A Redetermination of the Crystal Structure of Galenobismutite, PbBi₂S₄*

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The crystal structure of galenobismutite (PbBi₂S₄) has been redetermined in order to establish the structural relationship between this sulfosalt and berthierite (FeSb₂S₄).
The lattice constants and the space group are:

$$a = 11.79 \pm 0.007, \quad b = 14.59 \pm 0.008, \quad c = 4.10 \pm 0.005 \text{ Å}, \quad D_{2h}^{16}\text{-}Pnam \,.$$

The structure was refined by Fourier and three-dimensional least-squares methods based on newly determined intensity data. Bismuth and lead atoms could be distinguished by comparing their coordination. The structure contains two BiS₂-chains which are bound together to form composite chains Bi₄S₈. The present interpretation of the structure, in contrast of the previous work, shows that it is more similar to that of berthierite, but is not isostructural with it.

Introduction

The crystal structure of galenobismutite, PbBi₂S₄, was proposed by Wickman (1951), who based his conclusions on X-ray data obtained with Fe $K\alpha$-radiation and only the heavy lead and bismuth atoms could be located directly. The sulfur atoms were placed by space considerations assuming a similar arrangement to that found in stibnite Sb₂S₃ and bismuthinite Bi₂S₃. Recent structure determinations of berthierite, FeSb₂S₄ (Buerger & Hahn, 1955) and scleroclase, PbAs₂S₄ (Nowacki, Iitaka *et al.*, 1961) indicated that the arrangement of antimony (or arsenic) and sulfur atoms in these crystals is not quite the same as in stibnite or bismuthinite. Moreover, the similar cell constants and the identical space group suggest a very close structural relationship between galenobismutite and berthierite. We have initiated the refinement of the crystal structure of galenobismutite in order to establish the structural relationships among these sulfosalt minerals.

Experimental

The specimens of galenobismutite were kindly presented by Prof. F. E. Wickman. The material was from Nordmark Mines, Värmland, Sweden, from the collection at the Naturhistoriska Riksmuseet, Stockholm, with catalog No. g 4030. They form indistinctly columnar aggregates elongated along the the *c*-axis and showing poor longitudinal cleavage.

Very thin acicular crystals about 0·02 mm. thick were chosen for the *c*-axis X-ray specimens. A small spherical crystal of diameter 0·11 mm. was ground from the fragment by Bond's method (Bond, 1951) and was used for the *a*-axis specimen.

Table 1. *Cell constants of galenobismutite*

	Berry (1940) (Å)	Wickman (1951) (Å)	Present determination (Å)
a	11·72 ± 0·03	11·65 ± 0·05	11·79 ± 0·007
b	14·52 ± 0·03	14·49 ± 0·03	14·59 ± 0·008
c	4·07 ± 0·02	4·08 ± 0·03	4·10 ± 0·005

The lattice constants were calculated by the least-squares method using 16 $hk0$ and 14 $0kl$ reflections recorded on zero-layer Weissenberg photographs. These values are listed in Table 1 together with the published data of Berry (1940) and Wickman (1951).

The systematic absences confirmed the space group to be D_{2h}^{16}-$Pnam$ (or C_{2v}^{9}-$Pna2$) as reported by Berry (1940) and Wickman (1951). The unit cell contains four formula units of PbBi₂S₄. The intensity data were obtained from equi-inclination integrated Weissenberg photographs taken with Cu $K\alpha$-radiation.

These were: *c*-axis, using the acicular crystal (0·02 mm. thick), zero-layer with Ni-filter, 1st, 2nd, 3rd layers no filter; *a*-axis, using the spherical crystal (0·11 mm. diameter), zero-layer no filter. The multiple-film technique was used and the intensities were recorded with a photometer (Joyce–Loebl double beam automatic recording Microdensitometer, Mark III). Errors caused by the variation of the spot-size in upper-layer Weissenberg photographs, and by the variation of the absorption effect due to the irregular shape of the crystal specimen, were minimized by using the mean intensity values for the two sets of equivalent reflections on either side of the Weissenberg photograph.

The intensities were corrected for Lorentz and polarization factors and for absorption. The acicular *c*-axis specimen was regarded as a cylinder with a μR-value of 1·80, and the *a*-axis specimen as a sphere with a μR of 8·8. The linear absorption coefficient

