

## Refinement of the crystal structure of zinckenite, $\text{Pb}_6\text{Sb}_{14}\text{S}_{27}$ \*

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### Auszug

Die Kristallstruktur von Zinckenit,  $\text{Pb}_6\text{Sb}_{14}\text{S}_{27}$ , wurde mit Hilfe von dreidimensionalen Röntgendaten bis zu einem  $R$ -Wert von 0,13 verfeinert. Die Intensitäten wurden mit einem Supper-Pace-Autodiffractometer unter Verwendung von  $\text{CuK}\alpha$ -Strahlung gemessen. Die hexagonale Elementarzelle mit  $a = 22,148(6)$  und  $c = 4,333(6)$  Å enthält  $1\frac{1}{2}$  Formeleinheiten. Die Ergebnisse der Verfeinerungen in den Raumgruppen  $P6_3/m$  und  $P6_3$  werden mit dem „Hamilton  $R$ -Ratio Test“ verglichen.  $P6_3$  ergibt sich als die richtige Raumgruppe.

Die Struktur enthält drei reine Pb-Lagen und eine gemischte (Pb,Sb)-Lage. Pb(1) besitzt Achter-Koordination während Pb(2) und Pb(3) von 9 nächsten S-Nachbarn umgeben sind. Die Pb(2)- und Pb(3)-Lagen sind nur zu 20% besetzt. Die mittleren (Pb–S)-Abstände für Pb(1), Pb(2) und Pb(3) sind 3,14, 3,23 und 3,24 Å. Die (Pb,Sb)-Lage hat eine dem Pb(1) ähnliche Koordination; der mittlere [(Pb,Sb)–S]-Abstand beträgt 3,09 Å. Alle drei Sb-Ionen sind von 6 S-Ionen in Form eines verzerrten Oktaeders umgeben. Betrachtet man nur (Sb–S)-Abstände, die kleiner als 2,7 Å sind, so erhält man für Sb(1) eine trigonalpyramidale, für Sb(2) und Sb(3) hingegen eine planare Dreier-Koordination. Die  $\text{SbS}_3$ -Gruppen sind zu unendlichen Ketten verknüpft, welche als Spiralen um die  $2_1$ -Achsen liegen. Die Spiralen werden von den Pb-Ionen zusammengehalten.

### Abstract

The crystal structure of zinckenite,  $\text{Pb}_6\text{Sb}_{14}\text{S}_{27}$ , has been refined to an  $R$  value of 0.13 with the aid of three-dimensional x-ray data. The intensities were measured by means of a Supper-Pace autodiffractometer, using  $\text{CuK}\alpha$  radiation. The hexagonal unit cell, with  $a = 22.148(6)$  and  $c = 4.333(6)$  Å, contains  $1\frac{1}{2}$  formula units. Results of refinements in the space groups  $P6_3/m$  and  $P6_3$  are compared according to HAMILTON'S  $R$ -ratio test. The latter space group is the correct one.

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The structure has three pure Pb positions and one mixed (Pb,Sb) position. Pb(1) has an eight coordination while Pb(2) and Pb(3) are surrounded by 9 S nearest neighbours. The Pb(2) and Pb(3) positions are only occupied by 20%. The average Pb—S distances for Pb(1), Pb(2) and Pb(3) are 3.14, 3.23 and 3.24 Å respectively. The coordination of (Pb,Sb) is similar to that of Pb(1); the average (Pb,Sb)—S distance is 3.09 Å. All three Sb ions are coordinated by 6 S ions in a distorted octahedron. Considering only Sb—S distances smaller than 2.7 Å Sb(1) has a trigonally pyramidal coordination while Sb(2) and Sb(3) have planar threefold coordinations. The  $\text{SbS}_3$  groups are joint in endless chains which form spirals around the  $2_1$  axes. These spirals are held together by the Pb ions.

### Introduction

VAUX and BANNISTER (1938) were the first to investigate zinckenite by x-ray techniques. They determined the Laue group  $6/m$  and the cell dimensions,  $a = 44.06$  and  $c = 8.60$  Å, from crystals originating from the antimony mine at Wolfsberg (Germany). They suggested the composition  $\text{Pb}_6\text{Sb}_{14}\text{S}_{27}$  ( $= 6\text{PbS} \cdot 7\text{Sb}_2\text{S}_3$ ) and  $Z = 12$  on the basis of earlier chemical analyses and the possible space groups  $C_{6h}^2 = P6_3/m$  and  $C_6^6 = P6_3$ . Reflection spots on the odd layers of the  $a$  and  $c$  axis were very weak and unsharp, giving rise to a pseudocell with half the above quoted dimensions as lattice periods, the same possible space groups and  $Z = 1\frac{1}{2}$ .

