

The crystal structure of rathite-I*

By F. MARUMO and W. NOWACKI

Abteilung für Kristallographie und Strukturlehre,
Mineralogisches Institut, Universität Bern, Schweiz

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Auszug

Die Kristallstruktur von Rathit-I wurde mittels dreidimensionaler Intensitätsdaten bestimmt. Vier Formeleinheiten $(\text{Pb,Tl})_3\text{As}_4(\text{As,Ag})\text{S}_{10}$ sind in der Einheitszelle der Symmetrie $P2_1/a$ mit $a = 25,16 \text{ \AA}$, $b = 7,94 \text{ \AA}$, $c = 8,47 \text{ \AA}$, $\beta = 100^\circ 28'$ enthalten. Die wahre Symmetrie von Rathit-I ist möglicherweise triklin. Die Lösung lieferten die Ähnlichkeit der Struktur mit derjenigen von Rathit-III und spezielle Verhältnisse der Röntgendiagramme.

Von drei unabhängigen Pb(Tl)-Atomen sind zwei von neun S-Atomen umgeben, das andere von sieben. Die As-Atome weisen trigonal-pyramidale Koordination durch die S-Atome auf. Von einem As-Atom wird angenommen, daß es statistisch von zwei verschiedenen trigonal-pyramidalen S-Koordinationen umgeben wird. Ein anderes As-Atom ist teilweise durch Ag ersetzt.

Die Struktur besteht aus zweierlei Schichten parallel zu (100). Die erste Art hat die Zusammensetzung $(\text{Pb,Tl})\text{S}_3$ und besteht aus den Koordinationspolyedern um die Pb(Tl)-Atome mit Neuner-Koordination. Die zweite Art ist aus Pb(Tl)-, As(Ag)- und S-Atomen zusammengesetzt, welche ein deformiertes PbS-Gitter bilden. Trigonale As-S₃-Pyramiden sind zu Ketten endlicher Länge vereinigt.

Abstract

The crystal structure of rathite-I has been determined with the use of three-dimensional intensity data. Four chemical units of $(\text{Pb,Tl})_3\text{As}_4(\text{As,Ag})\text{S}_{10}$ are contained in the unit-cell of the symmetry $P2_1/a$ with $a = 25.16 \text{ \AA}$, $b = 7.94 \text{ \AA}$, $c = 8.47 \text{ \AA}$, $\beta = 100^\circ 28'$. The true symmetry of rathite-I may be triclinic. The solution was obtained from the similarity of the crystal structure to that of rathite-III and from a peculiar feature of the x-ray diagrams.

Among three independent Pb(Tl) atoms two are surrounded by nine S atoms and the other is surrounded by seven S atoms. As atoms have trigonal-pyramidal coordinations by S atoms. One As atom, however, is believed to occupy statistically two different trigonal-pyramidal S coordinations. Another As atom is partially replaced by Ag.

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The structure is composed of two kinds of layers parallel to (100). Layers of the first kind have the composition $(\text{Pb,Tl})\text{S}_3$, and consist of coordination polyhedra around the Pb(Tl) atoms which are coordinated by nine S atoms. The layers of the second kind are composed of Pb(Tl) , As(Ag) and S atoms, having a deformed PbS -type structure. Trigonal As-S_3 pyramids are linked into strings of finite length.

1. Introduction

Rathite-I, $(\text{Pb,Tl})_3\text{As}_4(\text{As,Ag})\text{S}_{10}$, is a mineral of a sulfosalt group, to which rathite-II, rathite-III, rathite-IV, dufrenoyite, baumhauerite and scleroclase belong. A characteristic feature of these minerals is that they have periods of 8.4 Å and 7.9 Å along two mutually perpendicular directions. Though most of the structures have already been investigated, no precise structure has yet been revealed owing to the large absorption effects and the large unit-cell dimensions. Some of the structures reported contain unreasonable features such as, for example, infinite chains of As-S_3 pyramids along the 8.4 Å axes which, as was pointed out by Y. IITAKA and W. NOWACKI (1961), cannot exist.

The structure determination of rathite-I was carried out in order to obtain precise information concerning the structural principles of this group of minerals. It was also desired to clarify the relationship of rathite-III and rathite-I, which are dimorphous if the small amount of Tl and Ag in the latter plays no significant role in the formation of the mineral and can be replaced by Pb and by As respectively.

Rathite-III (LE BIHAN, 1962) has hitherto not been found by us in the Lengenbach quarry. It is important to mention that the rathite-I of LE BIHAN (1962) is almost identical with dufrenoyite and was called rathite-Ia by us (NOWACKI *et al.*, 1964). Rathite-II was first described by BERRY (1953). The lattice constants, space group and chemical composition are:

Mineral	Formula	<i>a</i>	<i>b</i>	<i>c</i>	β	Space group
Rathite-I	$(\text{Pb,Tl})_3\text{As}_4(\text{As,Ag})\text{S}_{10}$	25.16	7.94	8.47	100° 28'	$P2_1/a$ ($P\bar{1}$)
Rathite-III	$\text{Pb}_3\text{As}_6\text{S}_{10}$	24.52	7.91	8.43	90°	$P2_1$
Rathite-II	$\text{Pb}_9\text{As}_{18}\text{S}_{28}$	8.43	70.9	7.91	90°	$P2_1$

Thus, rathite-I and -III form two modifications of a single species and should perhaps have a name different from rathite-II; it is not, however, possible for us to introduce one. In the Lengenbach quarry rathite-II is frequently found, whereas rathite-I occurs rarely, and

then usually polysynthetically twinned. The microprobe analysis (NOWACKI und BAHEZRE, 1963) yielded the composition $\text{Pb} = 41.2 \pm 1$, $\text{As} = 27.0 \pm 0.5$, $\text{S} = 28 \pm (1 - 2)$, $\text{Tl} = 3.6 \pm 1$, $\Sigma = 99.7\%$.