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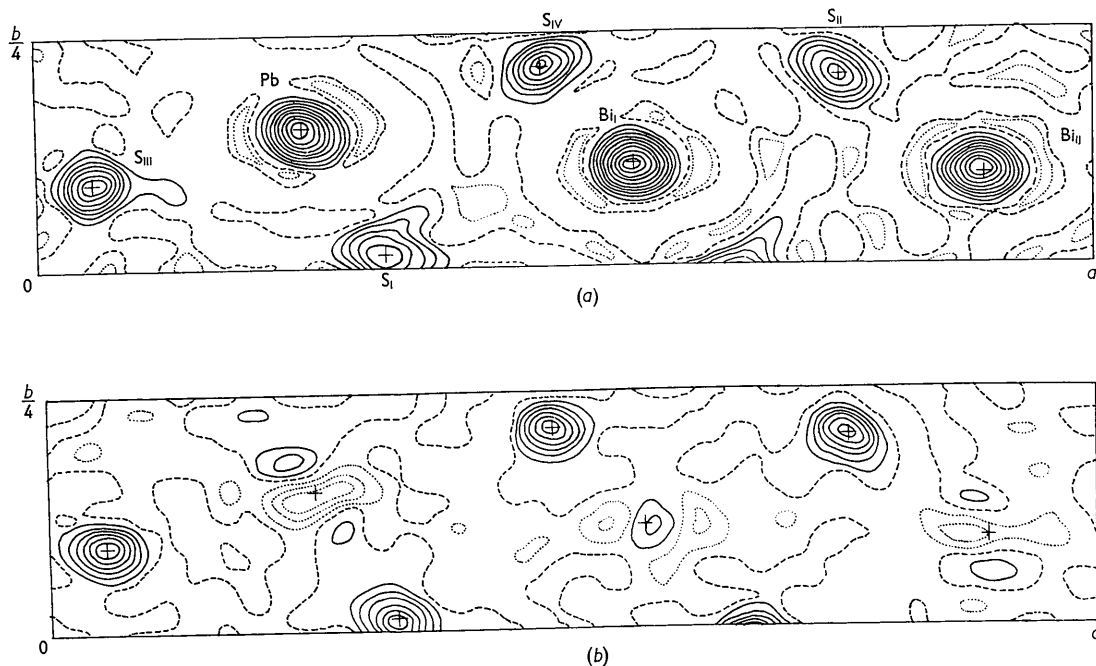
Fig. 1. (a) Galenobismutite: Fourier projection along the c-axis. Contours at intervals of 20 e.Å^{-2} for lead and bismuth atoms, and 5 e.Å^{-2} for sulfur atoms. Broken lines indicate 0 e.Å^{-2} and dotted lines negative contours of 5 e.Å^{-2} interval. (b) Galenobismutite: Difference Fourier projection along the c-axis. Lead and bismuth atoms are subtracted. Contours at intervals of 5 e.Å^{-2}. Broken lines indicate 0 e.Å^{-2} and dotted lines negative contours.

(μ) for Cu $K\alpha$-radiation was calculated to be 1580 cm.$^{-1}$, and the absorption factors were taken from the *International Tables of X-ray Crystallography*, Vol. II (1959).

The relative $|F_o|^2$-values were then placed on an absolute scale by Wilson's method and at the same time an average temperature factor of 1·38 Å^2 was obtained.

Refinement of the structure

Preliminary $hk0$ structure-factor calculations based on Wickman's model gave an R-factor of 36% using our observed structure factors. This factor became 40% omitting the contribution from the sulfur atoms. A trial projection calculated from one third of the total $F(hk0)$'s indicated no anomalous features and the

Table 2. *The refinement process*

	R_1	R_2	$w(F_o^2-F_c^2)^2$
Start	11·5%	17·2%	512575
After 1st cycle	10·5	13·4	407374
After 2nd cycle	9·8	11·1	338572
After 3rd cycle	9·4	9·7	299599

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_2 = \Sigma w(F_o^2-F_c^2)^2/\Sigma w F_c^4$

Table 3. *Atomic parameters of galenobismutite*

	Wickman (1951)			Present determination			
	x	y	z	x	y	z	B (Å^2)
Pb*	0·250	0·645	0·250	0·24792 ±0·00015	0·65126 ±0·00011	0·25000	1·56 ±0·03
Bi$_I$†	0·072	0·400	0·250	0·06750 ±0·00014	0·39009 ±0·00010	0·25000	1·23 ±0·03
Bi$_{II}$	0·110	0·900	0·250	0·10427 ±0·00014	0·90559 ±0·00011	0·25000	1·42 ±0·03
S$_I$	0·333	0·035	0·250	0·33072 ±0·00092	0·01411 ±0·00069	0·25000	1·10 ±0·08
S$_{II}$	0·285	0·285	0·250	0·26091 ±0·00088	0·29968 ±0·00074	0·25000	0·89 ±0·07
S$_{III}$	0·077	0·090	0·250	0·05499 ±0·00093	0·09269 ±0·00071	0·25000	1·04 ±0·09
S$_{IV}$	0·013	0·735	0·250	0·01808 ±0·00097	0·71199 ±0·00070	0·25000	1·06 ±0·08

* Reported as Bi$_I$ by Wickman (1951).　　† Reported as Pb by Wickman (1951).

