Zeitschrift für Kristallographie, Bd. 141, S. 79—96 (1975)

Refinement of the crystal structure of zinckenite, $Pb_6Sb_{14}S_{27}$ *

By **Jan C. Portheine**** and **Werner Nowacki**
University of Bern

(Received 15 January 1974)

Auszug

Die Kristallstruktur von Zinckenit, $Pb_6Sb_{14}S_{27}$, 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 Cu$K\alpha$-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 trigonal-pyramidale, für Sb(2) und Sb(3) hingegen eine planare Dreier-Koordination. Die 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, $Pb_6Sb_{14}S_{27}$, 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 Cu$K\alpha$ 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.

---

* Contribution no. 253; part 76 on sulfides and sulfosalts; Dept. Crystallography, University, CH-3012 Bern, Sahlistr. 6.

** Present address: Laboratoire de Cristallographie aux Rayons X de l'Université, 24 Quai Ernest Ansermet, 1211 Genève 4, Switzerland.

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 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 $Pb_6Sb_{14}S_{27}$ ($= 6PbS \cdot 7Sb_2S_3$) 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 week 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 $PbSb_2S_4$ ($= PbS \cdot Sb_2S_3$) 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 $AgBi_3S_5$. In Table 1 observed weight

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

	Locality			$Pb_6Sb_{14}S_{27}$ (calc.)	$PbSb_2S_4$ (calc.)
	Cerro Bonete	Wolfsberg			
	Analysis number				
	640-1973[a]	182-1967[b]	208-1967[b]		
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
Σ	99.8	99.2	99.2	100	100
Pb/Sb	0.75	0.76	0.75	0.73	0.85

[a] Analyst: H. Walter, Laboratorium für Mikroröntgenspektroskopie der Universität Bern.

[b] Analyst: G. Burri, Laboratorium für Mikroröntgenspektroskopie der Universität Bern.

percentages of the constituent elements are compared with calculated values for the two compositions mentioned in the introduction. The composition $Pb_6Sb_{14}S_{27}$ 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 week 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 hewever that the ordering is not perfect and that there is no additional ordering in directions perpendicular to $\mathbf{c}$. 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 ($a_{Si} = 5.4301$ Å) 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 θ 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 ω-scan technique using Ni-filtered Cu radiation. Because of the high μ 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*

$Pb_6Sb_{14}S_{27}$, $M = 3813$ g · mole^{-1},
space group $P6_3$, $Z = 1\frac{1}{2}$,
$F(000) = 2457$ electrons, $\lambda = 1.54178$ Å,
$\mu = 1117$ cm^{-1}

a	22.148(6)	Å
c	4.333(6)	
ϱ_{obs}*	5.36	g · cm^{-3}
ϱ_{calc}	5.16	
V_{cell}	1841	Å^3

* Measured by NUFFIELD (1946, Berman balance).

The independent reflections were obtained by averaging as follows: $F_0 = \sum_i W(F_i) \cdot F_i / \sum_i W(F_i)$ and $W(F_0) = \sum_i W(F_i)$, where the summation goes over the equivalent reflections (i). F_0 was considered observed if $33\,{}^0/_0$ or more of the individual observations were significant at the $1\,{}^0/_0$ level $[F \geq 2.33 \times W^{-1/2}(F)]$. There resulted 956 observed reflections and 266 unobserved ones, together comprising $87\,{}^0/_0$ of the independent reflections in the Cu sphere. The discrepancy between equivalent reflections expressed as the average of $\sum_i W(F_i) \cdot |F_i - F_0| / \sum_i W(F_i) \cdot F_i$ amounted to 0.11.

Some diffraction data are given in Table 2.