2. Experimental

We looked through a large number of specimens from Lengenbach for a suitable rathite-I crystal as described by PEACOCK and BERRY (1940), but could not find one untwinned. Finally, through the kindness of Dr. L. G. BERRY (Queens University, Kingston, Canada) we obtained a good crystal (also from Lengenbach) for intensity measurements.

The unit-cell dimensions obtained from Weissenberg photographs are,

$$\begin{aligned} a &= 25.16 \pm 0.02 \text{ \AA}, & b &= 7.94 \pm 0.01 \text{ \AA}, & c &= 8.47 \pm 0.01 \text{ \AA}, \\ \alpha &= 90^\circ \pm 10', & \beta &= 100^\circ 28' \pm 10', & \gamma &= 90^\circ \pm 10'. \end{aligned}$$

Although the space group of rathite-I was reported as $P2_1/a$, the Weissenberg photographs showed small discrepancies between the intensities of hkl and $\bar{h}k\bar{l}$ reflections, indicating triclinic symmetry for this crystal. Moreover, several weak reflections with $h = \text{odd}$ were observed among the $h0l$ reflections. The true space group must, therefore, be $P1$ or $P\bar{1}$. However, it is difficult to say whether these small deviations from monoclinic symmetry are common to all rathite-I crystals or whether they are only a special characteristic of the crystal examined, caused by a small content of Tl and Ag. For the structure determination the space group $P2_1/a$ was assumed, and the average intensities of the hkl and $\bar{h}k\bar{l}$ reflections were used, the difference being very small.

A sphere with a radius of 0.06 mm was prepared for the intensity measurement from a piece of the crystal. The integrated Weissenberg photographs were taken with $\text{CuK}\alpha$ radiation up to the 7-th layer around the b axis and up to the second layer around the c axis. The intensities were measured with a Joyce-Loebl microdensitometer, and corrected for the Lorentz-polarization and absorption effects with the programme of Y. IITAKA for the Bull Γ AET electronic computer. The linear absorption coefficient of the crystal is 855 cm^{-1} for $\text{CuK}\alpha$ and the absorption-correction factors for the sphere range between 180 at $\theta = 0^\circ$ and 14 at $\theta = 90^\circ$.

The chemical analysis of the crystal was carried out by W. NOWACKI and C. BAHEZRE (1963) with a Castaing x-ray microanalyser.

The unit-cell content calculated from the result, assuming 5.37 g/cm^3 (DANA's system of mineralogy, Vol. I, 1944) for the density, is $\text{Pb}_{10.7}\text{Tl}_{0.9}\text{As}_{19.3}\text{S}_{40.1}$, or approximately $\text{Pb}_{11}\text{Tl}_1\text{As}_{20}\text{S}_{40}$. In the actual structure-factor calculations, the Tl atoms were taken as Pb atoms, since the differences between the atomic scattering factors of these two elements are quite small, and since the number of Tl atoms in the unit cell is less than the value required by the space group $P2_1/a$.

3. Structure analysis

Since the $hk0$ x-ray diffraction diagram of rathite-I is almost identical with that of rathite-III (M.-TH. LE BIHAN, 1962), the c axis projection of the structure should have the same atomic arrangement as that of rathite-III. Actually the values $a \sin\beta$, b and c for rathite-I (24.75 Å, 7.94 Å, 8.47 Å) are nearly equal to the values found for rathite-III (24.52 Å, 7.91 Å, 8.43 Å) and the chemical contents of their unit cells are identical if the Tl atoms in rathite-I are replaced by Pb atoms ($\text{Pb}_{12}\text{As}_{20}\text{S}_{40}$). Calculation of the $hk0$ structure factors were, therefore, carried out with a programme by Y. IITAKA for Bull Γ AET utilizing the atomic coordinates of rathite-III; fairly good agreement between the observed and the calculated structure factors was obtained, the R -factor being 0.38. This projection was refined by difference Fourier syntheses until the R -value was reduced to 0.16.

The z coordinates were obtained from a special feature of the $h0l$ x-ray diagram. Since the $h0l$ intensity distribution along the c axis direction in reciprocal space is periodic to a fairly good approximation with the period 4, all atoms should lie nearly on a set of equally spaced planes perpendicular to the c axis, the interplaner spacing being $c/4$. There are two possible sets of planes which satisfy both this condition and the symmetry requirement for $P2_1/a$:

$$z = \frac{1}{8} + \frac{x}{2} = \frac{1}{8} - x \cos\beta, \quad z = \frac{3}{8} + \frac{x}{2}, \quad z = \frac{5}{8} + \frac{x}{2}, \quad z = \frac{7}{8} + \frac{x}{2},$$

and

$$z = \frac{x}{2}, \quad z = \frac{1}{4} + \frac{x}{2}, \quad z = \frac{2}{4} + \frac{x}{2}, \quad z = \frac{3}{4} + \frac{x}{2}.$$

The structural similarity to rathite-III as well as crystallochemical considerations suggested that the correct set should be the former, and furnished two probable models of the structure. The true structure was found after several cycles of refinements of these models tested with the $h0l$ difference Fourier projection. The R value of the correct model was reduced from the initial value 0.49 to 0.19 for the $h0l$ reflections during the refinement.

4. Refinement

During the preliminary study with two-dimensional data, it was found from the Fourier projections that the As(5) atom has a lower electron density than the other As atoms and that there is a peak at a position about 0.6 Å apart from the position postulated for As(5). The agreement between the observed and the calculated structure factors becomes worse if As(5) is put at this peak. Therefore it was suspected that the As(5) atom statistically occupies both positions.