Table 4. *Observed and calculated structure factors*

Negative signs of F_c are designated by 0 printed between F_o and F_c

H	K	L	F O	F CAL		H	K	L	F O	F CAL		H	K	L	F O	F CAL
2	0	0	2 5	0	8	6	7	0	2 4 5	0	2 5 5	0	1 6	0	2 2 6	0	2 3 1
4	0	0	8 5		6 7	7	7	0	8 4		8 0	1	1 6	0	1 1 1		1 0 7
6	0	0	5 2 9	0	5 7 3	8	7	0	1 0 5	0	8 4	2	1 6	0	3 3		3 3
8	0	0	9 7		9 0	9	7	0	2 7	0	3 9	3	1 6	0	1 0 4		9 3
1 0	0	0	1 1 9	0	1 1 4	1 0	7	0	1 7 6		1 5 6	4	1 6	0	3 2	0	8
1 2	0	0	1 9 4		1 9 8	1 1	7	0	1 6	0	6	5	1 6	0	1 1 8		1 1 9
1 4	0	0	1 0 6	0	1 1 1	1 2	7	0	2 3 1		2 2 8	6	1 6	0	1 4 9		1 4 4
1	1	0	1 3	0	1 2	1 3	7	0	1 1	0	2	1	1 7	0	1 3 5	0	1 3 7
2	1	0	3 0		3 0	0	8	0	2 0 1		2 1 0	2	1 7	0	3 4	0	1 7
3	1	0	9 7	0	9 9	1	8	0	3 8 2		4 3 0	3	1 7	0			1 4
4	1	0	1 3 6		1 2 9	2	8	0	7 3		5 6	4	1 7	0	3 5	0	3 5
5	1	0	1 4 3	0	1 4 5	3	8	0	8 4		7 9	5	1 7	0	1 1 6		1 2 5
6	1	0	1 6 9		1 4 4	4	8	0	3 5	0	1 9	6	1 7	0	8 1	0	8 4
7	1	0	1 1 9		1 1 0	5	8	0	2 3 5		2 2 2	0	1 8	0	6 3	0	4 2
8	1	0	7 7		7 3	6	8	0	1 2 3	0	1 2 0	1	1 8	0		0	8 8
9	1	0	2 5 0		2 3 4	7	8	0	3 2 4	0	3 3 0	2	1 8	0	9 4		
1 0	1	0	1 7 3	0	1 7 1	8	8	0	1 1 7	0	1 0 5	3	1 8	0	1 3 3		1 5 4
1 1	1	0	6 2		5 1	9	8	0	1 8		3	2	0	1	4 7 8	0	4 9 5
1 2	1	0	1 5 8	0	1 5 1	1 0	8	0	6 7	0	6 5	4	0	1	5 2 9		4 7 1
1 3	1	0	1 6 8	0	1 4 2	1 1	8	0	1 2 8	0	1 2 3	6	0	1	2 5		1 9
1 4	1	0	1 0 1	0	9 4	1 2	8	0	7 1		5 7	8	0	1	2 2 3	0	1 9 7
1 5	1	0	1 1 7	0	1 2 1	1 3	8	0	1 3 6		1 3 0	1 0	0	1	8 6	0	5 9
0	2	0	6 2		5 9	1	9	0	1 2 2	0	1 1 3	1 2	0	1		0	1
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3	2	0	6 9 7	0	7 1 8	4	9	0	7 1		6 2	1	1	1	7 8		7 3
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6	2	0			4	7	9	0	1 2 1		1 0 3	4	1	1	1 1 1		9 5
7	2	0	5 2		1 6	8	9	0	1 0 8	0	1 1 0	5	1	1	3 1 8	0	3 3 2
8	2	0	1 4 2	0	1 2 3	9	9	0	1 7 9		1 9 0	6	1	1	9 1	0	8 2
9	2	0	3 3 4		3 2 1	1 0	9	0	6 1		6 4	7	1	1	4 6	0	3 1
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5	4	0	1 7 2	0	1 6 2	9	1 1	0	1 4 9		1 3 9	3	3	1	2 1 3	0	2 0 3
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Table 4 (cont.)

