

The crystal structure of dufrenoyite, $\text{Pb}_{16}\text{As}_{16}\text{S}_{40}$ *

By F. MARUMO** and W. NOWACKI

Abteilung für Kristallographie und Strukturlehre, Universität Bern

(Received July 8, 1966)

Auszug

Dufrenoyisit wurde strukturell untersucht. In der Einheitszelle befinden sich zwei Formeleinheiten $\text{Pb}_8\text{As}_8\text{S}_{20}$. Die Raumgruppe ist $C_2^2-P2_1$ und die Gitterkonstanten sind $a = 7,90$, $b = 25,74$, $c = 8,37$ Å, $\beta = 90^\circ 21'$.

Die Grundstruktur ist dieselbe wie bei Rathit-I, Rathit-Ia und Rathit-III; die Unterschiede liegen in der chemischen Zusammensetzung und in kleinen dadurch bedingten Atomverschiebungen. Jedes von vier der acht unabhängigen Pb-Atome ist von neun, jedes der anderen vier Pb-Atome von sieben (6 + 1) S-Atomen umgeben. Das siebente der nächsten S-Atome des letzten Typus ist relativ weit weg gelegen. Alle As-Atome scheinen eine trigonal-pyramidale S-Koordination aufzuweisen. Sieben unabhängige AsS_3 -Pyramiden sind über S-Atome unter Bildung von As_4S_9 - und As_3S_7 -Gruppen miteinander verknüpft. Die achte AsS_3 -Pyramide ist wahrscheinlich isoliert.

Abstract

A structural investigation of dufrenoyite has been carried out. There are two chemical units of $\text{Pb}_8\text{As}_8\text{S}_{20}$ in a unit cell. The space group is $C_2^2-P2_1$, and the unit-cell constants are $a = 7.90$ Å, $b = 25.74$ Å, $c = 8.37$ Å, $\beta = 90^\circ 21'$.

The main structure is the same as that of rathite-I, rathite-Ia and rathite-III, the differences among them lying in the chemical composition and in small shifts of atoms due to the difference in composition. Each of four out of eight independent Pb atoms is surrounded by nine S atoms, the other four Pb atoms each being surrounded by seven (6 + 1) S atoms. The seventh of the nearest S atoms of the latter type is at a fairly distant position. All As atoms seem to have trigonal pyramidal coordinations of S atoms. Seven independent AsS_3 pyramids are joined by sharing S atoms, giving an As_4S_9 and an As_3S_7 group. The remaining AsS_3 pyramid is probably isolated.

* Publication no. 165, Department of Crystallography and Structural Sciences, University of Bern. — Part 28 of papers on sulfides and sulfosalts.

** Present address: University of Tokyo, Institute for Solid State Physics, Azabu-Shinryudo-cho, Minato-ku, Tokyo.

1. Introduction

The structure determination of dufrenoyite was undertaken to get a systematic knowledge on the crystal chemistry of lead arsenosulfide minerals, especially of the rathite group, to which rathite-I, rathite-III, dufrenoyite (NOWACKI *et al.*, 1964) and rathite-Ia (MARUMO and NOWACKI, 1966) belong. The detailed structure of rathite-I was reported by MARUMO and NOWACKI (1966) and structure determinations of rathite-III and rathite-Ia were published by LEBIHAN (1962). These structures are all composed essentially of two kinds of layers. One kind of layers consists of Pb atoms surrounded by nine S atoms, and the other kind of layers have a deformed galena-type structure. The differences between these structures lie in the chemical composition of the latter kind of layers.

There are several arsenosulfide minerals which have structures similar to the rathite-group minerals. Their structures are composed of layers of the same kind as in the rathite group minerals, but the thickness of the second kind of layers is not always the same as in the rathite group. Scleroclase, baumhauerite, rathite-II and probably jordanite are examples of this kind of minerals.

2. Experimental

A crystal from Lengenbach (B 348, labeled as „marrite“), Bin-natal, Switzerland was used in this investigation. Four pieces were cut off from the crystal for x-ray intensity measurement, chemical analysis, x-ray microanalysis and powder photography. The unit-cell dimensions measured by KUNZ (NOWACKI, ITAKA, BÜRKI and KUNZ, 1961) with the same material were adopted throughout this work (Table 1). The possible space groups obtained from x-ray diagrams are $C_{2h}^2-P2_1/m$ and $C_2^2-P2_1$. Since the crystal is strongly piezoelectric, the true space group of dufrenoyite is $C_2^2-P2_1$.