A model for the structure of the pseudocell was proposed by TAKEDA and HORIUCHI (1971; this publication, in Japanese, was brought to our attention only recently). This model was based on photographic data of Wolfsberg zinckenite. The lattice dimensions  $a = 22.09$  and  $c = 4.321$  Å correspond to the pseudocell of VAUX and BANNISTER (1938). The space group  $P6_3/m$  was assumed and the composition  $\text{PbSb}_2\text{S}_4$  ( $= \text{PbS} \cdot \text{Sb}_2\text{S}_3$ ) with  $Z = 10$  to  $\sim 10\frac{1}{2}$  was taken from NUFFIELD (1946). Because of the small amount of intensity data ( $hk0$  and  $hk1$  only) no thermal parameters were refined and the alternative space group  $P6_3$  was not tested.

The purpose of our investigation was to determine the space group of the pseudocell and to specify the structure more accurately. The correct space group will be shown to be  $P6_3$ .

### Experimental

Steel-gray needle-shaped crystals of zinckenite were taken from the sample A.K. 345—65 of the collection in this laboratory. This sample originates from the Bolivar mine in Cerro Bonete (Bolivia) and consists mainly of pavonite  $\text{AgBi}_3\text{S}_5$ . In Table 1 observed weight

Table 1. Observed (microprobe analysis) and calculated weight percentages of the constituent elements of zinckenite

	Locality			Pb <sub>6</sub> Sb <sub>14</sub> S <sub>27</sub> (calc.)	PbSb <sub>2</sub> S <sub>4</sub> (calc.)
	Cerro Bonete	Wolfsberg			
	Analysis number				
	640-1973 <sup>a</sup>	182-1967 <sup>b</sup>	208-1967 <sup>b</sup>		
Pb	32.6	33.6	33.0	32.60	35.79
Sb	43.2	44.1	44.2	44.70	42.06
S	24.0	21.5	22.0	22.70	22.15
$\Sigma$	99.8	99.2	99.2	100	100
Pb/Sb	0.75	0.76	0.75	0.73	0.85

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percentages of the constituent elements are compared with calculated values for the two compositions mentioned in the introduction. The composition Pb<sub>6</sub>Sb<sub>14</sub>S<sub>27</sub> will be assumed here since its Pb/Sb weight ratio is not different from the observed ratio if one accepts a standard error of 0.6 in the observed percentages. The same composition has been confirmed for zinckenite from Wolfsberg by HARRIS (1965) and in our laboratory (see Table 1).

Close inspection of Weissenberg and oscillation photographs revealed weak diffuse intensity halfway in between the *c*-axis layers of the pseudocell. Consequently there is an ordering in the structure along the hexagonal axis with a period of twice the corresponding pseudocell dimension, similar to earlier observations (VAUX and BANNISTER, 1938 and TAKEDA and HORIUCHI, 1971). The diffuse character of this intensity indicates however that the ordering is not perfect and that there is no additional ordering in directions perpendicular to *c*. Apparently in this case the pseudocell comprises the three-dimensional translation unit and consequently it will be referred to as unit cell afterwards.

The lattice parameters were determined with the aid of zero-level Weissenberg photographs about [001] (needle axis) and [100]. Cu radiation was used for the exposures, and Si powder lines ( $a_{\text{Si}} = 5.4301 \text{ \AA}$ )

were superposed on the films for the purpose of calibration. The values  $a = 22.148(6)^1$  and  $c = 4.333(6)$  Å were calculated from 66  $\theta$  values with the program LAPA of Dr. T. ITO (unpublished).

The systematic absences  $00l$  for  $l$  odd are consistent with the space groups  $P6_3/m$  and  $P6_3$ .

The collection of the intensity data was carried out by Dr. P. ENGEL on a crystal with dimensions  $0.04 \times 0.02 \times 0.2$  mm, which was mounted about [001] on a Supper-Pace autodiffractometer. Intensities of 2766 not-independent reflections were measured with the  $\omega$ -scan technique using Ni-filtered Cu radiation. Because of the high  $\mu$  value an ellipsoidal absorption correction was applied. Structure amplitudes  $F$  and associated weights  $W(F)$  were derived as described by GABE, GLUSKER, MINKIN and PATTERSON (1967).