---

[1] Throughout this publication numbers added in parentheses are estimated standard deviations σ 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 $\Sigma W(F_o) \cdot (F_o - F_c/k)^2$ 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 Å^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 $\Delta B = -2.1$ Å^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 $R_w = [\Sigma W(F_o) \cdot (F_o - F_c/k)^2 / \Sigma W(F_o) \cdot F_o^2]^{1/2}$ 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 $\Delta B = +0.8$ Å^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 $\mathcal{R}_{13,917,0.005} = 1.02$. Since the ratio is larger than $\mathcal{R}_{13,917,0.005}$ the latter space group is the correct one[2]. The suffixes of $\mathcal{R}$ 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 Å^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 Å^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 Å. Such a distance cannot be realized in sulfosalts and therefore the upper limit for the occupancies is less

---

[2] On the basis of Laue photographs of Wolfsberg zinckenite NUFFIELD (1946) decided for the same space group.

Table 3. *Positional coordinates*[a] *in fractions of the cell edges and occupancies of the ions in zinckenite*

Cationic position number		x		y		z		Occupancy[b]
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)[c]
3	Pb(3)	—	0	—	0	—	0.125(4)	0.18(3)[c]
4	(Pb,Sb)[e]	0.2009(5)	0.1994(2)	0.0400(5)	0.0399(3)	3/4	0.775(2)	0.85(2)[g]
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)[c]	0.116(3)	0.115(2)[c]	3/4	0.76(2)[d]	0.75[f]
	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)	

[a] The values of TAKEDA and HORIUCHI (1971) are given in the first column.

[b] Only occupancies different from 1.00 are given.

[c] Not refined in the final stage.

[d] Estimated from final difference map.

[e] For this ion the scattering factor $\frac{1}{2}(f_{Pb} + f_{Sb})$ was employed.

[f] Assumed.

[g] Dependent occupancy.

Table 4. *Thermal parameters*[a] *of the ions in zinckenite.*

	β_{11}	β_{22}	β_{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^2
(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^2	S(2)	2.0(3) Å^2	S(4)	1.8(3) Å^2	S(6)	1.1(3) Å^2
Pb(3)	1.8(3)	S(3)	1.3(3)	S(5)	1.8(3)	S(7)	1.3(2)

[a] The anisotropic temperature factor is defined as:

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

[b] 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*

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	h k l	F_o	F_c	h k l	F_o	F_c
1 1 0	76	38	7 17 0	63	60	18 2 0	47	43	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	333	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	291	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	10	83	79	14	206	198	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	42	5	50	32	3	38	58	1	60	63	15	74	83	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	139	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	104	105	7	45	47	6	109	107	5	122	111	5	153	155
13	100	116	12	52	20	9	118	113	8	72	66	7	87	101	6	44	31	6	136	142
14	62	71	13	38	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	230	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	13	36	23	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	139	171	11	140	131	20	85	94	16	43	22	2	191	214	14	49	32	14	96	106
4	206	189	13	96	98	21	53	52	17	61	19	3	234	237	16	38	58	15	34	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	3	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	63	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	194	220	1	81	79	6	113	100	10	114	76
17	133	130	13	190	179	8	70	69	8	302	307	2	72	64	8	72	23	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
2	49	62	16	69	76	10	63	58	10	105	110	4	57	52	10	55	27	2	404	402
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	55	37	7	37	52	13	209	217	8	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	93	7	138	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	63	4 0 2	43	48	13	75	80
18	47	50	10	136	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	930	971	14	38	45	3 0 1	260	275	3	149	149	5	58	50	4	53	63	3	49	42
2	99	74	15	30	9	1	342	397	4	227	247	6	112	106	5	74	82	4	119	128
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	52	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
5	51	55	13	41	51	19	48	16	3	64	64	6	117	117	5	83	101	10	89	93
6	161	150	15 3 0	196	223	20	74	64	4	44	50	7	56	70	6	63	15	11	42	35
7	68	60	4	44	30	21	92	105	6	104	105	8	57	70	7	117	94	12	51	55
8	59	71	5	98	104	4 0 1	136	140	7	79	85	9	38	45	8	47	34	13 0 2	85	91
9	142	136	6	64	81	1	228	212	9	64	51	18 0 1	121	133	9	89	74	1	86	73
11	115	107	8	53	65	2	93	81	10	118	115	1	55	53	10	63	46	2	42	33
12	241	248	11	62	73	3	43	58	11	156	166	2	118	131	11	111	16	4	95	76
15	180	191	12	71	60	4	109	105	13	41	48	3	63	92	12	86	93	5	35	37
17	90	101	16 0 0	100	107	5	361	368	14	45	44	4	106	114	13	63	22	6	128	109
18	97	108	2	59	57	6	91	96	15	90	95	5	30	31	15	64	74	7	105	99
7 1 0	112	85	3	64	57	7	55	39	16	90	95	6	60	62	16	52	81	8	57	49
2	47	21	5	96	120	8	51	50	17	55	57	19 0 1	115	106	17	84	80	11	86	95
3	213	222	6	139	131	9	42	17	10 0 1	77	66	1	50	49	18	169	159	14 0 2	140	144
4	47	32	8	64	63	10	240	269	1	55	62	2	70	74	6 0 2	80	73	1	52	38
5	97	89	10	36	30	11	85	111	2	87	62	3	49	9	1	73	74	2	50	56
6	234	231	17 0 0	240	237	12	50	43	3	73	38	4	137	134	2	50	41	5	201	201
8	89	77	2	43	60	13	96	92	4	76	83	5	41	21	3	127	123	9	55	69
9	208	226	4	52	52	14	135	138	5	192	211	6	40	28	4	148	150	15 2 2	65	30
11	142	138	5	45	62	15	135	154	6	59	72	20 0 1	51	42	5	63	59	3	160	174
12	90	106	7	36	59	16	115	137	7	81	41	1	40	39	6	119	120	4	47	51
14	58	17	8	126	148	17	98	97	8	82	81	2	83	81	7	50	29	5	58	58
16	91	106	9	44	47	18	60	63	9	147	151	4	29	46	8	67	8	6	78	84