H	K	L	FO		F CAL
4	6	1	227	0	226
5	6	1	171		150
6	6	1	36		43
7	6	1	159		141
8	6	1	135		111
9	6	1	14		9
10	6	1	71		66
11	6	1	42	0	26
12	6	1	29	0	43
13	6	1	60	0	45
0	7	1	122		107
1	7	1	211	0	239
2	7	1	77		73
3	7	1	36		30
4	7	1	198		191
5	7	1	186	0	176
6	7	1	138	0	116
7	7	1	221		241
8	7	1	194	0	187
9	7	1	54	0	54
10	7	1	211	0	214
11	7	1	74		70
12	7	1	57		55
13	7	1	64	0	70
1	8	1	208	0	231
2	8	1	116		101
3	8	1	69		61
4	8	1	150		148
5	8	1	269		267
6	8	1	90		70
7	8	1	151		141
8	8	1	83	0	67
9	8	1	77	0	82
10	8	1	58	0	61
11	8	1	92	0	60
12	8	1	116	0	94
0	9	1	19		17
1	9	1	126		119
2	9	1	174	0	185
3	9	1	183	0	183
4	9	1	259		280
5	9	1	88	0	79
6	9	1	106	0	97
7	9	1	184	0	190
8	9	1	36		38
9	9	1	117		112
10	9	1	212	0	214
11	9	1	92		77
12	9	1	69		64
1	10	1	59		52
2	10	1	236		269
3	10	1	24		21
4	10	1	251		278
5	10	1	14	0	1
6	10	1	14	0	21
7	10	1	86	0	91
8	10	1	114	0	102
9	10	1	164	0	129
10	10	1	82	0	67
11	10	1		0	27
12	10	1	30		35
0	11	1	250	0	294
1	11	1	163		179
2	11	1	99		94
3	11	1	64		57
4	11	1	136	0	136
5	11	1	32		32
6	11	1	207		228
7	11	1	138	0	160
8	11	1	48		43
9	11	1	44		36
10	11	1	201		188
11	11	1	64		51
1	12	1	203		227
2	12	1	43		50
3	12	1	20	0	26
4	12	1		0	5
5	12	1	143	0	148
6	12	1	98	0	84
7	12	1	128	0	113
8	12	1	75	0	85
9	12	1	10	0	4
10	12	1	53		62
11	12	1	58		50
0	13	1	20	0	3
1	13	1	42	0	37
2	13	1	44	0	21
3	13	1	213		258
4	13	1	114	0	136
5	13	1		0	3
6	13	1	54	0	51
7	13	1	117		106
8	13	1	123		107
9	13	1	150	0	150
10	13	1	119		134
1	14	1	49		59
2	14	1	142	0	159
3	14	1	79	0	81
4	14	1	157	0	147
5	14	1	69	0	72
6	14	1	19	0	21
7	14	1	24		35
8	14	1	73		67
9	14	1	105		103
0	15	1	201		266
1	15	1	34	0	42
2	15	1	12	0	12
3	15	1	16	0	32
4	15	1	72		65
5	15	1	52		45
6	15	1	196	0	209
7	15	1	82		91
8	15	1	53		58
1	16	1	134	0	121
2	16	1	119	0	122
3	16	1	57	0	55
4	16	1	68	0	61
5	16	1	61		56
6	16	1	44		42
7	16	1	119		111
0	17	1	56	0	53
1	17	1	27		19
2	17	1	1 0 1		93
3	17	1	222	0	248
				0	7
4	17	1	39		35
5	17	1	41	0	47
1	18	1	47		45
2	18	1	44		4
2	0	2	54	0	47
4	0	2	488		458
6	0	2	75	0	72
8	0	2	97		99
10	0	2	188	0	172
12	0	2			11
1	1	2	27		20
2	1	2	83		79
3	1	2	106	0	100
4	1	2	122		112
5	1	2	136	0	115
6	1	2	99	0	90
7	1	2	65	0	61
8	1	2	209	0	200
9	1	2	143		148
10	1	2	44	0	44
11	1	2	155		132
12	1	2	133		125
13	1	2	52	0	47
0	2	2	31		14
1	2	2	132	0	113
2	2	2	575		546
3	2	2	208		199
4	2	2	58	0	50
5	2	2	17		4
6	2	2	38	0	16
7	2	2	120		105
8	2	2	269	0	272
10	2	2	70	0	67
11	2	2	57		68
12	2	2	32		26
13	2	2	68	0	77
1	3	2	70	0	65
2	3	2	51		41
3	3	2	113	0	93
4	3	2	143	0	126
5	3	2	26		5
6	3	2	260	0	255
7	3	2	76		76
8	3	2	130	0	111
9	3	2	63		45
10	3	2	131		125
11	3	2	21		27
12	3	2	220		208
13	3	2	43	0	50
0	4	2	483		497
1	4	2	204		211
2	4	2	43		34
3	4	2	126		103
4	4	2	28	0	4
5	4	2	137		128
6	4	2	415	0	399
7	4	2	199	0	181
8	4	2	12		9
9	4	2	63	0	70
10	4	2	10	0	6
11	4	2	95		88
12	4	2	94		90
13	4	2	62		48
1	5	2	95		87
2	5	2	116	0	112
3	5	2	77		72
4	5	2	75	0	61
5	5	2	18		2
6	5	2	171	0	153
7	5	2		0	6
8	5	2	191	0	187
9	5	2	39	0	46
10	5	2	105		89
11	5	2	18		13
13	5	2	143	0	137
0	6	2	130		128
1	6	2	19		3
2	6	2	299		324
3	6	2	347	0	357
4	6	2	287	0	293
5	6	2	12		4
6	6	2	90	0	73
7	6	2	90	0	86
8	6	2	148	0	138
9	6	2	177		163
10	6	2	194		166
11	6	2	16	0	21
12	6	2	80	0	83
13	6	2	52		58
1	7	2	103		104
2	7	2	21		23
3	7	2	92	0	82
4	7	2	124		104
5	7	2	102	0	93
6	7	2	202		216
7	7	2	72	0	69
8	7	2	95		72
9	7	2	36		34
10	7	2	161	0	137
11	7	2			5
12	7	2	205	0	201
0	8	2	161	0	171
1	8	2	289	0	349
2	8	2	60	0	47
3	8	2	71	0	65
4	8	2	22		18
5	8	2	196	0	185
6	8	2	102		102
7	8	2	262		281
8	8	2	104		92
9	8	2	15	0	1
10	8	2	61		57
11	8	2	122		108
12	8	2	55	0	51
1	9	2	103		96
2	9	2	87	0	94
3	9	2	85		87
4	9	2	57	0	52
5	9	2	44		25
6	9	2	103		97
7	9	2	102	0	90
8	9	2	96		96
9	9	2	169	0	167
10	9	2	63	0	57
11	9	2	21	0	9
0	10	2	193	0	214
1	10	2	18		4
2	10	2	241	0	275
3	10	2	36		32
4	10	2	220		239
5	10	2	117		107
6	10	2	68		61
7	10	2	30		28
8	10	2	165		152
9	10	2	29	0	28
10	10	2	120	0	120
11	10	2	103	0	98
1	11	2	104	0	107
2	11	2	57	0	57
3	11	2	25		33
4	11	2	132	0	133
5	11	2	88		104
6	11	2	76	0	83
7	11	2			3
8	11	2	13		29
9	11	2	137	0	122
10	11	2	118		98
0	12	2	74	0	72
1	12	2	220		229
2	12	2	66		62
3	12	2	76		74
4	12	2	52		56
5	12	2	214		213
6	12	2	53		54
7	12	2	194	0	189
8	12	2	89	0	80
9	12	2	12		10
1	13	2	127	0	123
2	13	2	71		74
3	13	2	47	0	46
4	13	2	34	0	34
5	13	2	95		92
6	13	2	151	0	138
7	13	2	109		93
8	13	2	64	0	73
9	13	2	72		74
0	14	2	69		65
1	14	2	74	0	64
2	14	2	162		171
3	14	2	141		145
4	14	2	140	0	153
5	14	2	129	0	123
6	14	2	82	0	64
7	14	2	38	0	38

Tabelle 4 (cont.)