Table 2. Diffraction data of zinckenite from Cerro Bonete

Pb <sub>6</sub> Sb <sub>14</sub> S <sub>27</sub> , $M = 3813$ g · mole <sup>-1</sup> ,		
space group $P6_3$ , $Z = 1 \frac{1}{2}$ ,		
$F(000) = 2457$ electrons, $\lambda = 1.54178$ Å,		
$\mu = 1117$ cm <sup>-1</sup>		
$a$	22.148(6)	Å
$c$	4.333(6)	
$\rho_{\text{obs}}^*$	5.36	g · cm <sup>-3</sup>
$\rho_{\text{calc}}$	5.16	
$V_{\text{cell}}$	1841	Å <sup>3</sup>

\* Measured by NUFFIELD (1946, Berman balance).

The independent reflections were obtained by averaging as follows:  $F_o = \sum_i W(F_i) \cdot F_i / \sum_i W(F_i)$  and  $W(F_o) = \sum_i W(F_i)$ , where the summation goes over the equivalent reflections ( $i$ ).  $F_o$  was considered observed if 33% or more of the individual observations were significant at the 1% level [ $F \geq 2.33 \times W^{-1/2}(F)$ ]. There resulted 956 observed reflections and 266 unobserved ones, together comprising 87% of the independent reflections in the Cu sphere. The discrepancy between equivalent reflections expressed as the average of  $\sum_i W(F_i) \cdot |F_i - F_o| / \sum_i W(F_i) \cdot F_i$  amounted to 0.11.

Some diffraction data are given in Table 2.

<sup>1</sup> Throughout this publication numbers added in parentheses are estimated standard deviations  $\sigma$  in terms of the last digit.

### Refinement

The structure was refined by Fourier and least-squares methods using computer programs written in PL/1 by Dr. P. ENGEL (unpublished). The quantity  $\sum W(F_o) \cdot (F_o - F_c/k)^2$  was minimized where  $F_c$  is the calculated structure amplitude and  $k$  the scale factor.

As a start cations at the positions 1 and 4–7 (see Table 3) were refined in the space group  $P6_3/m$ , according to TAKEDA and HORIUCHI (1971), on the basis of our observed reflections and associated weights. The position 0,0,0 was reported (TAKEDA and HORIUCHI, 1971) as tentative and therefore not considered in our case. Besides, the mentioned five positions suffice to accommodate the number of 30 cations in the unit cell. Position number 4 was occupied half by Pb and half by Sb [mixed cation (Pb,Sb)]. The S ions were contributing to  $F_c$  at fixed positions and the overall  $B$  was kept at the value  $2.45 \text{ \AA}^2$  from the Wilson plot. Scattering factors for neutral atoms were adopted from DOYLE and TURNER (1968). After two refinement cycles the conventional  $R$  amounted to 0.26.

Subsequently a difference map was evaluated in which only the cations contributed to  $F_c$ . The anions with exception of S(1) were found as well defined peaks at the expected positions. At the position of S(1) a very low peak appeared, which was elongated along [110]. The coordination of the cations at the positions 1 and 5–7 confirmed the different types: octahedra for Sb (pos. no. 5–7) and a trigonal prism for Pb (pos. no. 1) with two extra S ions outside the prism on normals to two side faces. The mixed cation (pos. no. 4) had a coordination similar to Pb if one includes S(1). The negative region at its site could indicate an occupancy less than 1.00 and/or a smaller Pb/Sb ratio. No density was found at the position 0,0,0, but at 0,0,0.38 a peak with the height of an S ion was discovered. For an accordingly located anion a temperature-factor shift  $\Delta B = -2.1 \text{ \AA}^2$  was calculated. A possible explanation for this shift is the presence of an ion heavier than S and as such an Sb ion with occupancy  $\frac{1}{2}$  was included in the following refinement cycles at that position (no. 2).

Now the positions of all S ions were refined additionally while the overall temperature factor was still fixed. When convergence was reached  $R$  was equal to 0.24 and the weighted factor  $R_w = [\sum W(F_o) \cdot (F_o - F_c/k)^2 / \sum W(F_o) \cdot F_o^2]^{1/2}$  amounted to 0.21. The ion on the  $c$  axis had a  $z$  value of 0.367 but there remained doubt about its location because of the calculated shift  $\Delta B = +0.8 \text{ \AA}^2$ .

