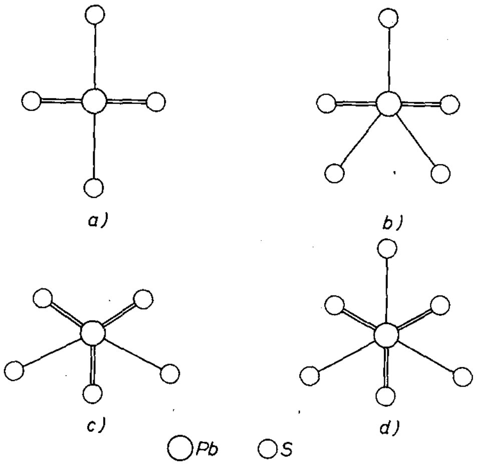

Fig. 4. Typical coordinations of sulfur atoms about lead atoms; (*a*) octahedral coordination, (*b*) seven-fold coordination, (*c*) eight-fold coordination and (*d*) nine-fold coordination

position is occupied by Tl atoms in the two (Pb,Tl) positions, it is impossible at present to decide definitively from the difference of the coordination nor from the x-ray data. Nevertheless position 2 seems to be more probable for Tl.

The Ag atom in hatchite is tetrahedrally surrounded by four S atoms. However, three of them are situated closer to the Ag atom than the remainder, yielding a rather flat trigonal-pyramidal coordination. This is one of the typical coordinations for Ag atoms in sulfosalt crystals. Examples are known in miargyrite (Knowles, 1964) and smithite (Hellner and Burzlaff, 1964). Another type of a very common coordination around silver is the two-fold one, which is observed in proustite (Engel and Nowacki, 1966), pyrargyrite (Engel and Nowacki, 1966), stromeyerite (Frueh, 1955) and miargyrite. Sometimes octahedral coordinations are reported in structures which are not well refined. The Ag—S distances of hatchite are in good agreement with those of Ag atoms with three-fold coordination in miargyrite.

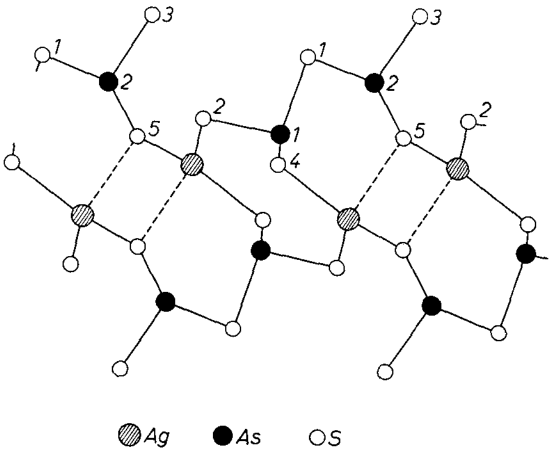

Fig. 5. The double chain of the composition $Ag_2As_4S_{10}$ occurring in the hatchite structure

The As atoms have a trigonal-pyramidal coordination of S atoms, as in ordinary arsensulfide crystals. Two crystallographically independent As—S_3 pyramids are joined by sharing an S atom to form As_2S_5 group. These As_2S_5 groups are connected to each other by the Ag—S_3 trigonal pyramids, forming infinite double chains of composition $AgAs_2S_5$. The chains run along the $[01\bar{1}]$ direction (primed cell).

These double chains may also be described as consisting of AgS_4 double tetrahedra (having a common edge) of the composition Ag_2S_6, joined together by As_2S_5 groups, yielding the total composition $Ag_2As_4S_{10}$ (Fig. 5).

The structure is composed essentially of slabs of double chains which are parallel to the cleavage plane (011) (primed cell). The slabs are stacked closely along the *a'* axis direction, while there is a fairly large space along [011] (primed cell). The (Pb,Tl) atoms are situated in this space thus combining the chains laterally. This feature of the structure explains well the type of cleavage.

Hatchite contains a small amount of copper, as shown in Table 1. The Cu atoms are probably occupying the Ag positions, since the number of Ag atoms in an asymmetric unit is less than one, while it becomes one if the copper atoms are added. This seems reasonable also from a crystallochemical viewpoint. Cu atoms usually have tetrahedral coordinations of sulfur in sulfide and sulfosalt crystals, and the Ag position is surrounded tetrahedrally by S atoms.

