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A redetermination of the crystal structure of cosalite, $Pb_2Bi_2S_5$ *

By **T. Srikrishnan**** and **Werner Nowacki**

Department of Crystallography and Structural Sciences
University of Bern***

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Auszug

Die Kristallstruktur von Cosalit, $Pb_2Bi_2S_5$, wurde mit Hilfe von Diffraktometerdaten neu bestimmt, um die Koordinationen von Pb und Bi zu erhalten und sie mit denjenigen anderer Pb-Bi-Sulfide zu vergleichen. Die Gitterkonstanten und die Raumgruppe sind $a = 19{,}098 \pm 0{,}004$ Å, $b = 23{,}890 \pm 0{,}005$ Å, $c = 4{,}057 \pm 0{,}001$ Å und D_{2h}^{16}—*Pbnm*, mit 8 Formeleinheiten in der Elementarzelle (zwei in der asymmetrischen Einheit). Mittels Ausgleichsmethoden wurde die Struktur bis zu einem *R*-Wert von 10,8% für alle 1432 Reflexe (9,6% für die beobachteten 1217 Reflexe) verfeinert.

Alle Atome liegen in den Spiegelebenen der Raumgruppe bei $z = 1/4$ und 3/4. Die Bi-Atome konnten von den Pb-Atomen durch Vergleich ihrer Koordinationen unterschieden werden. Bi(1) hat eine quadratisch-pyramidale Koordination von fünf S in Abständen von 2,57 bis 2,83 Å, dazu ein zusätzliches S im Abstand von 3,21 Å. Die anderen drei Bi-Atome weisen eine deformiert-oktaedrische Sechserkoordination auf, mit Bi—S = 2,57 bis 3,45 Å (mittlere Standardabweichung = 0,01 Å), ebenso Pb(1) und Pb(2). Die beiden anderen Pb-Atome, Pb(3) und Pb(4), haben eine Achter-Koordination (trigonal-prismatisch plus zwei). Die (Pb—S)-Abstände liegen im Bereich von 2,72 bis 3,47 Å. Außerdem befindet sich in der Struktur ein „statistisches Kupferatom", dessen Koordination ein deformiertes Tetraeder ist (Cu—S = 2,21 bis 2,61 Å).

Die Strukturformel von Cosalit kann als $[Bi_2S_4|S|Pb^{VI}Pb^{VIII}]$ geschrieben werden, Typus III.a_3 entsprechend der Klassifikation der Sulfosalze von Nowacki (1969).

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** Present address: Organic Chemistry Laboratory, Swiss Federal Institute of Technology, Zürich, Switzerland.

*** CH–3012 Bern, Sahlistraße 6, Switzerland.

Abstract

The crystal structure of cosalite, $Pb_2Bi_2S_5$, has been redetermined with the help of diffractometric data, with a view to study the coordinations of Pb and Bi atoms in the structure and to compare them with that found in other lead-bismuth sulfides. The cell dimensions and space group are $a = 19.098 \pm 0.004$, $b = 23.890 \pm 0.005$, $c = 4.057 \pm 0.001$ Å and D_{2h}^{16}–*Pbnm*. There are eight formula units in the unit cell and two in the asymmetric unit. The structure was refined by the method of least squares, to a final R value of 10.8% for all the 1432 reflections (9.6% for the observed 1217 reflections).

All the atoms lie on the mirror planes of the space group at $z = 1/4$ and $3/4$. Bismuth atoms could be distinguished from the lead atoms by a comparison of their coordination. Bi(1) has a coordination of five sulfur atoms in the range of 2.57 to 2.83 Å, which could be described as a square pyramid, plus an additional sulfur atom at a distance of 3.21 Å. The other three independent Bi atoms in the structure have a coordination of six, making up a distorted octahedron in each. These Bi—S distances are in the range 2.57 to 3.45 Å and the average standard deviation in them is 0.01 Å. Six sulfur atoms around Pb(1) and Pb(2) form a distorted octahedron. The other two lead atoms, Pb(3) and Pb(4), have a coordination of eight (in the corners of a trigonal prism plus two). The Pb—S distances are in the range of 2.72 to 3.47 Å; the mean standard deviation is 0.01 Å. There is, in addition, a "statistical copper" atom in the structure. The coordination around the copper atom is a distorted tetrahedron and the Cu—S distances are in the range of 2.21 to 2.61 Å.