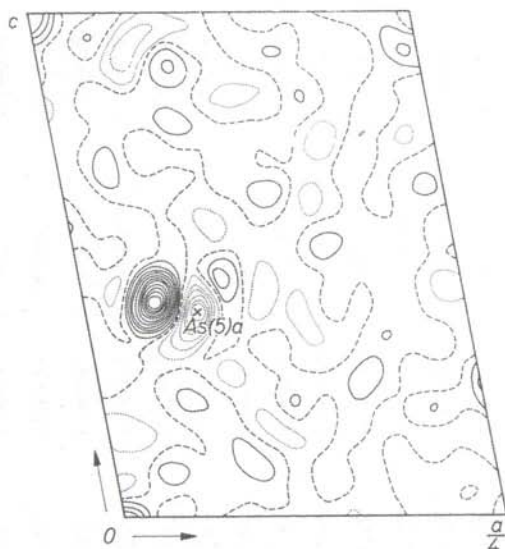


Fig. 1. A section of the three dimensional difference FOURIER map through the As(5) atom. Contours are at intervals of $4 e \cdot \text{Å}^{-3}$. The zero contour is shown as a dotted line and negative contours as broken lines

To clarify this point, a three-dimensional difference Fourier including 3477 diffraction data was calculated with the O. S. MILLS' programme for the Mercury computer at the calculating center of Oxford University. A part of the section through the As(5) atom is shown in Fig.1, in which a negative region at the postulated As(5) position and the peak near it is clearly observed, suggesting a statistical distribution of the As(5) atom between the two positions.

Three-dimensional least-squares refinements using equal weights for all reflections and assuming the statistical distribution of the As(5) atom were then carried out with the programme written by C. T. PREWITT for the I.B.M. 7090 computer. Anisotropic temperature

Table 1. The final positional coordinates and the populations of the As (5) atoms

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	population	$\sigma(w)$
Pb(1)	0.79493	0.00005	0.24587	0.00016	0.52425	0.00013		
Pb(2)	0.29663	0.00006	0.25004	0.00020	0.02117	0.00015		
Pb(3)	0.07201	0.00005	0.08812	0.00017	0.90401	0.00014		
As(1)	0.65908	0.00010	0.14956	0.00036	0.70133	0.00030		
As(2)	0.64775	0.00011	0.16774	0.00037	0.24983	0.00034		
As(3)	0.45735	0.00013	0.15358	0.00044	0.31332	0.00043		
As(4)	0.44043	0.00010	0.16767	0.00037	0.86116	0.00030		
As(5) <i>a</i>	0.07434	0.00024	0.0154	0.00080	0.4164	0.00065	0.807	0.015
As(5) <i>b</i>	0.05005	0.00031	0.0316	0.00112	0.4270	0.00093	0.402	0.013
S(1)	0.26381	0.00025	0.0017	0.00082	0.2580	0.00073		
S(2)	0.72350	0.00023	0.0211	0.00081	0.2494	0.00071		
S(3)	0.17470	0.00024	0.1793	0.00077	0.4949	0.00068		
S(4)	0.18042	0.00025	0.1696	0.00081	0.9056	0.00074		
S(5)	0.88749	0.00024	0.1612	0.00078	0.3051	0.00069		
S(6)	0.87973	0.00025	0.1200	0.00080	0.8307	0.00072		
S(7)	0.40154	0.00024	0.0184	0.00082	0.6328	0.00068		
S(8)	0.40741	0.00030	0.0078	0.00087	0.0405	0.00078		
S(9)	0.01249	0.00032	0.1999	0.00100	0.5872	0.00082		
S(10)	0.00907	0.00025	0.1833	0.00089	0.1798	0.00074		

Table 2. *Temperature factors*

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

atom	$\beta_{11} \cdot 10^6$	$\sigma(\beta_{11}) \cdot 10^6$	$\beta_{22} \cdot 10^6$	$\sigma(\beta_{22}) \cdot 10^6$	$\beta_{33} \cdot 10^6$	$\sigma(\beta_{33}) \cdot 10^6$	$\beta_{12} \cdot 10^6$	$\sigma(\beta_{12}) \cdot 10^6$	$\beta_{23} \cdot 10^6$	$\sigma(\beta_{23}) \cdot 10^6$	$\beta_{13} \cdot 10^6$	$\sigma(\beta_{13}) \cdot 10^6$
Pb(1)	158	2	1394	43	1032	17	-11	5	72	15	74	4
Pb(2)	216	3	2104	47	1225	22	-172	7	526	20	2	6
Pb(3)	153	2	1644	44	1229	18	23	5	284	16	127	5
As(1)	101	4	1126	61	781	36	5	11	-12	33	87	9
As(2)	103	4	1026	64	1132	39	54	12	184	36	99	10
As(3)	149	6	1391	75	1729	49	80	15	252	46	259	13
As(4)	98	4	1178	61	775	36	-14	11	-9	33	66	9
As(5)a	153	12	2030	117	1412	86	8	27	230	72	90	23
As(5)b	50	11	1299	160	930	116	23	30	-111	96	80	26
S(1)	107	9	821	98	847	76	47	23	103	70	71	20
S(2)	86	8	889	94	804	73	38	22	3	67	62	19
S(3)	105	8	676	93	704	71	-18	21	-111	65	70	19
S(4)	108	10	802	127	905	90	-42	28	-139	84	129	24
S(5)	94	8	753	96	767	74	-33	22	65	68	56	20
S(6)	111	9	711	99	828	77	33	23	74	70	37	21
S(7)	102	8	945	94	650	73	-25	22	49	67	85	19
S(8)	172	11	837	134	862	95	11	30	110	90	164	26
S(9)	174	12	1252	143	896	104	55	32	0	97	64	28
S(10)	97	9	1133	99	856	77	22	23	-169	70	73	21

Table 3. (Continued)

Table with multiple columns containing numerical data and sub-headers like 'h k l', 'F_o', 'F_c'. It is a continuation of Table 3, listing various numerical values under different sub-headers.