An ordinary chemical analysis was carried out by Fa. Fresenius (Wiesbaden) and an x-ray microanalysis by NOWACKI and BAHEZRE

Table 1. *A comparison of dufrenoyite and the related minerals*

Mineral	Formula	a_0	b_0	c_0	β	Space group
dufrenoyite	$Pb_{16}As_{16}S_{40}$	7.90	25.74	8.37	$90^\circ 21'$	$P2_1$
rathite-Ia	$Pb_{14}As_{18}S_{40}$	7.91	25.80	8.43	90°	$P2_1$
rathite-I	$(Pb,Tl)_{12}As_{16}(As,Ag)_4S_{40}$	25.16	7.94	8.47	$100^\circ 28'$	$P2_1/a$ ($P\bar{1}$)
rathite-III	$Pb_{12}As_{20}S_{40}$	24.52	7.91	8.43	90°	$P2_1$

Table 2. *Chemical analyses of dufrenoyite*

	Pb	As	S	Total
Ordinary chemical analysis	55.72 ^o / _o	19.94 ^o / _o	23.72 ^o / _o	99.38 ^o / _o
X-ray microanalysis	54.8	20.6	26.7	102.1
Ideal formula Pb ₁₆ As ₁₆ S ₄₀	57.20	20.68	22.12	100.00

(1963). The results of the two analyses are in good agreement (see Table 2). If the density of the crystal is assumed to be 5.53 g/cm³ (DANA's System of Mineralogy, Vol. I, 1944) the values obtained by the chemical analysis give the empirical formula Pb_{15.33}As_{15.18}S_{42.18}. However, it is certain that dufrenoyite is a member of the rathite-group minerals from its similarity to rathite-I and rathite-Ia in unit-cell dimensions and *hk0* x-ray diffraction patterns. Since in the rathite-group minerals the number of S atoms in the unit cell is 40 and the total number of metallic atoms is 32, the ideal empirical formula of dufrenoyite should be Pb₁₆As₁₆S₄₀. The experimental formula becomes Pb_{14.54}As_{14.40}S₄₀, if we assume the number of S atoms in the unit cell to be 40.

As can be seen in Table 1, dufrenoyite and rathite-Ia have the same symmetry and identical unit-cell dimensions within experimental error. The chemical composition of these two minerals is also very similar. However, there is a fairly large difference between the powder data for dufrenoyite given by BERRY and THOMPSON (1962) and that for rathite-Ia given by LEBIHAN (1962). A powder photograph was, therefore, taken with FeK α radiation for identification of the material. The spacings and the relative intensities of the main lines are shown in Table 3, together with those of dufrenoyite and rathite-Ia. The crystal used was unequivocally identified as dufrenoyite.

In order to simplify the absorption correction, the piece used for x-ray intensity measurement was ground to a sphere with a diameter of about 0.15 mm. The absorption-correction factor for the sphere ranged between 4.98 at $\theta = 0^\circ$ and 19.2 at $\theta = 90^\circ$ for

Table 3. *Powder data of the crystal studied, dufrenoyite (BERRY, 1962) and rathite-Ia (LEBIHAN, 1962)*

Crystal		Dufrenoyite		Rathite-Ia	
I	d	I	d	I	d
		1	7.50 Å		
		2	6.81		
		1	5.99		
		2	4.98		
		2	4.27		
		2	4.11		
4	4.10 Å	1	3.93		
9	3.73	10	3.74		
6	3.53	5	3.56		
5	3.38	7	3.40		
6	3.17	6	3.21		
4	3.10	2	3.12	5	3.140 Å
10	2.98	9	3.00	10	2.918
6	2.88	5	2.90		
5	2.78	4	2.80		
7	2.71	8	2.70		
2	2.58	1	2.58		
3	2.43	1	2.44		
9	2.34	6	2.36	6	2.253
3	2.30				
3	2.21	6	2.23	5	2.166
		2	2.16		
5	2.08	3	2.09	7	2.049
5	2.03	3	2.03		
				6	1.570
				5	1.537
				3	1.083

CuK α radiation. Integrated Weissenberg photographs were taken around the a and the c axis. The relative intensities of the $0kl$ and $hk0$ reflections were measured with a microdensitometer and Lorentz-polarization and absorption factors were applied.