The structural formula of cosalite could be written as $[Bi_2S_4|S|Pb^{VI}Pb^{VIII}]$ and belongs to the type III.a_3, in the classification of sulfosalts by Nowacki (1969).

Introduction

Cosalite is a lead bismuth sulfide and derives its name from its occurence at the Cosala mines, Sinaloa, Mexico. It is not an uncommon mineral, formed at moderate temperatures, in contact metamorphic deposits (Vaskö, Rézbánya, Fahlun and Nordmark) and in pegmatites. It occurs at the Cosala mines, Mexico, at the Bjelke mine, Nordmark, Sweden, at the Forno glacier, Switzerland and at a number of other places in the world (Dana, 1944). It has a chemical composition of $Pb_2Bi_2S_5$, but contains small amounts of Cu, Ag, and Fe, which is depending on its source.

Cosalite was first investigated by Berry (1939), during the course of his studies of complex sulfosalts and he gave the cell dimensions and the possible space group and chemical composition (Table 2). Weitz and Hellner (1960) carried out the crystal-structure investigation of cosalite by three-dimensional Patterson and Fourier methods. Their analysis was not based on complete three-dimensional diffraction data and distinction between the lead and bismuth atoms was impossible, because of the small differences in their scattering factors and also because of the relatively inaccurate coordinates of the sulfur atoms.

Quite recently accurate analyses of some of the lead-bismuth sulfides are undertaken in this laboratory (IITAKA and NOWACKI, 1962; OHMASA and NOWACKI, 1970) and a distinction between lead and bismuth atoms has been made from a comparison of their coordination. We have undertaken this redetermination, so as to get an accurately refined structure, with the help of diffractometric data and hence distinguish between lead and bismuth atoms by a comparison of their coordination.

Experimental

Crystals of cosalite are opaque, lead-gray to steel-gray in colour and have a metallic luster. They are most frequently found elongated as needles, the needle axis being the *c* axis, as capillary forms and also as feathery or fibrous aggregates. Because of the fibrous nature of these crystals, some of the reflections have an inherent small faint streak associated with them. Also the existence of a perfect cleavage in the (001) direction rendered the problem of selecting a good crystal rather difficult.

The crystal used for the present study was prepared from a sample of cosalite from the Cariboo gold mines at Wells in British Columbia, Canada. It was a thin and fibrous needle, with dimensions 0.674 × 0.126 × 0.085 mm, with approximately cylindrical cross section. An electron-probe analysis of the sample yielded the values given in Table 1. The chemical composition of cosalite is essentially $Pb_2Bi_2S_5$, although there are some minor traces of Cu and Ag. We shall discuss about the presence of Cu in a later section.

Table 1. *Microprobe analysis of cosalite sample*

	Analysis No. 438	Theoretical
Pb	39.5%	41.75%
Bi	39.9	42.10
S	18.3	16.15
Cu	1.3	—
Ag	0.8	—
	99.8%	100%

Analysis No. 438: Cosalite sample from Cariboo gold mine, British Columbia, Canada (found with gold and quartz).

Theoretical: $Pb_2Bi_2S_5$.

Table 2. *Crystallographic data of cosalite*

	Berry (1939)	Weitz and Hellner (1960)	Present study
Cosalite	$a = 19.07$ Å	19.101 Å	19.098 ± 0.004 Å
$Pb_2Bi_2S_5$	$b = 23.87$	23.913	23.890 ± 0.005
	$c = 4.055$	4.061	4.057 ± 0.001

Space group D_{2h}^{16}–$Pbnm$, $Z = 8$, $d_x = 7.17$ g cm^{-3}, $V = 1851$ Å^3, $F(000) = 3309$.

The lattice constants were determined with the help of back-reflection Weissenberg photographs, on which the diffraction pattern of silicon have been superposed to calibrate the effect of film shrinkage. The precise lattice constants determined from a least-square best fit of 24 $hk0$ and 10 $h0l$ reflections are given in Table 2, together with the values of Berry (1939) and Weitz and Hellner (1960). The calculations were done with the aid of a program written by N. D. Jones (unpublished).