Table 5. *(Continued)*

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	h k l	F_o	F_c	h k l	F_o	F_c
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	41	25	5	174	187	15	34	50	2	44	24	5	40	36	8	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
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
5	91	105	1	94	128	9	51	39	4	103	113	6	41	47	1	48	37	2	65	32
6	109	100	3	124	135	10	132	156	5	129	143	8	41	53	4	49	56	3	44	74
8	54	58	4	180	179	11	48	81	6	59	76	9	81	78	17 0 3	41	39	4	41	62
17 0 2	197	184	5	42	60	12	40	56	7	101	112	11	70	82	2	43	23	5	43	32
1	52	37	6	151	145	13	49	56	8	169	186	11 0 3	49	66	3	33	90	9	53	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
4	39	27	8	57	61	15	67	86	10	48	67	2	53	98	1	28	37	3	77	85
5	45	59	9	82	88	16	80	103	11	54	59	3	88	83	1 3 4	40	41	5	42	71
6	38	66	10	70	56	5 0 3	47	44	12	29	60	5	70	88	5	48	67	6	52	55
7	45	60	11	33	38	1	43	34	14	37	48	6	53	44	7	46	61	9	37	47
18 0 2	38	47	12	53	53	3	89	102	8 0 3	40	32	12 0 3	41	80	8	63	94	8 1 4	37	27
1	64	41	13	40	34	4	193	195	1	164	174	4	60	51	10	60	63	2	38	67
3	36	27	14	57	68	5	76	94	2	204	213	5	89	112	11	59	75	4	90	35
19 1 2	52	61	16	51	42	7	41	39	3	73	66	6	60	78	12	45	16	5	75	106
2	56	54	17	66	83	8	55	60	4	128	144	7	62	74	2 2 4	37	75	6	50	67
3	40	41	3 0 3	145	186	9	54	74	5	72	73	8	53	63	4	47	60	8	93	69
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
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
21 0 2	67	55	3	199	209	12	40	36	9	58	62	1	53	68	10	87	112	5	49	48
1	98	102	4	54	42	13	33	57	12	62	77	2	121	134	11	57	59	6	133	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
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
4	122	134	7	56	43	1	37	69	1	74	88	5	72	79	5	45	72	2	44	38
5	68	89	8	119	125	3	61	29	2	85	82	6	36	32	8	50	27	3	38	37
6	51	50	9	69	58	4	63	83	3	45	18	7	36	60	9	47	46	4	45	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
8	82	63	12	86	85	7	40	84	6	64	82	1	47	79	2	44	40	1	94	55
9	54	54	14	33	38	8	39	45	7	52	59	2	51	76	3	44	17	13 0 4	68	59
10	144	153	15	31	36	9	40	46	8	44	51	3	104	112	5	37	36	1	37	4
11	37	71	16	69	88	10	59	59	9	48	42	4	47	46	7	190	240	14 0 4	59	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^2 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[3]. The final parameter shifts are smaller than $\frac{1}{4}$ except for z and B of ions Pb(2) and Pb(3),