H	K	L	FO	F	CAL
8	14	2	139	0	152
1	15	2	36		33
2	15	2	130		136
3	15	2	46	0	41
4	15	2	89		91
5	15	2	31	0	53
6	15	2	28		21
0	16	2	191		202
1	16	2	94	0	93
2	16	2	33	0	29
3	16	2	94	0	83
4	16	2	23		7
5	16	2	95	0	105
1	17	2	107		122
2	17	2	29		16
2	0	3	309	0	308
4	0	3	308	0	311
6	0	3	23	0	16
8	0	3	137		142
10	0	3	65		47
0	1	3	95	0	106
1	1	3	44		46
2	1	3	141		147
3	1	3	130	0	121
4	1	3	63	0	59
5	1	3	228		223
6	1	3	61		49
7	1	3	32		22
8	1	3	211	0	230
9	1	3	50		54
10	1	3	62	0	42
11	1	3	185	0	188
12	1	3	37	0	42
1	2	3	238	0	255
2	2	3	86	0	69
3	2	3	44		29
4	2	3	85	0	81
5	2	3	250		244
6	2	3	27		26
7	2	3	145		129
8	2	3	98		82
9	2	3	11		4
10	2	3			4
11	2	3	95	0	84
12	2	3	14		10
0	3	3	44	0	23
1	3	3	215	0	219
2	3	3	169		159
3	3	3	140		127
4	3	3	95		78
5	3	3	213	0	214
6	3	3	62		52
7	3	3	78		74
8	3	3	232	0	237
9	3	3	113	0	100
10	3	3	145	0	126
11	3	3	172		169
12	3	3	9		
1	4	3	168	0	163
2	4	3	252		269
3	4	3	44		33
4	4	3	195		187
5	4	3	115		96
6	4	3	26		24
7	4	3	56		53
8	4	3	114	0	111
9	4	3	82	0	74
10	4	3	106	0	89
11	4	3	55	0	38
0	5	3	94		86
1	5	3	69		56
2	5	3	201	0	207
3	5	3	19	0	7
4	5	3	170		164
5	5	3	68	0	62
6	5	3	85		78
7	5	3	165	0	165
8	5	3	125		129
9	5	3	79		68
10	5	3	120	0	110
11	5	3	195		175
1	6	3	178		188
2	6	3	228		235
3	6	3	50		44
4	6	3	160		158
5	6	3	114	0	105
6	6	3	26	0	28
7	6	3	107	0	105
8	6	3	106	0	82
				0	7
9	6	3	53	0	51
10	6	3	32		19
11	6	3	78	0	74
0	7	3	144		157
1	7	3	53	0	57
2	7	3	19	0	16
3	7	3	138	0	133
4	7	3	120		124
5	7	3	88		86
6	7	3	174	0	175
7	7	3	155		144
8	7	3	44		38
9	7	3	173		163
10	7	3	38	0	53
11	7	3	144		159
1	8	3	75	0	72
2	8	3	64	0	43
3	8	3	103	0	108
4	8	3	188	0	196
5	8	3	56	0	53
6	8	3	120	0	106
7	8	3	68		51
8	8	3	61		60
9	8	3	47		48
10	8	3	13	0	12
0	9	3	79	0	82
2	9	3	114		131
3	9	3	122		133
4	9	3	174	0	203
5	9	3	62		62
6	9	3	66		73
7	9	3	150		141
8	9	3	30	0	27
9	9	3	89	0	86
10	9	3	159		163
1	10	3	43	0	40
2	10	3	164	0	198
3	10	3	17	0	15
4	10	3	201	0	208
5	10	3	15		2
6	10	3	14		14
7	10	3	68		70
8	10	3	91		77
9	10	3	113		100
0	11	3	191		218
1	11	3	121	0	131
2	11	3	74	0	67
3	11	3	49	0	43
4	11	3	100		100
5	11	3	22	0	23
6	11	3	178	0	173
7	11	3	112		121
8	11	3	38	0	36
1	12	3	169	0	171
2	12	3	32	0	37
3	12	3	14		19
4	12	3			5
5	12	3	116		113
6	12	3	76		64
7	12	3	90		88
0	13	3	13		4
1	13	3	27		24
2	13	3	33		17
3	13	3	183	0	195
4	13	3	92		102
5	13	3	7	0	2
6	13	3	43		39
1	14	3	45	0	44
2	14	3	120		122
3	14	3	65		62
4	14	3	117	·	114
5	14	3	47		55
0	15	3	196	0	204
1	15	3	26		32
2	15	3	7		6
0	0	4	558		495
0	2	4	25		27
0	4	4	280	0	292
0	6	4	92	0	83
0	8	4	96		109
0	10	4	123		146
0	12	4	46		45
0	1	5	58		52
0	3	5	21		7
0	5	5	34	0	44

refinement was further continued. In this structure, all atoms must occur on the mirror planes with z-parameters ¼ or ¾, and the structure was mainly refined by successive Fourier syntheses and difference projections along the c-axis. Later, three-dimensional least-squares refinement was carried out. The atomic scattering factors were computed by the three term Gaussian expansion. The coefficients of the formula were taken from the paper by Forsyth & Wells (1959). For lead and bismuth they evaluated the coefficients from the tabulated values of atomic scattering factors by James & Brindley (1931) and for sulfur, the values of Viervoll & Øgrim (1949) were used.