The crystal belongs to the orthorhombic system. The possible space groups, as deduced from the systematic absences in Weissenberg photographs, are D_{2h}^{16}–$Pbnm$ or C_{2v}^{9}–$Pbn2_1$. But the former space group has been assumed for the following two reasons. Firstly an examination of the Weissenberg photographs taken about the c axis revealed that the intensity distribution in the zero, second, fourth layers are alike as well as in the first and third. This is possible only in the space group *Pbnm*, in the fourfold special positions (on the mirror planes at $z = 0.25$ and 0.75). Secondly, an analysis of the distribution of the normalized structure amplitudes also indicated in favour of the centric space group rather than the acentric one (see Table 3). There are eight formula units in the unit cell and two in the asymmetric quarter.

Table 3. *Distribution of normalized structure factors for cosalite*

	Experimental	Theoretical	
		Centric	Acentric
$< \lvert E \rvert >$	0.740	0.798	0.886
$< \lvert E^2 \rvert >$	1.005	1.000	1.000
$< E^2 - 1 >$	1.103	0.968	0.736
$\lvert E \rvert > 3.0$	1.2%	0.3%	0.01%
$\lvert E \rvert > 2.0$	6.4%	5.0%	1.8%
$\lvert E \rvert > 1.0$	26.6%	32.0%	37.0%

Three-dimensional intensity data were collected by a Weissenberg counter diffractometer (Supper-Pace Autodiffractometer) using Cu$K\alpha$ radiation. The intensities were corrected for Lorentz and polarization factors. Correction for absorption was made with the help of an ICR-10 program (Johnson, 1963), because of the high linear absorption coefficient of the material ($\mu = 1460$ cm^{-1} for Cu$K\alpha$ radiation).

Structure determination and refinement

The coordinates of the heavy atoms were located from the Patterson synthesis. Because of the fact that the atoms lie on the mirror planes at $z = 1/4$ and $3/4$, the Patterson interactions are confined to the sections at $w = 0$ and $1/2$. This confirmed the coordinates of the metal atoms in Weitz and Hellner's model.

A structure-factor calculation was attempted with the coordinates of the heavy atoms, with the scattering factor of bismuth. The R factor for all the 1432 reflections was 25%. A three-dimensional Fourier synthesis was computed with the coordinates of the heavy atoms. The sulfur atoms were found from the above Fourier map and this confirmed the sulfur coordinates of Weitz and Hellner's model.

Three-dimensional least-squares refinement was started with the coordinates of all atoms. The initial R factor was 22%. After a series of isotropic refinements, the R factor dropped to 15%. At this stage, the interatomic distances were calculated and marked difference was observed in the coordination of the Pb and Bi atoms. Based on their coordination, Pb atoms were distinguished from Bi atoms and further refinements were made with the individual atomic scattering factors for Pb and Bi. Neutral-atom form factors as given by Thomas, Umeda and King were used for the Pb and Bi atoms, and those given by Dawson were employed for S atoms[1].

Also, from a study of the difference Fourier at this stage, a vacant site was found at $x = 0.40$, $y = 0.06$, $z = 0.75$. Considerations of the dispositions of the sulfur atoms in the neighbourhood, and also the fact that there is a trace of Cu content in the sample (as evidenced by microprobe analysis), suggested that this could be the site of the Cu atom in the structure. From the percentage of content from microprobe and the peak height in the Fourier map, the occupancy factor for Cu was estimated to be not more than 0.12 (this was also verified by the least-squares refinement). The Cu atom was refined, at first isotropically

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[1] *International tables for x-ray crystallography*, vol. III. Kynoch Press, Birmingham, 1962, p. 201—212.