3. Structure determination

Dufrenoyite is quite similar to rathite-Ia (see Table 1). They have identical unit-cell dimensions within experimental error, the same symmetry, and similar chemical composition. In addition, dufrenoyite gives for the $hk0$ reflections, relative intensities almost identical to those of rathite-Ia, indicating that their structures have identical projections along the c axes. Since LEBIHAN (1962) gives the intensity data of rathite-Ia only for the $hk0$ reflections, we cannot make a further search for the structural similarity using three-dimensional intensity data. However, it is reasonable to assume from the above mentioned similarities that dufrenoyite and rathite-Ia have essentially the same structure. The difference lies in the ratio of Pb to As atoms. A part of the As atoms in rathite-Ia are apparently replaced by Pb atoms in dufrenoyite.

The structure determination was, therefore, carried out by successive refinements of the a - and the c -axis projections with the aid of difference Fourier syntheses, starting from the rathite-Ia structure given by LEBIHAN. In the first difference Fourier projections, it was observed that two of the nine independent As atoms are accompanied by salient peaks corresponding to about one third of a Pb atom, while these As atoms themselves are in negative holes corresponding to about minus one third of an As atom. This indicates that part of the As atoms in rathite-Ia are replaced by Pb atoms in dufrenoyite and explains well the difference in chemical composition of the two crystals. Five cycles of refinement were carried out assuming the partial replacement by Pb atoms. The discrepancy factor, $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, decreased from the initial value of 0.49 for $F(0kl)$ and 0.26 for $F(hk0)$ to 0.23 and 0.14, respectively. During the course of the refinement, some of the Pb atoms were recognized to have fewer electrons than a normal Pb atom. Fractional populations were assumed for such Pb atoms.

Although the total number of Pb atoms in the structure thus obtained coincides well with the number of Pb atoms in a unit cell as determined by chemical analyses, the assumption of the statistical distribution of Pb atoms was discarded for the following reasons. The popula-

tions of two Pb atoms which were supposed to be statistically replacing As atoms increased during the course of the refinement and the sum of the populations of the Pb atoms approached one. Since the structure is nearly centrosymmetric and the two As atoms are related by a pseudo-centre of symmetry, this kind of apparent partial replacement would be brought about in a Fourier map phased for the structure having

Table 4. *The atomic coordinates of dufrenoyite*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	σ_x	σ_y	σ_z	σ_B
Pb(1)	0.017	0.001	0.871	3	0.003	0.0007	0.002	0.33
Pb(2)	0.978	0.4975	0.636	3	0.003	0.0007	0.002	0.33
Pb(3)	0.518	0.096	0.868	3	0.003	0.0007	0.002	0.33
Pb(4)	0.522	0.096	0.368	3	0.003	0.0007	0.002	0.33
Pb(5)	0.202	0.226	0.876	3	0.003	0.0007	0.002	0.33
Pb(6)	0.308	0.3725	0.135	3	0.003	0.0007	0.002	0.34
Pb(7)	0.660	0.256	0.639	3	0.003	0.0007	0.002	0.33
Pb(8)	0.187	0.2285	0.395	3	0.003	0.0007	0.002	0.32
As(1)	0.954	0.139	0.199	3	0.008	0.0016	0.006	0.85
As(2)	0.950	0.136	0.609	3	0.008	0.0016	0.006	0.86
As(3)	0.552	0.4595	0.884	3	0.008	0.0016	0.006	0.85
As(4)	0.548	0.451	0.433	3	0.008	0.0016	0.006	0.83
As(5)	0.883	0.363	0.373	3	0.007	0.0017	0.006	0.90
As(6)	0.871	0.351	0.947	3	0.007	0.0016	0.006	0.87
As(7)	0.258	0.351	0.632	3	0.008	0.0018	0.006	0.85
As(8)	0.625	0.233	0.104	3	0.008	0.0017	0.006	0.82
S(1)	0.263	0.031	0.123	3	0.017	0.004	0.014	1.9
S(2)	0.786	0.073	0.115	3	0.017	0.004	0.013	1.9
S(3)	0.110	0.113	0.830	1	0.012	0.002	0.009	1.1
S(4)	0.409	0.181	0.119	1	0.011	0.002	0.009	1.1
S(5)	0.222	0.691	0.082	1	0.011	0.002	0.010	1.0
S(6)	0.428	0.315	0.423	4	0.021	0.004	0.018	2.3
S(7)	0.426	0.309	0.839	2	0.014	0.003	0.012	1.4
S(8)	0.047	0.296	0.646	3	0.017	0.004	0.013	1.8
S(9)	0.042	0.299	0.115	3	0.017	0.004	0.013	1.8
S(10)	0.080	0.415	0.909	3	0.017	0.003	0.014	1.8
S(11)	0.375	0.487	0.061	2	0.014	0.003	0.012	1.3
S(12)	0.740	0.405	0.183	4	0.022	0.005	0.017	2.3
S(13)	0.738	0.399	0.600	1	0.011	0.002	0.009	1.1
S(14)	0.274	0.020	0.614	4	0.022	0.005	0.015	2.3
S(15)	0.783	0.068	0.620	1	0.011	0.002	0.009	1.1
S(16)	0.124	0.104	0.435	4	0.021	0.004	0.017	2.4
S(17)	0.407	0.181	0.623	2	0.013	0.003	0.011	1.4
S(18)	0.774	0.201	0.302	4	0.023	0.005	0.016	2.2
S(19)	0.106	0.417	0.424	3	0.017	0.004	0.014	1.8
S(20)	0.392	0.481	0.669	2	0.013	0.003	0.011	1.4