Table 3. (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
17 7 1	0	-13	11 7 3	28	23	14 7 5	36	-31	13 8 0	0	8	4 9 0	20	-11
18	20	21	12	58	50	-1 7 5	102	82	14	30	28	5	25	-12
19	0	6	13	25	27	-2	54	40	15	72	80	6	93	92
20	46	48	14	31	-23	-3	0	-8	16	41	-48	7	0	3
21	36	35	15	0	10	-4	145	135	17	38	34	8	82	-79
-1 7 1	0	0	16	21	-26	-5	57	47	18	27	-36	9	45	-35
-2	89	-83	17	33	-28	-6	61	53	19	21	26	10	15	-6
-3	11	-4	18	17	16	-7	105	90	20	42	-32	11	66	-69
-4	34	-31	19	40	-38	-8	52	36	1	35	-27	12	30	45
-5	146	140	-1 7 3	20	7	-9	112	-112	2	23	4	13	28	26
-6	80	-76	-2	95	-85	-10	29	40	3	39	34	14	82	-46
-7	109	115	-3	85	81	-11	23	-26	4	38	-35	15	26	-23
-8	17	-13	-4	30	29	-12	46	-41	5	117	110	1	30	-33
-9	27	32	-5	60	51	-13	57	62	6	33	31	2	0	-7
-10	83	82	-6	92	84	-14	83	-82	7	45	37	3	29	-9
-11	58	-62	-7	75	-71	-15	50	42	8	94	86	4	58	37
-12	88	92	-8	113	94	-16	53	53	9	41	-28	5	31	-29
-13	64	-59	-9	63	-46	-17	16	-10	10	0	-4	6	46	41
-14	32	-37	-10	70	-61	-18	37	32	11	83	-71	7	27	23
-15	25	-27	-11	0	10	-19	0	3	12	17	-20	8	42	32
-16	31	-28	-12	93	-89	-20	8	-6	13	45	-39	9	26	-22
-17	13	11	-13	55	-45	0 7 6	79	7	14	27	6	10	31	-29
-18	0	-2	-14	39	-36	1	44	31	15	23	-15	11	19	-7
-19	29	27	-15	146	144	2	90	-98	16	15	-9	12	35	-23
-20	27	-27	-16	2	4	3	25	11	17	15	-6	13	33	30
-21	37	31	-17	72	73	4	58	62	18	15	-13	14	42	46
-22	18	-18	-18	47	34	5	0	-15	19	53	-79	15	57	-48
-23	38	-47	-19	0	5	6	50	-53	20	0	8	-3	26	28
0 7 2	39	31	-20	31	28	7	12	7	-3	65	-53	-4	103	-87
1	0	0	-21	18	-19	8	39	33	-4	0	-12	-5	62	-53
2	95	-109	-22	56	66	9	36	42	-5	0	11	-6	69	63
3	65	-68	0 7 4	64	59	10	73	83	-6	22	16	-7	35	-48
4	153	165	1	33	-22	11	45	-56	-7	22	18	-8	29	33
5	26	29	2	240	-236	-1 7 6	23	13	-8	0	-2	-9	0	6
6	148	-151	3	35	20	-2	44	-41	-9	88	74	-10	64	54
7	101	113	4	117	107	-3	51	-44	-10	0	6	-11	41	-36
8	24	25	5	76	-67	-4	27	-24	-11	29	-26	-12	48	51
9	0	11	6	63	56	5	0	-12	-12	60	37	13	0	-5
10	37	-31	7	79	-77	-6	53	50	-13	0	-4	-14	32	-23
11	57	-63	8	52	47	-7	50	-37	-14	82	-73	0 9 2	59	-54
12	148	-169	9	23	-24	-8	116	-111	-15	30	-32	1	45	-48
13	40	48	10	70	72	-9	0	3	-16	13	-2	2	79	89
14	77	88	11	101	86	-10	69	69	-17	80	-70	3	0	6
15	43	-50	12	20	-12	-11	59	57	-18	15	15	4	66	-67
16	24	-23	13	21	9	-12	38	-39	-19	0	-6	5	0	5
17	16	-20	14	45	50	-13	18	24	0 8 2	92	93	6	99	105
18	57	65	15	16	5	-14	13	-9	1	101	-111	7	69	-75
19	17	-13	16	62	-69	-15	19	12	2	43	-44	8	45	-52
20	8	5	17	36	35	-16	46	49	3	29	-38	9	44	51
21	36	41	-1 7 4	102	92	-17	14	20	4	31	25	10	0	-15
-1 7 2	37	33	-2	57	47	0 7 7	18	-17	5	98	107	11	0	-6
-2	0	-3	-3	92	88	1	15	-11	6	51	55	12	0	19
-3	-3	5	-4	57	-48	2	17	15	7	66	65	13	13	2
-4	84	-90	-5	0	-15	3	9	-7	8	77	-90	-1 9 2	0	-3
-5	64	63	-6	218	206	4	41	-43	9	25	35	-2	47	-40
-6	197	207	-7	0	8	5	24	20	10	111	110	-3	66	68
-7	51	-45	-8	89	-89	6	13	-5	11	25	35	-4	119	127
-8	170	-179	-9	59	-51	-1 7 7	16	16	12	49	-57	5	0	12
-9	132	-142	-10	60	60	-2	26	6	13	0	-25	-6	42	-47
-10	21	3	-11	0	-10	-3	43	-26	14	71	72	-7	0	21
-11	43	-46	-12	122	-105	-4	16	16	15	86	-82	-8	110	115
-12	0	9	-13	45	-34	-5	58	-58	16	0	10	-9	73	73
-13	15	23	-14	35	-34	-6	35	-32	-11	53	35	-10	0	-7
-14	139	-152	-15	93	88	-7	32	-22	-2	65	-66	-11	0	-20
-15	19	43	-16	79	80	-8	22	-29	-3	99	-98	-12	17	-16
-16	41	43	-17	0	-8	-9	62	64	-4	0	19	-13	0	5
-17	39	41	-18	63	-71	-10	59	-60	-5	38	-36	-14	24	-24
-18	41	-47	-19	28	-32	-11	53	46	-6	45	-33	0 10 0	43	-52
-19	20	14	-20	80	92	-12	25	24	-7	52	64	1	21	33
-20	63	69	-21	0	-8	-13	19	-27	-8	27	-30	2	51	59
-21	38	34	0 7 5	106	-92	-14	19	-27	-9	82	77	3	14	-7
-22	9	-11	1	58	54	0 8 0	117	105	-10	80	87	4	12	-3
-23	31	-35	2	14	-15	1	43	29	-11	22	28	5	34	35
0 7 3	14	10	3	34	-28	2	151	-141	-12	104	-105	0 10 1	45	43
1	38	-33	4	97	-91	3	0	19	-13	34	-32	1	12	3
2	22	10	5	49	-38	4	35	35	-14	73	-82	2	15	-13
3	59	-60	6	30	27	5	65	-66	-15	22	-20	3	46	56
4	38	4	7	54	-6	6	56	-66	-16	56	60	-10 1	16	-12
5	25	-27	8	69	-66	7	40	-38	-17	76	-66	-2	0	9
6	81	68	9	55	48	8	38	-31	-18	15	-22	-3	29	-29
7	15	-18	10	21	17	9	0	17	-19	25	26	-4	12	-16
8	51	46	11	18	-9	10	121	115	1 9 0	43	44	5	45	-52
9	50	50	12	26	26	11	63	-67	2	101	98	6	34	35
10	29	32	13	18	15	12	106	-114	3	20	5	7	29	-29