Table 4. *Observed and calculated structure amplitudes*

h	$\|F_o\|$	F_c
h 0 0		
4	147	119
10	906	820
12	267	-219
14	188	-182
16	539	-456
18	310	-275
22	162	172
h 1 0		
1	75	55
3	208	-200
4	92	-102
7	133	-90
13*	27	-3
14	163	-157
16	237	210
17	173	-162
18	218	177
19*	31	23
h 2 0		
0*	19	-9
1*	21	-44
2	67	-39
3	268	278
4	393	386
5	445	480
6	420	-396
7	227	276
8	171	-154
9	145	169
10	235	-211
11	241	227
12*	30	36
13*	48	54
14	259	225
15	644	560
16	390	-346
17	76	-65
19	164	-162
21	255	268
22	121	152
23	116	-129
h 3 0		
2*	31	1
4	364	-417
5	1332	-1411
6	589	534
7*	29	7
8	517	-570
10*	47	-35
11	347	298
12	156	-136
13	117	117
14	297	251
15	140	-185
16	168	147
17	150	-144
19	210	204
20	63	73
21	172	161
22*	20	105
h 4 0		
1*	17	-10
4	479	-490
5	210	-176
6	770	-814
8	241	244
10*	50	-39
11	170	157
12	310	284
13	167	-151
14	102	-90
15	740	-660
16	278	-245
17	100	113
18	147	129
20	53	-72
22	324	351
23	213	-245
h 5 0		
1*	46	-42
3	237	280
5	419	428
6	293	-370
7	159	145
8	357	-429
9	440	-471
10	326	-360
11	142	155
12	431	-408
14	159	-161
16	420	-409
17	114	-94
18	151	164
19	265	-259
20	137	-136
21	158	168
23	46	-35
h 6 0		
0	759	704
2*	34	7
3	343	405
4	164	-188
8	107	-129
9*	20	-7
11	284	-321
12	415	444
13	261	271
14	79	-72
15	62	-61
16	53	-45
17*	24	24
18	227	-236
19	353	-375
20*	31	25
21	71	-83
22	143	151
h 7 0		
1	1038	909
2	318	-327
3*	16	-25
7	227	-251
8	161	149
9	463	505
11	245	262
12	430	-459
13	218	-240
14	193	184
15	254	-251
16	143	-148
17	252	-247
18	253	268
20	264	277
21*	25	-26
22	57	-70
h 8 0		
0	291	-331
1	325	-279
2	193	-213
3	166	165
4	139	134
5	117	-137
6*	5	-31
7	104	77
8	124	-133
10	129	140
11	309	329
12	64	89
13*	44	-32
14	366	404
16	125	-112
17	152	162
19	246	242
20	149	152
21	273	291
22	170	-187
h 9 0		
1*	21	38
2	158	158
3	93	111
4	182	-168
5	68	-72
8	148	-136
9	100	124
10	219	253
12	148	188
13	206	228
14	205	242
15	196	-215
16	159	169
17	287	-298
18	82	-83
19	121	135
20	37	-46
22	25	18
h 10 0		
1	120	92
2	164	132
3	461	-516
4	1133	-1045
5	396	-463
7	220	226
9	309	-374
12	179	224
13	236	-272
14	80	-85
15	180	-198
16	57	61
17	140	145
18	99	-83
19	44	-45
20	241	250
21	126	132
22	136	144
h 11 0		
1	166	156
2	215	181
3	233	-215
4	490	-538
6	170	245
7*	31	-44
9*	26	-72
10	281	310
12	107	-130
15	83	-100
16	237	-265
17	193	209
18	59	75
19	202	-219
20*	20	9
21	110	117
h 12 0		
0	252	-240
1	185	-158
3	130	-131
4*	58	47
5	121	-135
6	273	308
8	232	-267
10	80	-88
11	178	-193
13	101	-112
14	186	-215
15*	26	-34
16	167	196
17	114	-133
18	256	-265
19*	30	-25
20	52	-54
21	28	0
h 13 0		
2	484	-464
3*	35	-1
4	361	389
5	164	-169
6*	29	34
8	321	400
9	338	400
10*	35	15
11	178	212