The fourfold peak of this atom in the difference map might have been created artificially from a twofold peak due to erroneously retaining the space group  $P6_3/m$  where the real space group is  $P6_3$ . Therefore position refinement in the latter space group was undertaken. The equivalent in  $P6_3$  of an Sb ion at 0,0,0.367 in  $P6_3/m$  is a pair of Sb ions, at 0,0,0.367 and 0,0,0.133, with the same occupancies (It will be shown afterwards that these Sb ions have to be replaced by Pb). In the initial cycles of the  $P6_3$  refinement only the first Sb ion (pos. no. 2) was included. When convergence was reached the  $z$  of this ion had not changed. In the resulting difference map the peak that could be associated with Sb at 0,0,0.133 (pos. no. 3) was apparent. From these two facts we concluded that the four peaks on the  $c$  axis represent real ions and there did not exist a preliminary argument to reject  $P6_3/m$  as a space group (see also Discussion). Both Sb ions (pos. no. 2 and no. 3) were refined in the following cycles and the resulting  $R$  values were  $R = 0.20$  and  $R_w = 0.18$ .

According to HAMILTON's (1965) test the ratio of the  $R_w$  factors of the refinements in  $P6_3/m$  and  $P6_3$ ,  $0.21/0.18 = 1.2$ , was compared with  $R_{13,917,0.005} = 1.02$ . Since the ratio is larger than  $R_{13,917,0.005}$  the latter space group is the correct one<sup>2</sup>. The suffixes of  $R$  are respectively the number of parameters varied in  $P6_3$  while fixed in  $P6_3/m$  ( $z$  parameters of cation positions 1 and 3—7 and of the seven anions), the number of observed reflections minus the number of parameters varied in  $P6_3$  and the significance level.

In the following stage of the refinement the space group  $P6_3$  was used and the individual  $B$  values were allowed to vary as additional parameters. In the first few cycles the  $B$  of S(1) increased beyond  $7 \text{ \AA}^2$  and in connection with that the  $z$  did not converge properly. This could be expected because of the peak shape in the difference map and it was decided to omit S(1) in the following cycles (see also Discussion).

The high  $B$  values for the Sb ions at the positions 2 and 3 ( $4$  and  $6 \text{ \AA}^2$ ) could indicate that the real electron density at these positions is lower. The following geometric argument shows that this must be the case. If one locates more than one cation on the  $c$  axis, which is equivalent with cations with occupancies larger than  $\frac{1}{4}$  at the two twofold positions, then the average cation—cation distance along  $c$  would be smaller than  $4.333 \text{ \AA}$ . Such a distance cannot be realized in sulfosalts and therefore the upper limit for the occupancies is less

<sup>2</sup> On the basis of Laue photographs of Wolfsberg zinckenite NUFFIELD (1946) decided for the same space group.

Table 3. Positional coordinates<sup>a</sup> in fractions of the cell edges and occupancies of the ions in zinckenite

Cationic position number		<i>x</i>		<i>y</i>		<i>z</i>	Occupancy <sup>b</sup>
1	Pb(1)	0.5359(3)	0.5365(1)	0.2433(3)	0.2434(1)	1/4 0.238(2)	
2	Pb(2)	—	0	—	0	— 0.365(5)	0.19(3) <sup>c</sup>
3	Pb(3)	—	0	—	0	— 0.125(4)	0.18(3) <sup>c</sup>
4	(Pb,Sb) <sup>e</sup>	0.2009(5)	0.1994(2)	0.0400(5)	0.0399(3)	3/4 0.775(2)	0.85(2) <sup>g</sup>
5	Sb(1)	0.4004(4)	0.4002(2)	0.0555(4)	0.0551(2)	3/4 0.769(2)	
6	Sb(2)	0.3465(4)	0.3484(2)	0.2449(4)	0.2430(2)	3/4 0.744(3)	
7	Sb(3)	0.5168(4)	0.5178(2)	0.4084(4)	0.4090(2)	3/4 0.768(2)	
	S(1)	0.130(3)	0.127(2) <sup>c</sup>	0.116(3)	0.115(2) <sup>c</sup>	3/4 0.76(2) <sup>d</sup>	0.75 <sup>f</sup>
	S(2)	0.313(2)	0.314(1)	0.029(2)	0.031(1)	1/4 0.321(6)	
	S(3)	0.498(1)	0.498(1)	0.081(1)	0.082(1)	1/4 0.356(5)	
	S(4)	0.275(2)	0.276(1)	0.171(2)	0.172(2)	1/4 0.349(5)	
	S(5)	0.439(2)	0.443(1)	0.315(2)	0.320(1)	1/4 0.165(5)	
	S(6)	0.436(2)	0.435(1)	0.181(2)	0.179(1)	3/4 0.824(5)	
	S(7)	0.633(1)	0.635(1)	0.231(2)	0.233(1)	3/4 0.735(8)	

<sup>a</sup> The values of TAKEDA and HORIUCHI (1971) are given in the first column.