factors were introduced for the second cycle of the refinement. The atomic scattering factors given by B. DAWSON, by A. J. FREEMAN and R. E. WATSON and by L. H. THOMAS, K. UMEDA and K. KING (International Table, Vol. III, 1962) were used for S, As and Pb, respectively. Using this programme, the atomic coordinates, temperature factors, layer-scale factors and the population of the As(5)

atom at the two positions were refined. After three cycles of refinement, the R factor was reduced from the initial value of 0.23 to 0.102 for all 3477 reflections and 0.086 for the 3013 observed reflections. The experimentally determined relative layer-scale factors and the final values obtained by the least-squares refinement agree within 3%, except for those reflections with k larger than 7 which were obtained from the photographs around the c axis. The experimental layer-scale factor for these reflections was underestimated owing to the insufficient integration for $K\alpha_1$ – $K\alpha_2$ splitting in the higher Bragg-angle regions.

The final positional coordinates and the temperature factors are given in Table 1 and Table 2, respectively, with the standard deviations calculated by the least-squares programme. Since the dispersion effect was not taken into account, the actual temperature factors of the Pb atoms should be smaller than the values given in Table 2. The calculated and the observed structure amplitudes are given in Table 3. For the calculation of the structure amplitudes, the population of the As(5) atoms at the two positions were assumed to be 0.668 and 0.332 respectively.

The maximum and the average coordinate shifts in the last cycle of the refinement expressed as fractions of the standard deviations are 2.01 and 0.66. Since we obtained a good convergence with the full-matrix least-squares programme, it is not expected that further refinement will cause significant changes in the atomic coordinates unless a new weighting scheme is employed.

5. Description of the structure

The atomic distances and the bond angles are given in Table 4. From the temperature factors the r.m.s. deviations of the atoms along the principal axes of the vibration ellipsoids were calculated and are given in Table 5 along with the direction cosines of two principal axes.

Pb(1) and Pb(2) are surrounded by nine S atoms in the manner shown in Fig.2. The coordination polyhedra around Pb(1) and Pb(2) are joined together by sharing the bases to form PbS_6 strings along the c axis direction. The strings are laterally combined by sharing triangular faces of the polyhedra and form PbS_3 layers parallel to (100). Pb(3) has seven nearest-neighbouring S atoms. The mean Pb(3)–S distance is somewhat shorter than the mean Pb(1), Pb(2)–S distances.

As(1), As(2) and As(4) are each coordinated by three S atoms forming trigonal pyramids with them, and these are joined into strings by sharing S atoms (Fig.3). The mean As–S distances agree

Table 4. *Interatomic distances and bond angles in rathite-I*
 The mean values of the shortest three distances are given for the As(1)—, As(2)—, As(4)—, As(5a)— and As(5b)—S

	Pb(1)	Pb(2)	Pb(3)	As(1)	As(2)	As(3)	As(4)	As(5a)	As(5b)
S(1)	3.012 Å 3.231	3.032 Å 3.254		2.254 Å					
S(2)	2.998 3.212	3.118 3.423			2.234 Å				
S(3)	3.472 3.048			2.304	2.394			2.811 Å	3.299 Å
S(4)		3.419 2.979	2.801 Å	2.237	3.424				
S(5)	3.300	3.084	2.958			2.283 Å		2.762	2.944
S(6)	3.206	3.044	2.875				2.258 Å	2.784	3.277
S(7)	3.263			3.247	2.271	3.439	2.327		
S(8)		3.366	3.392	3.236	2.945	2.684	2.251		
S(9)			2.962			2.737	3.362	2.735	2.233
S(10)		3.143 2.964				2.277	3.158	2.770	2.408
Mean	3.194	3.191	3.014	2.265	2.300		2.279	2.761	2.371
σ		0.008				0.0085		0.010	0.012

Table 4. (Continued.) *S-S distances*
 The asterisk means that the S-S bond is an edge of an As-S₃ pyramid
 $\sigma = 0.011 \text{ \AA}$