13	180	204
14	178	198
15	225	-254
16*	30	-32
17	47	42
18	123	-134
19	162	-174
21	62	63
h 14 0		
0	229	281
2	681	626
3	169	-159
4	211	-199
6*	27	-23
7*	25	32
8	168	207
10*	17	18
12*	34	-51
14	91	-103
15	96	-106
16	129	-141
17	132	135
18	161	-161
19	425	442
20	53	50
h 15 0		
1	596	-536
3	71	-88
4	153	140
7	181	-220
8	298	363
10	72	61
11	200	-225
12	235	256
13	280	328
15	152	165
16*	17	24
18	225	235
19	191	211
20	87	92
h 16 0		
0	179	169
1	312	285
3	282	-284
4	139	-156
5	122	116
6	166	-189
7	235	263
8	258	-296
10	128	143
14	46	-60
15	53	55
16	174	-188
17*	18	-16
18	187	-162
19	39	-43
h 17 0		
2	274	-251
3	453	-453
4	372	-393
5	98	-111
6*	18	21
7	227	-240
8	147	168
9	166	185
10	144	-158
11	152	173
13	68	-62
14	422	-483
15	66	-56
16*	32	24
17	73	75
18	59	60
19*	17	22
h 18 0		
1	141	131
3	214	-206
4	138	160
5*	32	32
6	202	217
7	102	-104
8	130	-151
9	148	164
13	348	-382
14	126	-136
15	140	-140
16	103	112
17	239	-237
18	82	-84
h 19 0		
2	241	-220
3	228	252
5	56	65
6	260	-270
7	183	193
8	81	-86
9	99	-105
10	164	-167
11	130	141
12	128	-98
14	96	-84
15	59	-60
16	97	100
17	93	-93
h 20 0		
0	125	142
1	84	-78
2	309	287
3	207	-217
4	160	-158
5	232	230
6	224	-220
7	211	219
8	328	339
9	393	400
10*	39	49
11	99	96
12	159	160
15	87	86
16	169	-163
h 21 0		
2	120	-96
3	166	175
4	101	-96
5	119	-108
6	195	-186
7	150	161
8	379	379
9*	16	-45
10	69	88
11	138	-145
12	126	137
13	78	-72
14	169	-177
16	26	6
h 22 0		
1	88	102
2	263	-283
4	78	63
5*	29	-20
7	111	116
8	124	-122
9	68	60
10	51	-63
11	78	74
12*	10	32
13	182	177
14	151	145
15	109	-97
h 23 0		
2	232	-233
4	61	-51
5	85	-91
6*	16	24
7	141	-135
8	144	138
9	115	-106
10	155	-144
11	154	153
13	221	-220
14	58	-70
h 24 0		
0	223	239
2	299	-300
5	106	-100
6	51	-50
7	53	-46
8*	25	-28
9	99	91
10	144	141
11	117	-113
12	101	-98
13	286	-274
h 25 0		
1*	19	22
3	178	173
5	192	177
7	151	153
8*	27	-48
9	96	-92
10	145	133
11	87	-80
12	89	-90
h 26 0		
0	56	47
1	80	-75
2	81	78
3	61	-72
4	162	142
5*	10	-2
6	121	-115
7*	10	34
8	114	107
9	58	-49
10	30	25
h 27 0		
1*	22	29
2	55	-47
3	115	113
4	162	-156
5	140	-136
6	280	249
7	146	141
8	214	201
9*	5	13
h 28 0		
0	132	-106
2	80	-70
4	60	56
5	94	-89
6	41	52
7	72	79
h 29 0		
1	164	-164
3	128	-118
h 0 1		
3	380	346
7	1223	1095
9	399	324
17	454	440
19	195	-214
h 1 1		
6	179	-162
9	88	-82
10	81	-99
11	265	-206
12	139	89
14	627	521
15	179	163
16	85	-57
18	206	187
21	96	-107
22	111	90
h 2 1		
1	134	89
2	566	-544
3	906	827
4	275	-233
6	207	-155
11	155	149
13	266	226
16	112	103
19	272	-292
20	280	289
22	138	111
h 3 1		
5	277	239
6	259	197
11	194	-164
13	300	235
15	256	-213
17	255	-275
18	353	-357
21	103	126
h 4 1		
6	166	104