The new sets of coordinates for lead and bismuth were obtained by the trial (001) projection and a subsequent structure-factor calculation yielded the R-factor 30%. A difference projection was now computed omitting the contribution of all sulfur atoms to the F_c's. This synthesis not only indicated the coordinate shifts of the heavy atoms, but also had peaks corresponding to four sulfur atoms. The R-factor now fell down to 17% including the sulfur atoms.

After two cycles of refinement by difference projections, a (100) projection was computed confirming the z-parameters of the atoms. Three-dimensional structure-factor calculations were then carried out. The R-factors were: $R(hk0)=11\cdot9\%$ (corrected for extinction), $R(hk1)=13\cdot3\%$, $R(hk2)=11\cdot8\%$, $R(hk3)=10\cdot1\%$, $R(0kl)=17\%$. The relatively large value of the $R(0kl)$ could be attributed to irregularity of the absorption effect.

A comparison of F_o and F_c indicated a systematic depression of F_o values for some strongest reflections. $12(hk0)$, $6(hk1)$, $6(hk2)$, and $4(hk3)$ planes were then corrected for extinction assuming the relation

$$I_c = I_o/(1 - g.I_o),$$

where g was found by plotting

$$Lp|F_c|^2/I_o\,(=I_c/I_o) \quad \text{against} \quad Lp|F_c|^2\,(=I_c).$$

Fig. 1(a) and (b) show the final electron-density and difference projections, the latter utilizing the F_c-values for which the contributions of sulfur atoms are excluded. It indicates four peaks of the sulfur

atoms and anisotropy of the heavy atoms. No allowance, however, has been made for the anisotropic thermal motions.

The 775 (hkl) data were then submitted to three cycles of least-squares refinement. The programme was written for the Bull-Gamma-A.E.T. electronic computer to minimize the function

$$\Sigma w(hkl)\,(F_o^2(hkl) - F_c^2(hkl))^2$$

using diagonal approximations. It includes the refinement of an individual isotropic temperature factor for each atom. The weighting system was

$$w(hkl) = 1/F_o^4(hkl) \quad \text{if} \quad |F_o(hkl)| \geqq 4F_{o\ \min.}$$
$$w(hkl) = 1/256F_{o\ \min.}^4 \quad \text{if} \quad |F_o(hkl)| < 4F_{o\ \min.}$$

where, $F_{o\ \min.}$ is a minimum observable F_o-value and was taken as 15·00. The process of the refinement is outlined in Table 2. The maximum coordinate shift during the refinement was only 0·02 Å.

The final parameters are listed in Table 3, together with the standard deviations calculated from the diagonal element of the normal equations for the last least-squares cycle. The atomic coordinates reported by Wickman (1951) are also listed in the table. The observed and the final calculated structure amplitudes are shown in Table 4.

Discussion of the structure

The structure of galenobismutite projected along the c-axis is shown in Fig. 2. Some of the interatomic distances calculated from the coordinates given in Table 3 are listed in Table 5. The average standard deviation of the Pb–S and Bi–S distances is ±0·015 Å and that of the S–S distances is ±0·022 Å.

As shown in Table 3, the present analysis yielded new atomic parameters which depart significantly from those of Wickman (1951). The average parameter changes for the heavy atoms were 0·05 Å in the a- and 0·11 Å in the b-direction and for the sulfur atoms they were 0·16 Å and 0·22 Å respectively. Some of the sulfur atoms were moved as much as 0·34 Å.
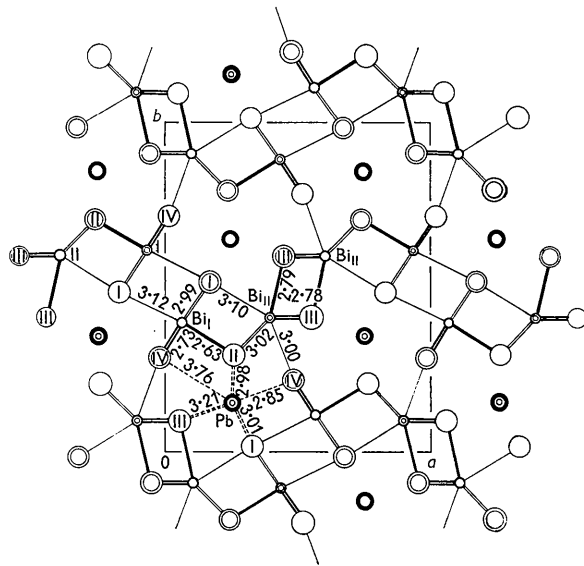
Fig. 2. Projection of the structure of galenobismutite along the c-axis. The largest circles indicate the sulfur atoms, the medium bold circles the lead, and the smallest circles the bismuth atoms. Double circles indicate atoms at $z=\frac{3}{4}$ and single circles at $z=\frac{1}{4}$.

Consequently, the interatomic distances between the heavy atoms and the sulfur atoms were changed by about 0·2 Å. The present interpretation of the structure, in contrast to that of Wickman, shows that it is more similar to that of bertherite, FeSb$_2$S$_4$, but it is not isostructural with the latter as was previously thought.