---

[3] Inclusion of these in the evaluation of R yields a value of 0.16.

which have shifts of $\sim \frac{1}{2}\,\sigma(z)$ and $\sigma(B)$ (see also Discussion). R_w amounts to 0.12.

The positional and thermal parameters are given in the Tables 3 and 4 respectively. Table 5 is the final list of observed and calculated structure amplitudes. The largest peak in the final difference map was identified with S(1). It had a height of 9 $e\text{Å}^{-3}$ and was elongated approximately along [210]. The x and y values estimated for the centroid correspond to the values obtained when S(1) was refined in $P6_3/m$ with fixed B. The latter values are given in Table 3. The only other peaks of any significance (heights between 2 and 5 $e\text{Å}^{-3}$) were found near the cationic positions. These must be due to systematic errors in the data and deficiencies in the model [*e.g.* S(1) was omitted in the refinement].

The ratio of the R_w values from isotropic and anisotropic refinements, 0.14/0.12, is larger than $R_{25,882,0.005} = 1.03$ which indicates that the anisotropic refinement is warranted. Introduction of anisotropic thermal parameters for the ions Pb(2), Pb(3) and S(2) to S(7) did not yield a significantly lower R_w value.

An attempt to establish the absolute configuration with the aid of the anomalous scattering of the cations was unsuccessful.

Discussion

In view of the discrepancy between equivalent reflections one could not have expected to find a much lower R_w value at the end of the refinement.

From Table 3 it is obvious that our x and y values are not different from those of TAKEDA and HORIUCHI (1971). There are however significant differences between the z values.

When the cations Pb(2) and Pb(3) were located the composition was preserved by decreasing accordingly the Pb occupancy of the mixed-cation position. A justification for this procedure was found in the comparison of residual electron densities in the different Fourier maps.

The number of anions in the unit cell is actually $40\frac{1}{2}$. So at least one of the seven sixfold S positions should be partially occupied. Since the S ions 2—7 had B values in the range of 1.1—2.3 Å^2 when that of S(1) blew up it was assumed that the S(1) position is the partially occupied one. The later found partial occupancies of the cations Pb(2), Pb(3) and (Pb, Sb) are concomitant with this assumption. With the occupancy fixed at $\frac{3}{4}$ the B of S(1) blew up as well which indicates that S(1) is also disordered as illustrated in the difference maps.

In the last cycles of the refinement the z values of Pb(2) and Pb(3) were oscillating, which is expressed in the size of the final shifts. This may indicate that these atoms are not independent. Assumption of the symmetry of $P6_3/m$ at the c axis would explain that the relation $z\,[\mathrm{Pb}(2)] + z\,[\mathrm{Pb}(3)] = \frac{1}{2}$ is satisfied within 2σ and that the occupancies are virtually equal. The region of this symmetry could be extended towards S(1) since the peak shape of this atom in the final difference map corresponds approximately to this symmetry. Since the employed refinement program has no options to apply the constraints: $z\,[\mathrm{Pb}(2)] + z\,[\mathrm{Pb}(3)] = \frac{1}{2}$, $B\,[\mathrm{Pb}(2)] = B\,[\mathrm{Pb}(3)]$ and occupancy [Pb(2)] = occupancy [Pb(3)] we have not verified this higher symmetry.