Table 5. Observed and calculated structure amplitudes of *dufrenoyite*

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
0 4 0	140	141	0 19 3	70	107	0 26 6	28	32	1 21 0	194	193	4 23 0	149	145
6	202	200	20	98	110	27	16	19	22	62	65	24	50	96
8	886	872	21	71	91	0 0 7	44	3	23	44	60	25	68	90
10	237	241	22	137	138	1	44	36	24	69	100	26	18	11
12	180	199	23	74	86	2	34	44	25	61	69	27	0	15
14	404	360	24	43	28	3	65	80	26	138	165	28	29	39
16	202	200	25	42	40	4	55	58	27	127	117	29	63	80
18	44	13	26	66	55	5	66	30	28	114	117	30	64	115
20	164	164	27	31	53	6	77	58	29	45	31	5 0 0	49	78
22	351	356	28	38	35	7	112	99	30	36	63	1	58	11
24	115	106	29	56	50	8	46	62	31	26	32	2	151	134
26	179	192	30	62	66	9	23	12	32	29	34	3	471	444
28	39	19	31	25	25	10	61	81	2 0 0	263	210	4	592	533
30	140	144	0 0 4	1204	1176	11	0	7	1	235	243	5	159	156
32	83	106	1	223	233	12	122	119	2	746	634	6	172	205
0 0 1	0	23	2	94	94	13	47	10	3	347	295	7	92	103
1	53	39	3	25	27	14	176	144	4	201	171	8	49	39
2	65	70	4	106	173	15	133	136	5	608	559	9	38	83
3	162	153	5	25	53	16	37	19	6	837	715	10	167	164
4	68	71	6	158	202	17	40	34	7	411	363	11	116	134
5	232	235	7	79	20	18	69	74	8	54	58	12	344	323
6	197	188	8	537	529	19	43	39	9	391	359	13	56	38
7	62	101	9	166	107	20	73	80	10	477	419	14	143	170
8	50	52	10	218	186	21	0	22	11	142	125	15	46	36
9	83	59	11	66	77	22	73	71	12	318	285	16	83	116
10	83	96	12	154	167	23	15	9	13	257	227	17	167	156
11	69	66	13	66	50	24	19	21	14	76	47	18	237	232
12	128	103	14	299	294	0 0 8	326	335	15	66	50	19	45	75
13	181	196	15	42	12	1	109	120	16	66	68	20	116	111
14	117	144	16	160	155	2	48	63	17	279	260	21	50	69
15	164	140	17	24	15	3	45	90	18	126	148	22	73	104
16	63	66	18	41	54	4	58	92	19	0	29	23	103	132
17	59	54	19	46	47	5	42	79	20	354	333	24	40	58
18	25	24	20	55	68	6	69	108	21	0	17	25	72	64
19	43	26	21	37	43	7	98	62	22	163	191	26	116	147
20	77	81	22	264	247	8	183	194	23	0	16	27	38	44
21	142	158	23	52	32	9	57	62	24	170	171	28	41	54
22	74	80	24	94	85	10	79	80	25	55	60	6 0 0	181	162
23	131	106	25	42	45	11	32	27	26	52	53	1	53	72
24	38	25	26	128	130	12	64	84	27	50	64	2	43	92
25	53	47	27	27	30	13	32	25	28	125	161	3	37	34
26	68	71	28	25	19	14	131	148	29	42	67	4	148	161
27	38	8	29	20	14	15	35	26	30	31	48	5	160	130
28	34	32	30	112	129	16	67	51	31	57	85	6	85	113
29	60	82	0 0 5	47	56	17	27	31	32	21	47	7	64	34
30	38	37	1	64	102	18	28	41	3 0 0	103	4	8	266	289
31	44	47	2	56	54	19	29	22	1	187	193	9	213	233
32	19	36	3	166	183	20	17	15	2	358	324	10	59	75