By X-ray methods it is very difficult to distinguish bismuth from lead. However, if we compare the environments of the three heavy atoms, it is found that two of them have the nearest approach of sulfur atoms at about 2·7 Å, while the third heavy atom has no short distance less than 2·85 Å. We may conclude that the former two are bismuth which form Bi–S bonds having much covalent character. The third heavy atom, which Wickman thought to be bismuth, is surrounded by seven sulfur atoms with

Table 5. *Interatomic distances in galenobismutite* ($\mathring{A}$)

	S$_I$	S$_{II}$	S$_{III}$	S$_{IV}$	Pb	Bi$_I$	Bi$_{II}$
Pb	3·01(2)	2·98(2)	3·21(2)	2·85(1) 3·76(1)	6·56	4·59	4·08 4·48
Bi$_I$	2·99(2) 3·12(1)	3·63(1)		2·73(2)		4·13	4·38
Bi$_{II}$	3·10(1)	3·02(2)	2·78(2) 2·79(1)	3·00(1)			4·22
S$_I$		4·51(2)	3·89(2) 4·25(1)	3·45(1) 3·96(2)			
S$_{II}$			3·88(1) 3·81(1)	3·55(2) 3·88(2)			
S$_{III}$				3·63(2) 3·61(2)			

(Numbers in parentheses indicate the number of distinct vectors of this length.)

distances ranging from 2·85 Å to 3·21 Å. These distances are in agreement with the Pb–S distances found in galena (2·97 Å) and in other sulfosalts, and we take this atom as lead.

A comparison of the coordination of sulfur around lead and bismuth as found in various sulfosalt minerals is given in Fig. 3. Although only a few bismuth compounds can be found for which the complete structure analysis has been made, it is evident that at least in these crystals given in Fig. 3 bismuth and sulfur atoms are bound together to form a trigonal pyramid, and the bond lengths are considerably shorter than what would be expected for ionic Bi^{+3}–S^{-2} bonds $(1·20 + 1·82 = 3·02$ Å$)$.
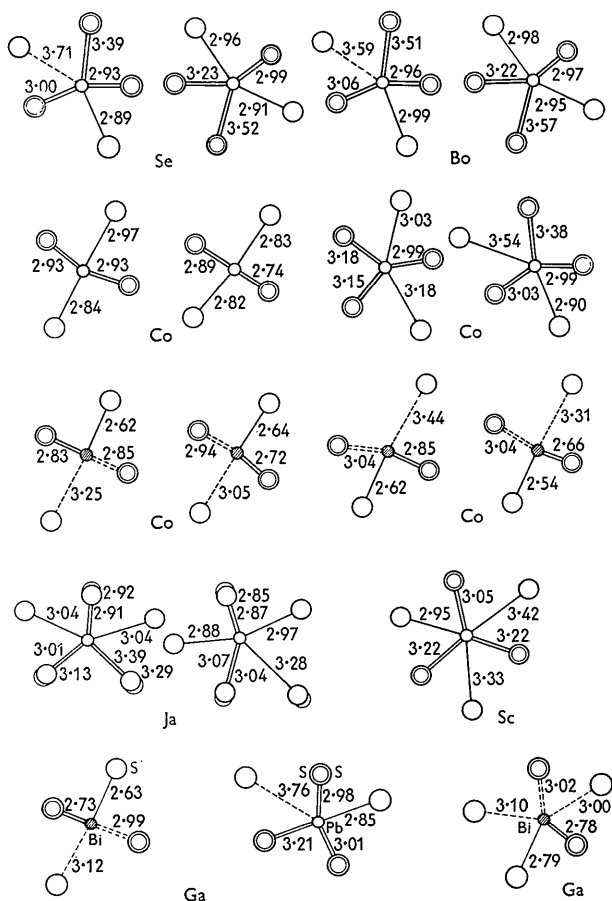
Fig. 3. Coordination of lead and bismuth in different sulfosalts. Large circles indicate sulfur atoms (double circles show overlapping of two sulfur atoms of different height); small circles indicate lead atoms and small shaded circles bismuth atoms.

Se: Seligmannite $CuPbAsS_3$ (Leineweber, 1956).
Bo: Bournonite $CuPbSbS_3$ (Leineweber, 1956).
Co: Cosalite $Pb_2Bi_2S_5$ (Weitz & Hellner, 1960).
Ja: Jamesonite $FePb_4Sb_6S_{14}$ (Niizeki & Buerger, 1957).
Sc: Scleroclase $PbAs_2S_4$ (Nowacki & Iitaka et al., 1961).
Ga: Galenobismutite $PbBi_2S_4$ (Iitaka & Nowacki, 1961)

The structure of galenobismutite contains two

crystallographically independent bismuth atoms (Bi_I and Bi_{II}), each constituting trigonal pyramidal BiS_3 groups which extend along the c-axis, sharing their edges to form the BiS_2-chains. The two $Bi_{II}S_2$-chains are, as shown in Fig. 2, joined together, forming a double chain.

This feature seems to be similar to berthierite $FeSb_2S_4$ and scleroclase $PbAs_2S_4$. All of these sulfosalts contain both single and double chains of antimony (arsenic, bismuth) atoms. The single chain (Bi_IS_2) in galenobismutite resembles the $Sb_{II}S_2$ and the As_IS_2 chains in berthierite and scleroclase. In the latter structures however, two SbS_2 chains (and also two AsS_2 chains) join together sharing one of the sulfur atoms to form a double chain of composition Sb_2S_4 (and As_2S_4). In galenobismutite, on the other hand, two $Bi_{II}S_2$ chains join together sharing two sulfur atoms so that the double chain has composition $Bi_{II}S$. Moreover, if we take into account the second smallest interatomic distances between the bismuth and sulfur atoms, it is found that these chains are not so distinct as in berthierite or scleroclase and the situation is thus quite different.