<sup>b</sup> Only occupancies different from 1.00 are given.

<sup>c</sup> Not refined in the final stage.

<sup>d</sup> Estimated from final difference map.

<sup>e</sup> For this ion the scattering factor  $\frac{1}{2}(f_{\text{Pb}} + f_{\text{Sb}})$  was employed.

<sup>f</sup> Assumed.

<sup>g</sup> Dependent occupancy.

Table 4. *Thermal parameters<sup>a</sup> of the ions in zinckenite.*

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$	$B^b$
Pb(1)	0.0016(1)	0.0018(1)	0.058(3)	0.0013(1)	0.004(1)	0.002(1)	3.24 Å <sup>2</sup>
(Pb,Sb)	14(1)	37(2)	42(5)	19(2)	9(2)	16(2)	3.72
Sb(1)	13(1)	14(1)	32(5)	16(2)	8(2)	15(2)	2.04
Sb(2)	14(1)	14(1)	49(5)	3(2)	10(2)	5(2)	2.93
Sb(3)	9(1)	11(1)	38(5)	7(2)	-7(2)	-11(2)	1.99
	$B$		$B$		$B$		$B$
Pb(2)	4.6(5) Å <sup>2</sup>	S(2)	2.0(3) Å <sup>2</sup>	S(4)	1.8(3) Å <sup>2</sup>	S(6)	1.1(3) Å <sup>2</sup>
Pb(3)	1.8(3)	S(3)	1.3(3)	S(5)	1.8(3)	S(7)	1.3(2)

<sup>a</sup> The anisotropic temperature factor is defined as:

$$\exp \{ - [h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk(2\beta_{12}) + hl(2\beta_{13}) + kl(2\beta_{23})] \}.$$

<sup>b</sup> These values are the equivalent  $B$ 's of HAMILTON (1959).

Table 5. Final list of observed and calculated structure amplitudes for zinckenite on 3/4 times absolute scale