0 0 2	49	37	4	144	116	21	25	24	3	70	64	11	118	116
1	442	421	5	273	273	0 0 9	0	1	4	255	277	12	138	129
2	55	89	6	70	91	1	54	70	5	54	37	13	142	147
3	106	111	7	59	85	2	30	26	6	447	435	14	144	134
4	56	59	8	55	93	3	89	91	7	289	291	15	65	113
5	246	222	9	108	93	4	111	69	8	637	598	16	57	36
6	0	0	10	66	113	5	82	98	9	487	451	17	200	210
7	142	137	11	69	86	6	16	22	10	153	165	18	137	154
8	133	112	12	55	43	7	0	16	11	82	67	19	42	37
9	1029	904	13	84	115	8	29	23	12	126	121	20	39	65
10	75	76	14	48	50	9	52	62	13	171	164	21	34	50
11	310	257	15	59	54	10	20	17	14	250	261	22	49	78
12	0	35	16	0	36	11	60	77	15	239	225	23	102	139
13	326	311	17	46	16	12	24	7	16	449	452	24	79	83
14	62	28	18	0	31	13	27	31	17	150	149	25	23	11
15	195	183	19	37	13	14	27	38	18	56	70	26	20	23
16	79	60	20	55	39	15	21	29	19	101	91	7 0 0	64	34
17	504	451	21	87	107	16	20	9	20	51	65	1	49	23
18	89	83	22	37	55	17	17	19	21	131	100	2	254	239
19	215	205	23	78	62	0 0 10	24	27	22	72	96	3	278	243
20	0	18	24	51	54	1	36	69	23	108	87	4	35	23
21	197	221	25	48	42	2	62	55	24	183	213	5	288	269
22	46	26	26	39	43	3	34	6	25	62	91	6	250	239
23	214	201	27	23	22	4	33	66	26	37	40	7	73	44
24	40	40	28	30	31	5	30	36	27	66	78	8	69	82
25	101	90	29	22	54	6	24	42	28	55	89	9	38	42
26	37	32	0 0 6	0	7	7	37	49	29	34	55	10	59	58
27	97	88	1	206	245	8	33	52	30	65	67	11	40	23
28	39	21	2	46	48	9	72	106	31	31	42	12	70	64
29	31	55	3	49	62	10	67	65	4 0 0	311	306	13	202	226
30	26	29	4	74	123	11	24	29	1	137	153	14	40	27
31	135	143	5	95	94	1 0 0	0	25	2	382	363	15	38	18
32	20	19	6	58	69	1	153	144	3	570	514	16	56	96
0 0 3	0	16	7	112	122	2	148	141	4	90	96	17	120	122
1	47	91	8	104	103	3	138	130	5	107	92	18	32	43
2	73	82	9	345	350	4	267	234	6	49	58	19	62	89
3	47	43	10	115	117	5	250	237	7	85	99	20	72	55
4	126	166	11	89	81	6	554	492	8	69	111	21	42	60
5	47	55	12	50	79	7	181	175	9	131	150	22	35	30
6	73	41	13	200	220	8	455	412	10	330	316	23	16	13
7	94	130	14	72	20	9	228	218	11	473	455	8 0 0	55	9
8	56	56	15	133	133	10	337	279	12	138	100	1	105	149
9	0	42	16	111	55	11	283	265	13	49	27	2	127	135
10	106	129	17	211	202	12	247	247	14	170	171	3	57	81
11	56	56	18	105	112	13	225	205	15	48	43	4	45	79
12	257	202	19	150	105	14	594	580	16	114	112	5	53	53
13	106	121	20	34	63	15	346	333	17	36	25	6	37	53
14	283	195	21	148	177	16	215	203	18	109	105	7	36	9
15	233	233	22	41	45	17	133	150	19	146	155	8	39	43
16	55	11	23	115	140	18	233	231	20	171	178	9	46	58
17	24	21	24	47	57	19	246	242	21	62	87	10	96	108
18	98	76	25	32	29	20	42	9	22	141	140	11	194	213