In the meantime TAKÉUCHI, OHMASA and NOWACKI (1967) have determined the structure of wallisite, $PbTlCuAs_2S_5$ (with some Ag), by comparison with that of hatchite, $PbTlAgAs_2S_5$ (with some Cu), and it turned out that these two compounds are isomorphous, one being the Cu and the other the Ag analogue.

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References

DON T. CROMER (1965), Anomalous dispersion corrections computed from self-consistent field relativistic Dirac-Slater wave functions. Acta Crystallogr. **18**, 17–23.

P. ENGEL und W. NOWACKI (1966), Die Verfeinerung der Kristallstruktur von Proustit, Ag_3AsS_3, und Pyrargyrit, Ag_3SbS_3. N. Jahrb. Miner., Mh. 181—184.

A. J. FRUEH (1955), The crystal structure of stromeyerite, AgCuS: A possible defect structure. Z. Kristallogr. **106**, 299—307.

E. HELLNER (1957), Über komplex zusammengesetzte sulfidische Erze II. Zur Struktur des Freieslebenits, $PbAgSbS_3$. Z. Kristallogr. **109**, 284—295.

E. HELLNER und H. BURZLAFF (1964), Die Struktur des Smithits $AgAsS_2$. Naturwissenschaften **51**, 35—36.

Y. IITAKA and W. NOWACKI (1962), A redetermination of the crystal structure of galenobismutite, $PbBi_2S_4$. Acta Crystallogr. **15**, 691—698.

C. R. KNOWLES (1964), A redetermination of the structure of miargyrite, $AgSbS_2$. Acta Crystallogr. **17**, 847—851.

M.-Th. LEBIHAN (1962), Étude structurale de quelques sulfures de plomb et d'arsénic naturels du gisement de Binn. Bull. Soc. Franç. Min. Cristallogr. **85**, 15—47.

G. LEINEWEBER (1956), Struktur-Analyse des Bournonits und Seligmannits mit Hilfe der Superpositions-Methoden. Z. Kristallogr. **108**, 161—184.

F. MARUMO and W. NOWACKI (1965), The crystal structure of rathite-I. Z. Kristallogr. **122**, 433—456.

F. MARUMO and W. NOWACKI (1967), The crystal structure of dufrenoysite, $Pb_{16}As_{16}S_{40}$. Z. Kristallogr. **124**, 409—419.

N. NIIZEKI and M. J. BUERGER (1957), The crystal structure of jamesonite, $FePb_4Sb_6S_{14}$. Z. Kristallogr. **109**, 161—183.

W. NOWACKI (1965), Über einige Mineralfunde aus dem Lengenbach (Binnatal, Kt. Wallis). Eclogae Geol. Helv. **58**, 403—406.

W. NOWACKI (1967), in preparation.

W. NOWACKI und C. BAHEZRE (1963), Die Bestimmung der chemischen Zusammensetzung einiger Sulfosalze aus dem Lengenbach (Binnatal, Kt. Wallis). Schweiz. Min. Petrogr. Mitt. **43**, 407—411.

W. NOWACKI, G. BURRI, PETER ENGEL und F. MARUMO (1967), Über einige Mineralstufen aus dem Lengenbach (Binnatal) II. N. Jahrb. Min., Mh., 43—48.

W. NOWACKI, Y. IITAKA, H. BÜRKI and V. KUNZ (1961), Structural investigations on sulfosalts from the Lengenbach, Binn valley (Ct. Wallis). Part 2. Schweiz. Min. Petrogr. Mitt. **41**, 103—116.

W. NOWACKI und V. KUNZ (1961), Gitterkonstanten und Raumgruppe von Hatchit und Trechmannit. N. Jahrb. Min., Mh., S. 94—95.

H. RÖSCH (1963), Zur Kristallstruktur des Gratonits—$9PbS \cdot 2As_2S_3$. N. Jahrb. Min., Abh. **99**, 307—337.

R. H. SOLLY and G. F. H. SMITH (1912), Hatchite, a new (anorthic) mineral from the Binnenthal. Min. Mag. **16**, 287—289.

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

Y. TAKÉUCHI, M. OHMASA and W. NOWACKI (1967), The crystal structure of wallisite, $PbTlCuAs_2S_5$, the Cu analogue of hatchite, $PbTlAgAs_2S_5$. Schweiz. Min. Petrogr. Mitt. **47** [in press]; Z. Kristallogr. [in press].

G. WEITZ und E. HELLNER (1960), Über komplex zusammengesetzte sulfidische Erze VII. Zur Kristallstruktur des Cosalits, $Pb_2Bi_2S_5$. Z. Kristallogr. **113**, 385—402.