	S(1)	S(2)	S(3)	S(4)	S(5)	S(6)	S(7)	S(8)	S(9)	S(10)
S(2)	4.130 Å									
	4.371									
	3.920									
	4.271									
S(3)	3.560	3.430 Å								
	3.486*	3.524*								
S(4)	3.580	3.318	3.455* Å							
	3.398*	3.814								
S(5)	4.069	4.216	3.686	3.449 Å						
S(6)	3.682	4.088	3.709	3.715	4.503 Å					
					4.001					
S(7)	4.255	3.483*	3.368*		3.734	3.419* Å				
S(8)	4.344	3.741		3.560	3.548*	3.454*	3.430* Å			
S(9)			4.296	4.587	3.601*	4.280	3.652	4.204 Å	3.510* Å	
					3.815	4.001	4.001			
S(10)			4.522		3.420*	3.705	3.655	3.585*	3.439*	4.178 Å
						4.011		3.995	3.720*	

Table 4. (Continued)

Bond angles			
S(1)—As(1)—S(3)	99.8°	S(5)—As(3)—S(9)	91.2°
S(1)—As(1)—S(4)	98.3	S(9)—As(3)—S(10)	86.1
S(3)—As(1)—S(4)	99.1	S(6)—As(4)—S(7)	96.4
S(2)—As(2)—S(3)	99.1	S(6)—As(4)—S(8)	100.0
S(2)—As(2)—S(7)	101.3	S(7)—As(4)—S(8)	97.0
S(3)—As(2)—S(7)	92.4	S(9)—As(5 <i>b</i>)—S(9')	98.2
S(5)—As(3)—S(8)	90.8	S(9)—As(5 <i>b</i>)—S(10)	99.3
S(5)—As(3)—S(10)	97.2	S(9')—As(5 <i>b</i>)—S(10)	93.8
S(8)—As(3)—S(10)	92.2	$\sigma = 0.44^\circ$	
As(1)—S(3)—As(2)	107.4	As(4)—S(8)—As(3)	99.5
As(2)—S(7)—As(4)	98.5	As(3)—S(10)—As(5 <i>b</i>)	92.6
		$\sigma = 0.40^\circ$	

well with the normal As—S covalent-bond distance. The S—As—S and As—S—As angles are in a good agreement with the values found in the structure of orpiment (N. MORIMOTO, 1954). As(3) is coordinated

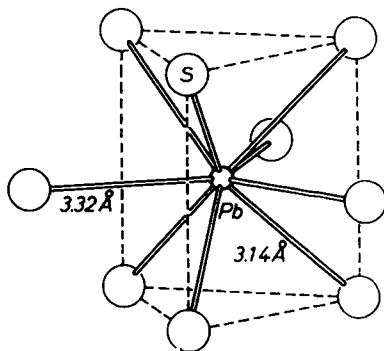


Fig. 2. The configuration of nine S atoms around a Pb atom

by S(5) and S(10) at distances of about 2.28 Å and by S(8) and S(9) at distances of about 2.7 Å. Although the former are in good agreement with the normal As—S covalent-bond distance, the distances of 2.7 Å are too long for As—S covalent bonds. The magnitude and anisotropy of the temperature motion of As(3) are very large in comparison to those of As(1), As(2) and As(4), which have a maximum r.m.s. deviation of 0.27 Å and a minimum deviation of 0.18 Å (Table 5). The As(3), S(8) and S(9) atoms are nearly on a straight line, and As(3) has the largest r.m.s. deviation nearly parallel to this line. Therefore, As(3) seems to form covalent bonds statistically with

Table 5. *The r.m.s. deviations of the atomic positions along the principal axes of the vibration ellipsoids and the direction cosines of the axes referred to the orthogonal axes X // to a*, Y // to b and Z // to c*

	r.m.s.d.	<i>l</i>	<i>m</i>	<i>n</i>
Pb(1)	0.223 Å 0.188 0.212	-- 0.946 -- 0.060	0.285 0.271	0.143 -- 0.959
Pb(2)	0.309 0.183 0.227	-- 0.590 -- 0.050	0.678 0.510	0.438 -- 0.858
Pb(3)	0.243 0.188 0.216	0.332 0.217	0.804 0.444	0.494 -- 0.869
As(1)	0.190 0.156 0.182	0.081 -- 0.442	0.996 0.058	-- 0.023 0.896
As(2)	0.212 0.164 0.176	0.465 -- 0.719	0.514 0.694	0.721 -- 0.030
As(3)	0.271 0.175 0.202	0.603 -- 0.791	0.342 0.153	0.721 0.588
As(4)	0.195 0.162 0.175	-- 0.192 0.317	0.981 0.035	-- 0.028 -- 0.949
As(5a)	0.261 0.215 0.218	0.051 0.280	0.926 0.354	0.383 -- 0.893
As(5b)	0.207 0.115 0.179	0.004 -- 0.938	0.943 0.124	-- 0.333 0.324
S(1)	0.191 0.153 0.170	0.823 -- 0.372	0.464 0.875	0.325 -- 0.310
S(2)	0.178 0.152 0.168	0.641 -- 0.749	0.752 0.570	0.150 0.340
S(3)	0.182 0.138 0.160	-- 0.951 0.042	0.209 0.819	-- 0.221 0.572

Table 5. (Continued)

	r.m.s.d.	<i>l</i>	<i>m</i>	<i>n</i>
S(4)	0.203	-0.746	0.347	-0.569
	0.151	-0.268	0.626	0.733
	0.155			
S(5)	0.176	-0.844	0.492	0.215
	0.145	0.361	0.817	-0.450
	0.167			
S(6)	0.190	0.930	0.185	-0.317
	0.145	-0.279	0.918	-0.283
	0.173			
S(7)	0.183	-0.832	0.542	-0.120
	0.140	0.307	0.258	-0.917
	0.173			
S(8)	0.235	0.963	0.070	0.259
	0.150	0.168	0.597	-0.785
	0.170			
S(9)	0.237	0.938	0.322	-0.136
	0.177	0.132	0.033	0.990
	0.195			
S(10)	0.200	0.082	0.869	-0.489
	0.155	-0.448	0.471	0.761
	0.178			

S(8) and S(9). If As(3) forms a covalent bond with S(8) the As(3)-S₃ trigonal pyramid is joined with the As(4)-S₃ pyramid.