A qualitative explanation for the diffuse intensity of zinckenite can be found in the assumption that the mixed-cation positions in consecutive cells along c are occupied alternatingly by Pb and Sb. The periodic positional disordering associated with such an alternating occupancy will effect the environment. Especially in the region of S(1), Pb(2) and Pb(3), that is around the c axis, one expects periodic deviations from the average positions and occupancies resulting from the x-ray experiment. On the other hand different regions are separated by a part of the structure without disordering and partial occupancies. Therefore it is plausible that there is no correlation between different regions: the ordering is only one-dimensional. If the local geometric adjustments are small the corresponding intensity will be determined approximately by the function $6\,(0.38\,f_{\mathrm{Pb}} - 0.50\,f_{\mathrm{Sb}})$, where f_{Pb} and f_{Sb} are the atomic scattering factors of Pb and Sb and the factor 6 is due to the fact that the involved position is sixfold. Comparison of the function value of 34 at $(\sin\theta)/\lambda = 0$ with $F(000)$ learns that the diffuse intensity should be of the order of 10^{-3} to 10^{-4} times the intensity of the strongest Bragg reflections. Photographic estimates do not contradict such a magnetude ratio.

Description of the structure

In Fig. 1 a projection of the zinckenite structure on (001) is shown. Interatomic distances and angles are tabulated in the Tables 6 and 7. The numerals of equivalent ions are illustrated in Fig. 2 where the cation coordinations are given.

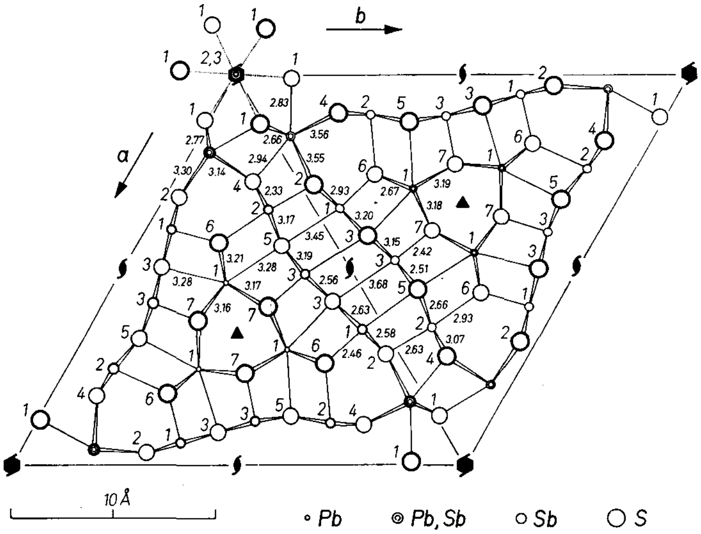

Fig. 1. Projection of the unit cell of zinckenite on (001). Ions drawn as thick circles have z values between 0.74 and 0.83 and as thin ones between 0.16 and 0.36. Distances towards Pb(2) and Pb(3), which are projected above each other, are represented as dotted lines

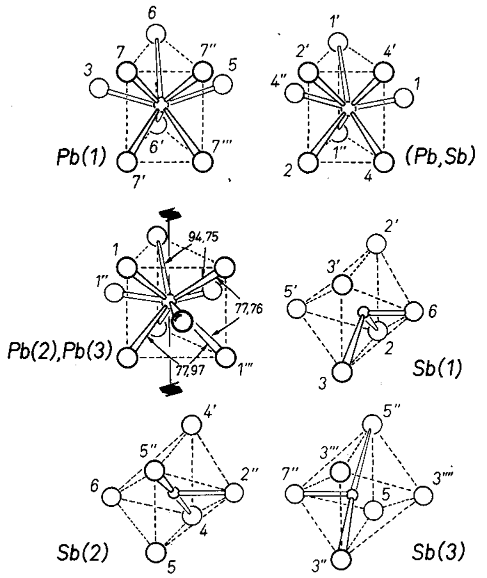

Fig. 2. Coordinations of the cations in zinckenite illustrating the numerals of equivalent anions used in the Tables 6 and 7. For Pb(2) and Pb(3) some interatomic angles are given in degrees. The coordinations of the latter ions are idealized