7	150	-152
8	506	455
9	488	-402
11	70	-77
13	304	-256
14	242	189
16	317	280
19	311	-295
h 5 1		
2	1359	1251
3	793	764
4	275	215
6	64	73
7	204	159
8	630	-550
9	325	240
10	101	98
11	219	-204
13	160	143
14	180	139
15	443	-396
16	117	107
19	177	-190
20	200	-201
21	123	-131
22	53	-50
h 6 1		
3	90	-103
7	191	146
8	157	-126
9	168	-199
10*	47	62
13	272	235
14	186	-154
15	94	80
16*	48	-54
17	359	326
18	291	-279
19	135	144
20	183	194
21*	7	11
22	144	163
h 7 1		
1*	32	5
5	158	154
6	348	332
7	156	-138
10	135	-108
11	89	-93
12	185	175
13	109	-75
14	336	291
15	134	-123
16	91	87
17	380	344
18	176	162
19	251	-258
20	151	-161
21	119	131
22*	23	30
h 8 1		
0*	47	-40
1*	19	4
2	157	-137
5*	13	-54
7	738	-724
8	155	-143
10	79	87
11	143	-153
12	139	-125
13	347	302
14	270	-248
15	209	182
16	350	329
17	105	-100
18	96	-77
20	78	83
21	30	-34
22	55	64
h 9 1		
2	153	128
7	487	-482
9	175	203
10	65	-62
11	87	103
12*	5	22
13	380	363
14	59	46
15	101	-95
16	120	-123
17	320	-303
18	291	-284
19	145	142
20	134	-136
21	217	227
h 10 1		
0	116	124
1	95	-103
4	246	213
7	160	-167
9	191	-219
10	67	81
11	377	-390
12	155	-164
13	342	-322
14	59	57
15*	46	52
16	291	-284
17	183	-188
18	229	-224
19	43	-38
20	99	114
21	123	-139
h 11 1		
1	111	93
2	448	397
3*	26	-3
4*	10	-22
6*	47	45
7	74	94
8	163	-176
10	312	-380
11	77	-97
12	377	376
13	112	119
14*	6	-19
15	93	94
16	168	164
17	89	83
18	241	-235
19	85	83
20	195	-208
21	243	-290
h 12 1		
1	706	693
2	370	363
3*	28	55
4*	18	40
5	177	167
6	65	-68
7	91	-91
9	231	-265
10	176	194
11	379	440
12	204	215
13	207	217
14	158	-162
15	91	99
16	236	-246
17	46	-46
18	203	-204
19	39	35
20	31	33
h 13 1		
2	147	-150
3	75	-90
6	106	118
7	107	-132
8	221	240
9	204	-221
12	302	294
13	101	110
14*	24	-15
16	336	345
17*	19	-10
18	47	49
19	191	-191
20	111	114
h 14 1		
3*	31	44
4	239	-201
5	376	387
6	60	-65
8*	33	-47
9	261	307
10	182	-218
12*	29	-10
13	107	105
14	176	-175
15	368	363
16	118	112
17	140	-136
18	68	62
19*	24	-16
20	101	-105
h 15 1		
1*	3	-3
2	85	79
3	62	-72
4	442	420
5	583	-587
6	755	-755
7	61	-73
8	280	-329
9	92	-71
10	212	-243
11	123	158
13*	38	28
14	69	68
15	70	-56
16	64	-59
17	37	-29
18	106	-99
19	73	79
h 16 1		
3	79	71
4	114	127
6	487	-479
7	87	-64
8*	10	-11
9	106	125
10	92	113
11	130	-147
12	211	237
14	210	206
15	220	-221
16	406	-410
17	107	-105
18	35	11
19	20	-20
h 17 1		
1	136	164
2	143	-162
3	214	203
4	93	-116
5	53	48
6	62	-56
7	94	100
8	56	69
9*	25	-23
10	396	-438
13	45	-43
14	96	-86
15	106	104
16*	30	1
17	213	-195
18	58	58
h 18 1		
0	646	653
1	270	285
2	159	-188
3	217	202
5	87	75
8	86	97
9	195	-179
10	328	356
11	155	155
12	78	-67
13	195	181
14	98	90
15	37	-39
16*	13	-10
17	39	32