hkl	F <sub>o</sub>	F <sub>c</sub>	hkl	F <sub>o</sub>	F <sub>c</sub>	hkl	F <sub>o</sub>	F <sub>c</sub>	hkl	F <sub>o</sub>	F <sub>c</sub>	hkl	F <sub>o</sub>	F <sub>c</sub>	hkl	F <sub>o</sub>	F <sub>c</sub>	hkl	F <sub>o</sub>	F <sub>c</sub>	
1 1 0	76	38	7 17 0	63	60	18 2 0	47	45	4 20 1	30	36	10 10 1	50	49	20 5 1	51	63	6 9 2	129	126	
3	77	86	18	89	89	3	55	24	5 0 1	49	64	11	135	135	21 0 1	41	35	11	136	111	
6	44	53	19	53	70	6	44	52	2	71	39	12	77	68	1	83	105	12	185	184	
7	63	87	8 0 0	97	56	8	71	77	3	217	235	13	68	80	2	37	15	13	65	46	
8	217	238	2	55	55	19 1 0	53	57	4	360	362	14	42	34	23 0 1	99	101	14	42	28	
9	94	58	3	156	183	3	60	57	5	144	148	15	37	8	1 1 2	52	65	15	135	143	
10	126	131	4	54	56	5	51	76	6	67	46	16	29	26	2	42	102	17	89	90	
11	361	335	5	159	160	6	148	156	7	45	43	11 0 1	102	122	4	49	63	7 0 2	47	61	
12	55	49	6	165	175	7	33	34	8	114	104	1	83	57	5	51	70	1	84	63	
13	66	50	7	81	79	20 0 0	173	180	9	67	68	2	65	94	7	67	91	2	48	59	
14	281	271	8	91	22	2	52	69	10	99	128	3	145	145	8	167	188	3	175	184	
15	138	119	9	90	116	3	33	24	11	74	82	4	54	61	9	78	45	4	44	65	
16	184	195	10	122	124	4	44	48	12	68	68	5	112	123	10	110	117	5	100	95	
17	111	117	12	96	93	5	48	35	13	42	46	6	83	80	11	231	219	6	166	147	
18	89	90	14	132	151	21 0 0	33	31	14	43	44	8	66	33	12	42	40	7	39	39	
20	39	56	16	34	32	1	129	127	15	79	60	9	52	50	13	54	48	8	70	79	
23	46	49	17	72	63	2	46	55	16	49	11	79	44	202	108	9	143	108	9	143	148
2 2 0	164	147	18	59	53	3	59	67	17	60	65	11	74	78	15	84	76	11	128	122	
3	55	61	9 0 0	46	13	22 0 0	57	59	19	92	89	12	103	104	16	149	148	12	104	107	
4	50	44	1	108	106	23 0 0	53	53	20	55	61	13	37	45	17	101	108	14	57	36	
5	188	161	4	305	316	1 1 1	44	50	6 0 1	105	103	14	101	48	18	50	53	16	65	78	
6	76	82	5	50	52	1	38	58	7	60	63	15	89	85	2 0 2	39	58	17	54	54	
7	59	76	6	58	40	4	266	281	2	90	90	12 1 1	54	41	1	45	40	8 0 2	71	48	
8	355	320	7	89	90	5	156	163	3	55	43	2	54	46	2	120	132	1	69	53	
10	177	179	8	314	322	6	149	143	4	91	83	4	88	81	3	37	30	2	89	77	
11	128	159	10	58	55	7	204	215	5	80	59	5	132	147	4	86	85	3	104	114	
12	107	119	11	72	86	8	101	105	6	45	47	6	6	107	5	122	111	5	153	155	
15	100	116	12	52	20	9	118	113	8	72	66	7	87	101	6	44	31	6	136	142	
14	62	71	13	58	25	10	211	224	9	89	98	8	95	107	7	67	72	7	42	78	
15	77	52	10 2 0	561	578	11	110	117	10	123	129	9	143	157	8	229	208	8	40	60	
17	58	54	4	91	98	12	250	238	11	205	215	11	39	15	9	57	30	9	70	78	
19	55	61	5	162	187	13	248	251	12	80	88	12	80	85	10	162	172	10	101	99	
20	41	29	6	42	18	14	74	60	13	152	148	14	36	17	11	125	117	11	40	33	
21	40	34	9	81	97	16	98	78	14	159	168	13 0 1	125	119	12	62	59	12	70	68	
3 1 0	76	64	10	93	104	17	91	76	15	40	38	1	108	115	13	63	76	13	40	40	
2	159	171	11	140	151	20	85	94	16	43	22	2	191	214	14	49	32	14	96	106	