Table 6. *Cation-anion distances*[a] *in zinckenite*

Pb(1)—S(6′)	2.67(2) Å	(Pb,Sb)—S(1′)	2.66(8) Å	Sb(2)—S(4)	2.33(2) Å
—S(7)	3.16(3)	—S(1″)	2.77(8)	—S(2″)	2.63(1)
—S(7″)	3.17(3)	—S(1)	2.83(3)	—S(5″)	2.66(2)
—S(7′)	3.18(3)	—S(4″)	2.94(1)	—S(6)	2.93(1)
—S(7‴)	3.19(3)	—S(4)	3.14(2)	—S(4′)	3.07(2)
—S(6)	3.21(2)	—S(2)	3.30(2)	—S(5)	3.17(2)
—S(3)	3.28(1)	—S(2′)	3.55(2)	Average[b]	2.54
—S(5)	3.28(1)	—S(4′)	3.56(2)		
Average	3.14	Average	3.09		
Pb(2)—S(1″)	3×2.73(4)	Sb(1) —S(6)	2.46(1)	Sb(3)—S(7″)	2.42(1)
—S(1)	3×3.19(6)	—S(2)	2.58(3)	—S(5″)	2.51(2)
—S(1‴)	3×3.76(7)	—S(3)	2.63(2)	—S(3″)	2.56(2)
Average	3.23	—S(2′)	2.93(3)	—S(3‴)	3.15(2)
		—S(3′)	3.20(2)	—S(5)	3.19(2)
Pb(3)—S(1″)	3×2.75(4)	—S(5′)	3.45(1)	—S(3$^{\mathrm{IV}}$)	3.68(1)
—S(1‴)	3×3.12(5)	Average[b]	2.56	Average[b]	2.50
—S(1)	3×3.85(7)				
Average	3.24				

[a] Only distances smaller than 4.0 Å are given.

[b] Average of the three shortest distances.

Table 7. *Angles between the cation-anion distances in zinckenite*

S(6) —Pb(1)—S(6′)	94.4°	S(1′) —(Pb,Sb)—S(1″)	106°
—S(7)	77.6	—S(2′)	79
—S(7″)	75.6	—S(4′)	75
—S(3)	69.2	—S(4″)	74
—S(5)	80.0	—S(1)	78
S(7) —Pb(1)—S(7′)	86.3	S(2′) —(Pb,Sb)—S(2)	78
—S(7″)	65.3	—S(4′)	61
—S(3)	68.1	—S(4″)	68
S(7″)—Pb(1)—S(7‴)	85.8	S(4′) —(Pb,Sb)—S(4)	80
—S(5)	74.9	—S(1)	73
S(6′) —Pb(1)—S(7′)	85.7	S(1″)—(Pb,Sb)—S(2)	83
—S(7‴)	83.3	—S(4)	81
—S(3)	80.0	—S(4″)	85
—S(5)	68.5	—S(1)	76
S(7′) —Pb(1)—S(7‴)	64.9	S(2) —(Pb,Sb)—S(4)	69
S(3) —Pb(1)—S(5)	133.8	S(4″)—(Pb,Sb)—S(1)	140
S(6) —Sb(1)—S(2)	95.3	S(3″)—Sb(3) —S(5″)	174.4
—S(3)	92.9	—S(7″)	92.6
S(2) —Sb(1)—S(3)	88.4	S(5″)—Sb(3) —S(7″)	93.0
S(2″)—Sb(2)—S(4)	95.6		
—S(5″)	91.1		
S(4) —Sb(2)—S(5″)	172.8		

Standard deviations are in the range 0.4—0.8° for Pb(1) and the Sb ions and in the range 1—2° for (Pb,Sb), Pb(2) and Pb(3). Angles for Pb(2) and Pb(3) are given in Fig. 2.