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
8 12 0	120	161	8 18 0	27	23	9 3 0	69	86	9 9 0	28	14	10 0 0	27	50
13	66	84	19	62	82	4	45	51	10	57	40	1	36	68
14	47	77	20	51	101	5	0	28	11	27	37	2	0	32
15	40	55	9 0 0	106	44	6	45	17	12	45	35	3	47	63
16	44	42	1	145	162	7	124	153	13	18	36			
17	22	36	2	81	40	8	53	22	14	20	22			

no replacement, even if one of the As atoms is fully replaced by a Pb atom. Also, anomalous dispersion was not taken into account, even though the dispersion effect is fairly large for a Pb atom. This might cause a decrease in the apparent number of electrons for the Pb atoms in a Fourier map. And the final reason is that electron deficiency is often caused by experimental errors, especially in substances which have large absorption coefficient. A further refinement of the structure was, therefore, also performed by the difference Fourier method without the assumption of a statistical distribution of atoms. For the two positions where As and Pb atoms were statistically distributed in the former calculation, the one which had the higher Pb atom population was chosen as a Pb atom and the other as an As atom. The final R value is 0.168 for $F(0kl)$ and 0.140 for $F(hk0)$.

The final atomic parameters are given in Table 4 and the calculated structure amplitudes in Table 5, together with the observed structure amplitudes for comparison.

4. Discussion

The interatomic distances are given in Table 6 and the bond angles in Table 7. The Pb—S distances range between 2.80 Å and 3.50 Å, just as in the structure of rathite-I. Each of four of the eight independent Pb atoms is surrounded by nine S atoms, the other four Pb atoms each being surrounded by six S atoms. For groups of the latter type there are seventh S atoms at distances of about 3.6 to 3.8 Å. The mean Pb—S distance is shorter for groups of the latter type than for those which have nine neighbouring S atoms. The same tendency is also observed in the rathite-I structure. All As atoms seem to have trigonal-pyramidal coordinations of S atoms as is usual in arsenosulfide crystals. Most of the As—S distances obtained are, however, somewhat longer than the normal covalent As—S bond length. This may be caused by the inaccuracy of the two-dimensional study and also by the large difference in atomic number between Pb and S. Since As(7) has the fourth-nearest atom at a fairly short distance, 2.68 Å, we cannot say anything conclusive about the coordination around this atom.

Table 6. *Interatomic distances*

	S(1)	S(2)	S(3)	S(4)	S(5)	S(6)	S(7)	S(8)	S(9)	S(10)
Pb(1)	2.96	3.31	3.00							2.93
Pb(2)	2.91	3.39								3.14
Pb(3)	3.39	3.02	3.45	3.09	3.30					
Pb(4)	3.35	3.05		3.09						
Pb(5)			3.03	2.83	(3.68)		2.86	2.86	2.99	
Pb(6)						2.82	3.02		2.93	2.83
Pb(7)					2.93	2.99	2.87	3.40		
Pb(8)				3.12		3.01		2.89	3.10	
As(1)	3.85	2.30	3.27		2.98					
As(2)			2.27		3.18					
As(3)	2.41									
As(4)						3.64				
As(5)								3.08	2.95	
As(6)							3.97	3.14	2.36	2.42
As(7)						2.37	2.41	2.27		3.12
As(8)				2.25	2.23	3.68	3.31		3.88	

The *a*-axis and the *c*-axis projections of the structure are shown in Fig.1 and Fig.2. The structure is composed of the same kinds of layers as in rathite-I, which are parallel to the plane determined by the 8.4 Å and 7.9 Å axes. The first kind of layers are PbS₃ layers and consist of the coordination polyhedra around those Pb atoms which are surrounded by nine S atoms. The second kind of layers have a deformed PbS-type structure containing Pb, As and S atoms. As-S₃ pyramids, except As(7)-S₃, are joined by sharing S atoms, giving two kinds of chains. One is four-membered: As(3)—As(4)—As(5)—As(6), and the other is three-membered: As(2)—As(1)—As(8). The As(7)-S₃ pyramid is isolated, assuming no bond between As(7) and S(19). The manner of linking is quite similar to that observed in the rathite-I structure, although the lengths of the strings are shorter than in rathite-I, owing to the high Pb content.