4	205	189	13	96	98	21	53	58	17	61	19	3	254	237	16	38	58	15	54	23	
5	83	91	15	51	54	22	26	24	18	58	39	4	73	75	17	58	50	9 0 2	70	101	
6	240	223	16	50	30	2 0 1	241	253	7 0 1	59	56	5	178	178	19	68	66	1	73	88	
7	62	59	11 2 0	163	140	1	174	209	1	118	112	6	60	53	20	36	34	2	76	77	
8	72	81	5	43	32	2	42	21	2	98	85	9	152	151	3 0 2	39	36	4	199	204	
9	136	138	4	132	144	3	254	305	3	43	69	10	89	49	1	62	70	6	42	17	
11	49	51	5	206	209	4	399	380	4	158	146	11	43	33	2	63	101	7	59	56	
13	288	289	7	54	56	5	92	99	5	195	220	13	30	16	4	153	148	8	248	239	
15	50	54	9	78	65	6	310	320	6	93	129	14 0 1	96	80	5	87	101	9	48	54	
16	92	92	10	81	99	7	448	454	7	144	220	1	81	79	6	113	100	10	114	76	
17	133	130	13	190	179	8	70	69	8	302	307	2	72	74	8	22	25	11	74	81	
4 0 0	78	99	14	78	75	9	122	121	9	64	65	3	177	180	9	95	94	10 1 2	39	8	
3	216	222	12 0 0	61	45	11	70	72	11	94	63	5	45	24	11	42	33	4	60	57	
4	58	48	1	145	143	12	78	64	12	60	44	6	48	20	12	41	19	5	136	138	
5	103	90	2	114	129	13	85	72	13	35	37	7	37	52	13	209	207	6	72	35	
7	730	727	4	128	141	14	97	89	14	77	83	8	55	47	14	54	23	9	77	84	
8	130	103	5	47	39	15	45	27	15	78	86	9	43	24	16	96	74	10	78	92	
10	52	34	6	76	88	16	63	65	16	48	15	10	129	131	17	83	87	11	100	92	
11	98	95	7	158	152	17	133	130	17	49	53	11	33	15	19	37	26	12	42	54	
14	103	103	9	50	1	18	146	138	18	49	44	12	46	43	4 0 2	43	48	13	15	60	
18	47	50	10	156	143	19	34	12	8 0 1	61	69	15 1 1	49	10	1	52	39	11 0 2	49	52	
21	40	42	11	59	54	20	34	18	1	283	299	3	63	76	2	55	45	1	56	39	
5 0 0	50	44	13	136	134	21	52	48	2	361	371	4	184	186	3	107	110	2	121	109	
1	950	971	14	38	45	3 0 1	260	275	3	149	149	5	58	50	4	55	63	3	49	42	
2	99	74	15	30	9	1	342	397	4	227	247	6	112	106	5	74	82	4	119	124	
3	63	72	13 0 0	80	72	2	131	177	5	76	62	7	46	42	6	70	58	5	147	136	
4	77	66	1	127	141	3	449	431	6	61	19	9	48	38	7	512	525	6	40	55	
5	79	85	4	98	115	4	124	135	7	100	117	10	109	112	8	104	93	7	70	77	
7	151	122	6	120	125	5	37	40	8	146	158	11	45	58	9	32	28	9	49	39	
9	94	70	7	99	99	6	169	170	9	72	55	16 0 1	149	161	10	64	71	10	80	85	
10	107	95	8	80	80	7	61	60	10	98	91	1	63	71	11	65	70	12	41	40	
12	87	83	10	39	70	8	176	170	11	68	25	3	50	17	13	47	25	13	144	144	
15	64	52	11	103	111	9	59	45	12	90	96	4	134	141	14	76	81	12 0 2	46	42	
16	61	66	12	44	42	11	229	223	13	115	115	5	54	60	16	61	26	1	127	120	
17	85	92	13	85	92	12	141	151	14	65	15	6	39	32	17	64	32	2	90	88	
18	215	215	14	30	33	13	74	52	15	72	71	7	55	54	18	47	50	3	43	49	
19	68	74	14 0 0	153	159	14	42	57	16	74	83	9	35	21	5 0 2	42	19	4	113	120	
6 0 0	81	90	2	70	93	15	76	58	17	55	53	17 0 1	45	53	1	632	678	5	47	48	
1	213	177	5	258	281	16	111	124	9 0 1	123	132	1	45	27	2	83	60	6	92	96	
3	150	134	9	51	70	17	51	32	1	109	116	3	79	59	3	42	67	7	119	124	
4	211	220	12	58	46	18	65	32	2	155	151	4	49	14	4	80	79	8	51	45	