The coordination of Pb(1) is approximately described as a trigonal prism of 6 S ions and two additional S ions outside the prism on normals from the cation to two side faces. Average Pb—S distances for Pb in similar eight coordinations are: 3.21, 3.18 (in bournonite and seligmannite respectively; EDENHARTER, NOWACKI and TAKÉUCHI, 1970), 3.11 and 3.15 Å (in cosalite; SRIKRISHNAN and NOWACKI, 1974). The average Pb(1)—S distance in zinckenite, 3.14 Å, lies in the range of these values. The unusual small value for the distance Pb(1)—S(6) in zinckenite is not significant.

The cation positions 2 and 3 are surrounded by 9 S(1) sites, six of which form a trigonal prism and three lie on normals to the three side faces. If one takes into account the partial occupancies of these positions and of S(1) then the actual coordination number 9 is found for Pb(2) and Pb(3). Pb ions with the same coordination in baumhauerite (ENGEL and NOWACKI, 1969) and dufrenoysite (RIBÁR, NICCA and NOWACKI, 1969) have average Pb—S distances between 3.15 and 3.24 Å. The agreement with these values of the averages for Pb(2) and Pb(3) in zinckenite confirms the Pb location at the positions 2 and 3. The discrepancies between the individual distances can be understood on the basis of a relation between the disordering of S(1) and the partial occupancies of Pb(2) and Pb(3). If the actual site of a S(1) ion depends on the fact whether or not the nearest Pb site is occupied, then the observed S(1) site, being the average for the two possibilities, will have too large or too small a distance towards the Pb site in question.

The coordination of the mixed cation is similar to that of Pb(1). Concomitant with the occupancy (50% Sb and 38% Pb) the average (Pb, Sb)—S distance is somewhat smaller than for Pb(1).

Each of the three Sb ions has six S neighbours at distances smaller than the sum of the van der Waals' radii of Sb and S ($2.2 + 1.85 = 4.05$ Å) in a distorted octahedral coordination. Sb(1) comprises the top of a trigonal pyramid with its three nearest S neighbours as basis corners. This coordination is to be expected when the bonds between Sb and S are covalent. The three nearest neighbours of Sb(2) and Sb(3) form approximately an isosceles orthogonal triangle where the Sb is located at the midpoint of the hypothenuse. In Fig. 2 only distances in the corresponding SbS_3 groups are drawn.

The "zone axes" of the coordination prisms of Pb(1) and (Pb, Sb) are parallel to *c*. Prisms of the same ion in cells adjacent along *c* are stacked on top of each other into infinite columns running parallel to *c*.

Three columns of Pb(1) prisms form together a threefold column about the threefold axis (see Fig. 3). In this case the elementary prisms of one column share two of the three parallel edges with prisms belonging to the other columns and in this way the composition PbS_4 is realized for the threefold column.

About the 6_3 axis six (Pb, Sb) columns form together a "ring wall" (see Fig. 3) in such a way that single column neighbours are shifted over $\frac{1}{2}\mathbf{c}$ with respect to each other. The Pb(2) and Pb(3) ions are enclosed by this "ring wall".

The SbS_3 groups form together endless chains by sharing of two S ions. These chains of composition SbS_2 wind as spirals around the 2_1 axes (see Fig. 4) and contain six units per winding period *c*.

The ratio φ of the numbers of S and Sb ions in the structure is equal to 1.93. Consequently zinckenite belongs to the type *V* ($1 < \varphi < 2$)

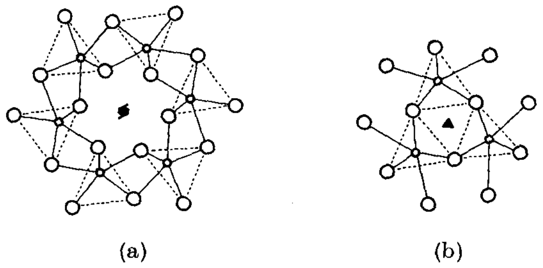

Fig. 3. (001) Projections of the "ring wall" of (Pb,Sb) prisms (a) and the threefold column of Pb(1) prisms (b) in zinckenite