The Bi_I-atoms, as illustrated in Fig. 2, are surrounded by six sulfur atoms in distorted octahedral arrangement, while the Bi_{II}-atoms are surrounded by seven sulfur atoms. Assuming that an ionic bond still exists between those bismuth and sulfur atoms which are separated by from 2·99 to 3·12 Å from each other (the calculated ionic bond distance is 3·02 Å), we can draw a sheet of bismuth and sulfur atoms extending parallel to the (010) plane. This sheet is made up of both kinds of chains and the S_I-atoms and has the composition BiS_2. It is linked to its neighbours through the lead atoms and by bonds between Bi_{II} and S_{IV}. The atomic configuration of the sheet resembles to some extent to those of the Sb_4S_6-chain in stibnite Sb_2S_3 (Hoffmann, 1933) and of the Bi_4S_6-chain in bismuthinite Bi_2S_3 (Hoffmann, 1933), but it is rather difficult to find such a sheet in berthierite and scleroclase. In Fig. 4 the bonding between bismuth and sulfur atoms within the sheet is schematically represented.

As described earlier, the lead atoms are surrounded by seven sulfur atoms with the distances 2·85 Å to 3·21 Å. There is one additional rather close approach of 3·76 Å. The arrangement of the sulfur atoms around the lead atom is, as shown in Fig. 2 and 3, very similar to that found in many sulfosalts. The PbS_7-polyhedra in galenobismutite extend parallel to the c-axis sharing three sulfur atoms with their translation equivalents and form a chain which fills up the interstices between the BiS_2 sheets.
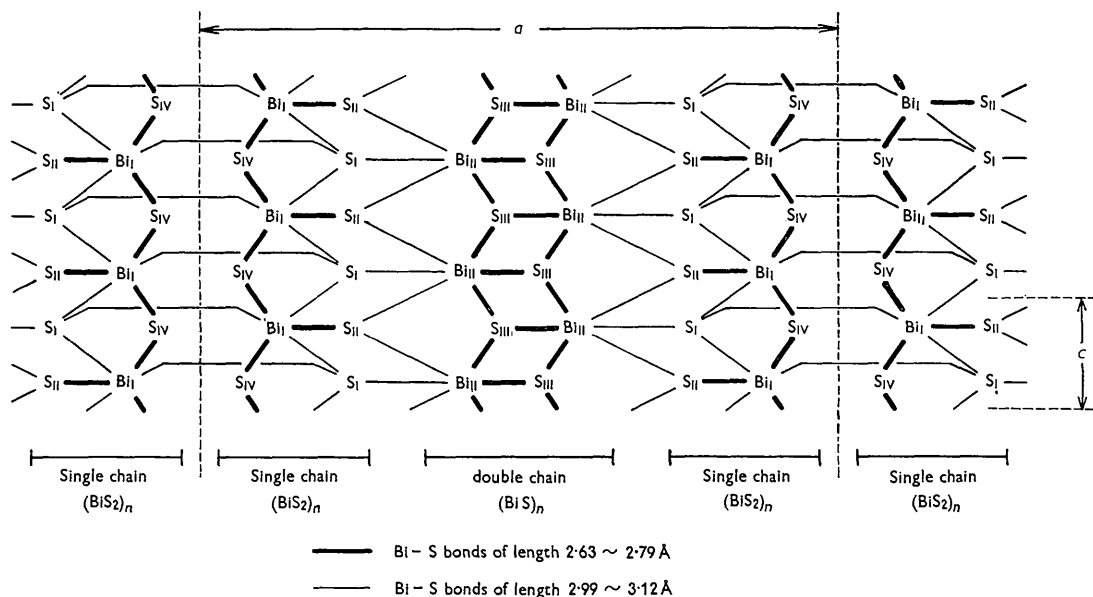
Fig. 4. Schematic representation of Bi–S bonds within a single sheet parallel to (010). Each sheet is linked to its neighbours through the Pb atoms and by bonds between Bi$_{\mathrm{III}}$ and S$_{\mathrm{IV}}$ (not shown).

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Die Kristallstruktur von Teineit. Ein Beispiel für die Korrektur einer chemischen Formel auf Grund der Strukturbestimmung

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The only existing chemical analysis of the rare secondary copper mineral teineite led to the composition 10 CuTeO$_4$.3 CuSO$_4$.26 H$_2$O. Determination of the crystal structure and comparison with CuSeO$_3$.2 H$_2$O showed, that the chemical composition should be CuTeO$_3$.2 H$_2$O, at least to a very good approximation. The atomic parameters have been refined in two projections. The shape of the TeO$_3$ group is within the limits of accuracy a trigonal pyramid with an angle O–Te–O $\sim$ 100° and distances Te–O $= 1\cdot88 \pm 0\cdot05$ Å. Copper has a $(4+1)$ coordination.

Vor kurzem konnten wir (Zemann & Zemann, 1960) zeigen, dass das seltene Mineral Teineit, welchem bisher die Formel 10 CuTeO$_4$.3 CuSO$_4$.26 H$_2$O (Yosi- mura, 1939) oder vielleicht auch Cu(Te,S)O$_4$.2 H$_2$O (Dana's System of Mineralogy, Vol. 2, 1951) zugeschrieben wurde, nach Gitterkonstanten und Raum-