As(5) was statistically distributed over two positions, (*a*) and (*b*), during the course of the refinement. The position (*a*) is surrounded octahedrally by six S atoms, while the position (*b*) has a trigonal pyramidal coordination of three S atoms, which is usual in crystal structures of arsenosulfides. It is suspected that the position (*a*) is not occupied by As but by a different kind of atom, since the distances from the position (*a*) to the surrounding S atoms are too long for As-S distances, and since the sum of the population factors for the positions (*a*) and (*b*), as obtained by the least-squares method, is much larger than one. Actually, a careful chemical analysis of the crystal used, carried out by G. BURRI with a CAMECA x-ray microanalyser, showed that the crystal contains a few weight percent of Ag. If the positions (*a*) are occupied by Ag atoms, the population factor for (*a*) becomes about 0.57 and the sum is nearly equal to one. Therefore,

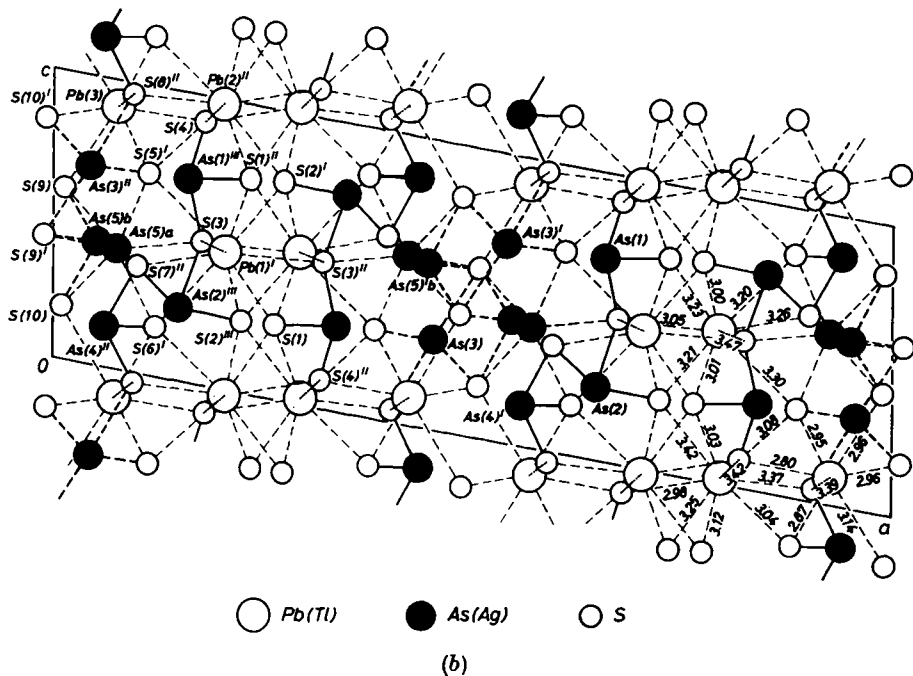
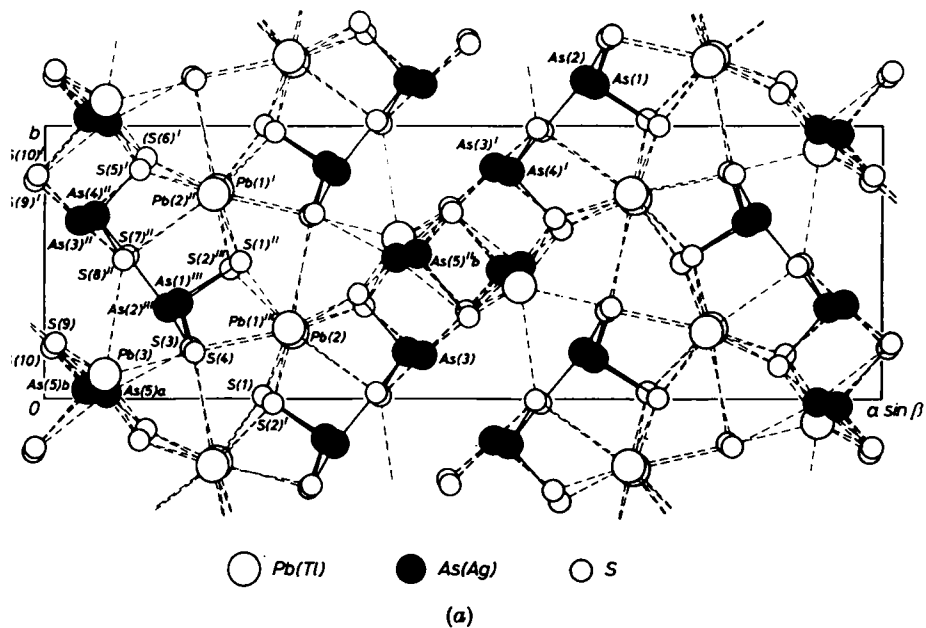


Fig. 3. The projection of the structure (a) along the *c* axis and (b) along the *b* axis

the position (*a*) is probably occupied by Ag instead of As. I is not to be expected from the crystallochemical point of view that the As(5) atoms occupy all the (*b*) positions, since two As(5)—S₃ trigonal pyramids around a center of symmetry should share two S atoms if it occurs.