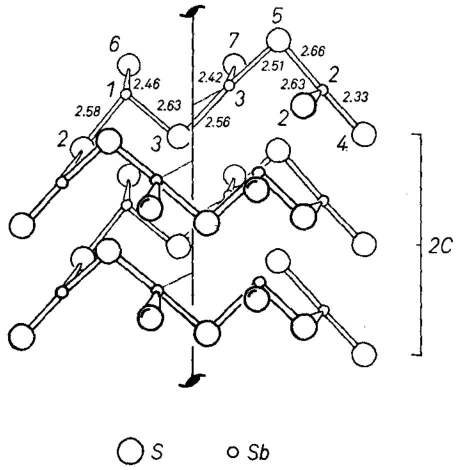

Fig. 4. Perspective view of two windings of a spiral with composition SbS_2 in zinckenite

of NOWACKI's (1969) classification of sulfosalts. Accordingly the structure is characterised by the spirals of SbS_3 groups and additional Sb and S ions. The extra Sb ions are found at the (Pb, Sb) sites while the S(1) sites contain the extra S ions.

Acknowledgements

Our thanks are due to Dr. P. ENGEL who collected the intensity data. The calculations were performed on the IBM 1620 of our University (data reduction) and on the IBM 370/155 of the Bernische Datenverarbeitungsgesellschaft BEDAG. We acknowledge the financial support of the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung (Proj. No. 2.516.71) and of the Stiftung Entwicklungsfonds Seltene Metalle.

References

P. A. Doyle and P. S. Turner (1968), Relativistic Hartree-Fock x-ray and electron scattering factors. Acta Crystallogr. A **24**, 390—397.

A. Edenharter, W. Nowacki und Y. Takéuchi (1970), Verfeinerung der Kristallstruktur von Bournonit [$(SbS_3)_2|Cu_2^{IV}Pb^{VII}Pb^{VIII}$] und von Seligmannit [$(AsS_3)_2|Cu_2^{IV}Pb^{VII}Pb^{VIII}$]. Z. Kristallogr. **131**, 397—417.

P. Engel und W. Nowacki (1969), Die Kristallstruktur von Baumhauerit. Z. Kristallogr. **129**, 178—202.

E. J. Gabe, J. P. Glusker, J. A. Minkin and A. L. Patterson (1967), X-ray crystal analysis of the substrates of aconitase. VII. The structure of lithium ammonium hydrogen citrate monohydrate. Acta Crystallogr. **22**, 366—375.

W. C. Hamilton (1959), On the isotropic temperature factor equivalent to a given anisotropic temperature factor. Acta Crystallogr. **12**, 609—610.

W. C. Hamilton (1965), Significance tests on the crystallographic *R* factor. Acta Crystallogr. **18**, 502—510.

D. C. Harris (1965), Zinckenite. Canad. Mineral. **8**, 381—382.

Werner Nowacki (1969), Zur Klassifikation und Kristallchemie der Sulfosalze. Mineral. Petrogr. Mitt. **49**, 109—156.

E. W. Nuffield (1946), Studies of mineral sulfo-salts. XII—Fülöppite and zinckenite. University of Toronto Studies, Geological Series **50**, 49—62.

B. Ribár, Ch. Nicca und W. Nowacki (1969), Dreidimensionale Verfeinerung der Kristallstruktur von Dufrenoysit, $Pb_8As_8S_{20}$. Z. Kristallogr. **130**, 15—40.

T. Srikrishnan and Werner Nowacki (1974), A redetermination of the crystal structure of cosalite, $Pb_2Bi_2S_5$. Z. Kristallogr. **140**, 114—136.

H. Takeda and H. Horiuchi (1971), Symbolic addition procedure applied to zinckenite structure determination. Journ. Miner. Soc. Japan **10**, 283—295.

G. Vaux and F. A. Bannister (1938), The identity of zinckenite and keeleyite. Min. Mag. **25**, 221—227.