The differences among the structures of dufrenoyite, rathite-I, rathite-III and rathite-Ia lie in the metallic atom compositions of the second kind of layers. The composition is Pb₄As₈ in dufrenoyite, Pb₂AgAs₉ in rathite-I, Pb₂As₁₀ in rathite-III and Pb₃As₉ in rathite-Ia. Since dufrenoyite and rathite-Ia have the same symmetry and the same unit-cell dimensions, they might be considered as the same kind of mineral. The discrepancies between the powder data of dufrenoyite

(in Å) in dufrenoyite

	S (11)	S (12)	S (13)	S (14)	S (15)	S (16)	S (17)	S (18)	S (19)	S (20)	Mean	σ
Pb (1)	3.35	3.23		3.01	3.27				3.34		3.16	
Pb (2)			3.25	2.94	3.38	2.92			2.88	3.50	3.15	
Pb (3)	3.00			3.46	3.06		3.06				3.20	
Pb (4)				3.46	3.03	3.38	3.13	3.47		3.06	3.22	0.06
Pb (5)							2.89				2.91	0.19
Pb (6)	3.06	(3.73)							3.07		2.96	
Pb (7)			(3.75)				2.87	3.17			3.04	
Pb (8)						3.26	2.84	(3.60)			3.04	
As (1)						2.51		2.34			2.38	
As (2)					2.24	2.17	4.00	3.29			2.23	
As (3)	2.16	3.16	3.15							2.23	2.27	
As (4)	3.40	2.82	2.46	2.35					3.80	2.41	2.41	0.09
As (5)		2.20	2.36						2.36		2.31	0.25
As (6)		2.58	3.20								2.45	
As (7)									2.68	3.54	2.35	
As (8)								2.16			2.21	

and rathite-Ia were probably caused by the difference in the conditions of recording the powder patterns.

There are dufrenoyite crystals (L3207-64) which give diffuse streaks along the b^* direction. This means that the periodicity along the b axis is imperfect in these crystals. There are several possibilities to explain these diffuse streaks. (1) The structure is centrosymmetric if we neglect the difference between Pb and As atoms in the second kind of layers and small shifts of atoms. Therefore it might be possible

Table 7. Bond angles in dufrenoyite

S(2)—As(1)—S(16)	107.0°	S(12)—As(5)—S(13)	92.6°
S(2)—As(1)—S(18)	102.1	S(12)—As(5)—S(19)	104.7
S(16)—As(1)—S(18)	110.5	S(13)—As(5)—S(19)	92.8
S(3)—As(2)—S(15)	97.6	S(9)—As(6)—S(10)	91.1
S(3)—As(2)—S(16)	89.6	S(9)—As(6)—S(12)	99.1
S(15)—As(2)—S(16)	98.6	S(10)—As(6)—S(12)	91.9
S(1)—As(3)—S(11)	102.0	S(6)—As(7)—S(7)	87.0
S(1)—As(3)—S(20)	100.2	S(6)—As(7)—S(8)	105.1
S(11)—As(3)—S(20)	90.0	S(7)—As(7)—S(8)	98.0
S(13)—As(4)—S(14)	95.0	S(4)—As(8)—S(5)	102.2
S(13)—As(4)—S(20)	96.4	S(4)—As(8)—S(18)	101.3
S(14)—As(4)—S(20)	103.1	S(5)—As(8)—S(18)	87.8

to insert an enantiomorphous layer in place of some layer without a large change of the structure. Then we would get a one-dimensionally disordered structure. (2) It might be possible to put the second kind of layers of dufrenoyseite and those of rathite-I into the structure