Table 5. (Continued)

h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>	
15 8 2	49	40	1 16 3	53	38	4 4 3	52	68	6 14 3	107	103	10 1 3	61	36	15 4 3	102	112	5 3 4	40	42	
16 0 2	106	105	17 4 1	25	5	174	187	15 3	34	50	2	44	24	5	40	36	8	47	41	47	41
2	65	45	18 42	20	6	54	47	7 1 3	88	89	3	72	79	6	61	90	9	40	48	48	48
3	62	65	2 0 3	119	145	8	53	55	2	84	66	5	128	148	16 0 3	105	130	6 1 4	40	70	70
5	91	105	1	94	128	9	51	39	4	103	113	6	41	47	1	48	37	2	65	32	32
6	109	100	3	124	135	10	132	156	5	129	143	8	41	53	4	49	36	3	44	74	74
8	54	58	4	180	179	11	48	81	6	59	76	9	81	78	17 0 3	41	39	4	41	62	62
17 0 2	197	184	5	42	60	12	40	56	7	101	112	11	70	82	2	43	23	5	43	32	32
1	52	37	6	151	145	13	49	56	8	169	186	11 0 3	49	66	3	33	90	9	53	71	71
2	61	77	7	225	212	14	74	73	9	46	42	1	40	28	18 0 3	64	86	7 0 4	118	60	60
4	39	27	8	57	61	15	67	86	10	48	67	2	53	98	1	28	37	3	77	85	85
5	45	59	9	82	88	16	80	103	11	54	59	3	88	83	1 3 4	40	41	5	42	71	71
6	38	66	10	70	56	5 0 3	47	44	12	29	60	5	70	88	5	48	67	6	52	55	55
7	45	60	11	33	38	1	43	34	14	57	48	6	55	44	7	46	61	9	37	47	47
18 0 2	38	47	12	53	53	3	89	102	8 0 3	40	32	12 0 3	41	80	8	65	94	8 1 4	37	27	27
1	64	41	13	40	34	4	193	195	1	164	174	4	60	51	10	60	63	2	38	67	67
3	36	27	14	57	68	5	76	94	2	204	213	5	89	112	11	59	75	4	90	35	35
19 1 2	52	61	16	51	42	7	41	39	3	73	66	6	60	78	12	45	16	5	75	106	106
2	56	54	17	66	83	8	55	60	4	128	144	7	62	74	2 2 4	37	75	6	50	67	67
3	40	41	3 0 3	145	186	9	54	74	5	72	73	8	53	65	4	47	60	8	95	66	66
20 0 2	143	149	1	177	243	10	64	83	7	54	79	9	81	85	5	44	49	9 4 4	74	75	75
2	44	44	2	62	83	11	45	69	8	85	110	13 0 3	106	90	8	54	75	10 2 4	112	165	165
21 0 2	67	55	3	199	209	12	40	36	9	58	62	1	53	68	10	87	112	5	49	48	48
1	98	102	4	54	42	13	33	57	12	62	77	2	121	134	11	57	59	6	133	70	70
1 2 3	49	20	5	42	55	15	45	53	13	62	77	3	142	153	3 1 4	35	46	11 0 4	43	48	48
3	35	61	6	95	100	6 0 3	54	68	9 0 3	66	85	4	45	40	4	50	67	1	38	26	26
4	122	134	7	56	43	1	37	69	1	74	88	5	72	79	5	45	72	2	44	38	38
5	68	89	8	119	125	3	61	29	2	85	82	6	36	32	8	50	27	3	38	37	37
6	51	50	9	69	58	4	63	83	3	45	18	7	36	60	9	47	46	4	45	63	63
7	99	114	11	143	166	5	51	38	5	43	33	14 0 3	68	75	4 1 4	43	53	12 0 4	79	43	43
8	82	63	12	86	85	7	40	84	6	64	82	1	47	79	2	44	40	1	94	55	55
9	54	54	14	33	38	8	39	45	7	52	59	2	51	76	3	44	17	13 0 4	68	59	59
10	144	153	15	31	36	9	40	46	8	44	51	3	104	112	5	37	36	1	37	4	4
11	37	71	16	69	88	10	59	59	9	48	42	4	47	46	7	190	240	14 0 4	59	86	86
12	129	130	4 0 3	86	112	11	114	119	10	37	28	5	27	24	8	54	40				
13	155	155	1	68	59	12	40	62	11	106	124	6	33	21	10	41	51				
14	35	21	2	56	99	13	90	93	10 0 3	55	75	15 3 3	30	46	5 1 4	146	300				

The unobserved reflections have been omitted since they were not used in the refinement.

than  $\frac{1}{4}$ . Consequently the maximum possible electron density on the  $c$  axis, effected if one locates Pb ions there, is smaller than the one corresponding to the two Sb ions with occupancies  $\frac{1}{2}$ .

In order to determine what the type and the occupancy of the ions on the  $c$  axis should be  $B$ 's and occupancies for both types, Pb and Sb, were refined with the aid of the program SITE of Dr. T. Ito (unpublished). Only for Pb ions at both positions occupancies smaller than  $\frac{1}{4}$  were calculated. In addition to that the unrealistic  $B$  values of 0.9 and 7.7 Å<sup>2</sup> were found for Sb at the positions 2 and 3 respectively. Therefore Pb ions were located at these positions. The resulting occupancies, 0.19 and 0.18 respectively, were included in the following refinement as fixed parameters. The composition was retained by setting the occupancy for the mixed cation at 0.85 which is virtually the same as defining a new mixed cation consisting of 50% Sb and 38% Pb ( $R_w = 0.14$ ).

After inclusion of anisotropic thermal parameters for the cations at the positions 1 and 4—7 convergence was reached at an  $R$  value of 0.13 for observed reflections only. The unobserved reflections have not been used in the refinement procedures<sup>3</sup>. The final parameter shifts are smaller than  $\frac{1}{4}$  except for  $z$  and  $B$  of ions Pb(2) and Pb(3),

<sup>3</sup> Inclusion of these in the evaluation of  $R$  yields a value of 0.16.