The projections of the structure along the *b* and *c* axis are shown in Fig. 3(*a*) and (*b*). The structure is composed of two kinds of layers parallel to (100). The first kind are the PbS₃ layers. The second kind have a structure closely related to the PbS structure. It is derived from the PbS structure by dividing it into layers which have the

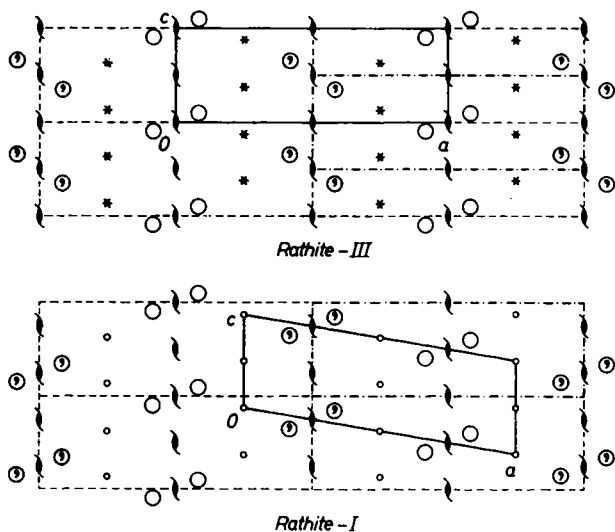


Fig. 4. A comparison of the unit cells and the symmetries of rathite-I and rathite-III. The local centres of symmetry in rathite-III are represented by asteriks. Both of the structures are composed of identical units bounded by the dashed and dotted lines

thickness of $a(\text{PbS})$ and are parallel to (100) of PbS, and by mutually shifting the layers in the [011] direction of PbS by a distance amounting to $a(\text{PbS})/2\sqrt{2}$. The layers in the rathite-I structure correspond to a zone bounded by two planes perpendicular to the [223] direction in the deformed PbS structure. Although each metallic atom in the deformed PbS structure is coordinated by seven S atoms, the As atoms in the rathite-I structure are coordinated by less than seven S atoms, owing to the fairly large deviation from the ideal atomic configuration caused by the difference in chemical character of As and Pb.

The main difference in the structure of rathite-I as compared to that of rathite-III (M.-TH. LE BIHAN, 1962) lies in the relative positions of Pb(3) and As(5). They are made up of the same structural unit, which has the volume of one unit cell (Fig.4). In rathite-III, Pb(3) and As(5) are exchanged in the next structural unit along the a -axis direction whereby the centre of symmetry which exists in the rathite-I structure is destroyed.

The crystal structures of rathite-II (M.-TH. LE BIHAN, 1962), dufrenoyite (W. NOWACKI, F. MARUMO and Y. TAKÉUCHI, 1964), baumhauerite (M.-TH. LE BIHAN, 1962) and scleroclase (W. NOWACKI, Y. IITAKA, H. BÜRKI and V. KUNZ, 1961) are also composed of PbS_3 layers and layers which have the deformed PbS structure. The differences between these structures lie in the chemical composition and in the thickness of the second kind of layers.

Although infinite chains of $As-S_3$ pyramids have been described in the structures of rathite-II, rathite-III and baumhauerite, it is impossible to adapt such chains to the PbS_3 layers, as has been pointed out by Y. IITAKA and W. NOWACKI (1961) and by Y. TAKÉUCHI, S. GHOSE and W. NOWACKI (1965). In the structure of rathite-I the $As-S_3$ pyramids form chains with finite lengths. The length of the chain is not fixed since there are several possibilities for the coordinations around the As(3) and As(5) atoms as explained above. In the most favourable case, the chain can contain six $As-S_3$ pyramids, in the order of $As(1)-As(2)-As(4')-As(3')-As(5'')-As(3)$.

Tl atoms are thought to be situated at the Pb position, replacing Pb atoms. It is not known whether the Tl atoms are in an ordered state or whether they are statistically distributed over several positions. Probable positions are the Pb(2) positions, since Pb(2) has a much larger anisotropic temperature factor than Pb(1) and Pb(3).

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References

- L. G. BERRY (1953), New data on lead sulpharsenides from Binnental, Switzerland. *Amer. Min.* **38**, 330.
- Y. IITAKA and W. NOWACKI (1961), A refinement of the pseudo crystal structure of scleroclase $PbAs_2S_4$. *Acta Crystallogr.* **14**, 1291–1292.
- M.-TH. LE BIHAN (1962), Étude structurale de quelques sulfures de plomb et d'arsenic naturels du gisement de Binn. *Bull. Soc. Franç. Min. Cristallogr.* **85**, 15–47.
- N. MORIMOTO (1954), The crystal structure of orpiment (As_2S_3) refined. *Mineral. Journal (Japan)* **1**, 160–169.
- W. NOWACKI und C. BAHEZBE (1963), Die Bestimmung der chemischen Zusammensetzung einiger Sulfosalze aus dem Lengenbach (Binnatal, Kt. Wallis) mit Hilfe der elektronischen Mikrosonde. *Schweiz. Min. Petr. Mitt.* **43**, 407–411 (Parker-Festschrift).
- W. NOWACKI, Y. IITAKA, H. BÜRKI and V. KUNZ (1961), Structural investigation on sulfosalts from the Lengenbach, Binn Valley (Ct. Wallis). Part 2. *Schweiz. Min. Petr. Mitt.* **41**, 103–116.
- W. NOWACKI, F. MARUMO und Y. TAKÉUCHI (1964), Untersuchungen an Sulfiden aus dem Binnatal (Kt. Wallis, Schweiz). *Schweiz. Min. Petr. Mitt.* **44**, 5–9.
- M. A. PEACOCK and L. G. BERRY (1940), Röntgenographic observations on ore minerals. *Univ. Toronto Studies, Geol. Ser. No.* **44**, p. 63.
- Y. TAKÉUCHI, S. GHOSE and W. NOWACKI (1965), The crystal structure of hutchinsonite, $(Tl, Pb)_2As_5S_9$. *Z. Kristallogr.* **121**, 321–348.