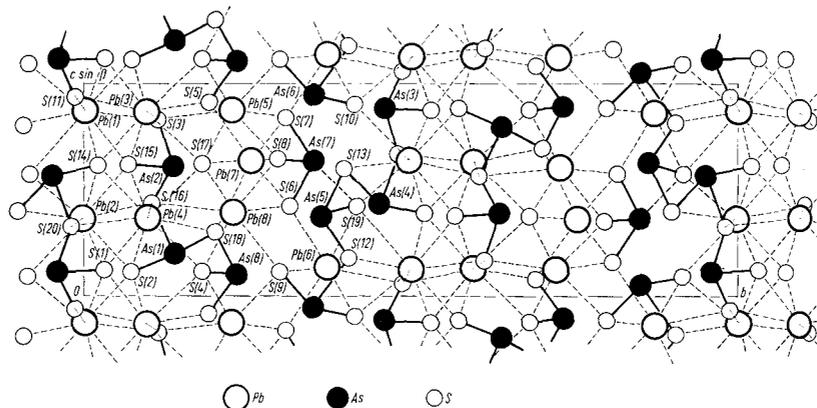


Fig. 1. The α -axis projection of the crystal structure of dufrenoyseite

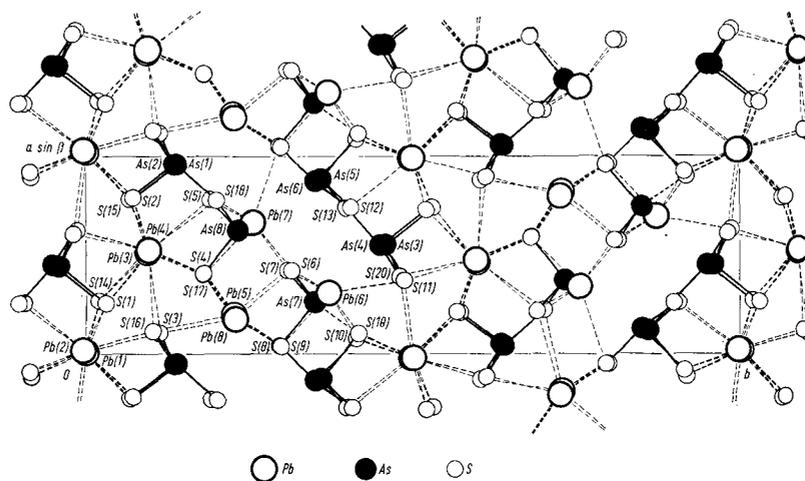


Fig. 2. The c -axis projection of the crystal structure of dufrenoyseite

at random, since the difference between the dufrenoyseite layer and the rathite-I layer is small. In this case, the chemical composition should be a little bit different from the ideal dufrenoyseite. It was found that the crystals are composed of microscopic blocks. According to an x-ray microprobe analysis (G. BURRI, analysis no. 124), the larger blocks

contain about 4% of Tl (Pb 52, Tl 4, As 23, S 21, Σ 100%), while the smaller blocks does not contain Tl (Pb 55, Tl —, As 23, S 21.5, Σ 99.5%). If the Tl atom can replace the Ag atoms in rathite-I, we can consider the Tl bearing block as a mixture of rathite-I and dufrenoyite as far as the chemical composition is concerned. Therefore, the second possibility is more probable for the explanation of the diffuse streaks.

Acknowledgments

We thank Prof. Dr. E. NICKEL (Fribourg) for putting at our disposal the B 348-crystal, Dr. N. D. JONES for his help in the English version of this paper and helpful criticism and Mr. G. BURRI for the electron-microprobe analysis. We are indebted to Schweizerische Nationalfonds (Project No. 2337), Kommission zur Förderung der wissenschaftlichen Forschung (Project No. 384) and Stiftung Entwicklungsfonds Seltene Metalle for financial support.

References

- L. G. BERRY and R. M. THOMPSON (1962), X-ray powder data for ore minerals: The Peacock Atlas. Geol. Soc. America, Mem. 85, New York.
- M.-TH. LEBIHAN (1962), Étude structurale de quelques sulfures de plomb et d'arsenic naturels du gisement de Binn. Bull. Soc. Franç. Min. Cristallogr. 85, 15–47.
- F. MARUMO and W. NOWACKI (1966), The crystal structure of rathite-I. Z. Kristallogr. 122, 433–456.
- W. NOWACKI und C. BAHEZRE (1963), Die Bestimmung der chemischen Zusammensetzung einiger Sulfosalze aus dem Lengenbach (Binnatal, Kt. Wallis) mit Hilfe der elektronischen Mikrosonde. Schweiz. Petr. Mitt. 43, 407–411.
- 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 and Y. TAKÉUCHI (1964), Untersuchungen an Sulfiden aus dem Binnatal (Kt. Wallis, Schweiz). Schweiz. Min. Petr. Mitt. 44, 5–9.