Table 4. *(Continued)*

h	$\|F_o\|$	F_c
h 19 1		
1	364	415
2	291	270
3*	31	32
5*	30	-3
7	90	-105
8	67	-62
10	180	214
11	323	342
12	111	110
13	154	-152
14	55	55
15	91	-90
16	141	130
17	332	-297
h 20 1		
1	230	-177
2	356	-342
3	128	-125
5	70	69
6	165	-163
7	105	111
8	75	-80
9	147	157
11*	19	26
12	138	134
13	119	-109
14	126	113
15	215	190
16	44	-37
h 21 1		
1	65	-47
2*	39	28
3*	23	45
4	129	134
5	346	-330
6	126	110
7	69	83
8	159	-159
9	61	-66
10	51	53
13	126	-112
14	169	142
h 22 1		
0*	21	-17
1*	42	-34
2	101	96
3	111	112
4	212	-225
5	210	-203
6	375	-370
7	159	-164
8	148	151
9	145	-139
10*	30	40
11	38	-42
12	179	166
h 23 1		
1	61	57
2	55	-60
3	116	117
4	148	-146
5	71	-70
6	137	134
8	39	38
9	58	-56
11	128	120
12	116	-107
13	120	113
h 24 1		
0	231	273
1	176	-145
2	62	50
3	51	-48
4	149	142
5	176	-156
6	92	96
9	146	-137
10	84	87
11	171	-148
12	32	-30
h 25 1		
1	225	205
2	145	157
3	140	-145
4	132	130
5*	18	3
6*	28	15
7	129	-126
9	155	132
10	206	172
11	237	199
h 26 1		
0	135	159
1	135	-152
3*	15	25
4*	10	-11
5*	7	-23
6	77	-80
7	46	31
8	202	-174
9	185	157
h 27 1		
1	150	-145
3*	19	-29
4	72	-57
5	62	-54
6	179	156
7	134	-110
h 28 1		
1	87	65
2	97	98
3*	17	43
h 0 2		
2	69	-66
10	702	-652
12	208	160
14	155	137
16	441	376
18	250	231
h 1 2		
2*	15	20
3	132	127
4	67	75
5*	21	-16
8*	24	-15
9*	35	16
12	87	72
14	146	126
16	198	-177
17	149	140
20	401	-447
h 2 2		
2*	44	41
3	169	-202
4	277	-285
5	323	-350
6	306	302
7	189	-201
8	131	119
9	132	-133
10	195	159
11	191	-179
12*	37	-39
13*	39	-43
14	210	-190
15	506	-456
16	307	283
17*	33	48
19	131	125
21	207	-226
h 3 2		
1*	19	-13
4	272	301
5	1055	1068
6	466	-393
8	422	424
9	66	-58
11	270	-244
12	123	106
13	110	-89
14	242	-205
15	130	153
16	102	-119
17	135	124
18*	33	23
19	163	-170
20	52	-39
21	133	-138
h 4 2		
3*	26	-21
4	380	376
5	189	160
6	640	611
7	385	-426
8	187	-187
9*	32	-76
11	139	-118
12	266	-228
13	153	128
14	100	71
15	613	543
16	246	210
17	94	-95
18	104	-105
20	34	59
21*	19	24
h 5 2		
2*	23	13
4	384	419
5	316	-301
6	234	263
7	119	-109
8	307	331
9	362	361
10	280	277
11	124	-128
12	375	336
13*	21	5
14	146	133
15	91	69
16	365	341
17	99	82
18	124	-131
19	227	217
20	114	116
h 6 2		
0	509	-545
5*	13	11
7	121	-147
8	104	93
10	474	-483
11	251	256
12	365	-255
13	230	-211
14	77	64
15	68	53
16*	44	46
17*	24	-23
18	193	202
19	309	312
20	31	-18
h 7 2		
3*	19	-1
4*	34	-3
5*	21	26
6	64	77
7	188	193
8	123	-122
9	393	-403
11	217	-220
12	396	371
13	191	181
14	171	-155
15	226	206
16	126	121
17	218	203
18	223	-222
20	228	-232
h 8 2		
0	213	246
7	76	-72
8	87	104
10	96	-115
11	268	-270
12	51	-68
13*	26	20
14	318	-316
16	100	97
17	132	-135
19	213	-202
20	116	-125
h 9 2		
1*	30	-20
3*	11	-76
5*	28	66
6	451	-542
7	291	320
8	118	110
9	80	-99
10	179	-204
11	284	324
12	135	-155
13	201	-195
14	195	-202
15	188	176
16	141	-138
17	253	245
18	64	66
19	100	-112
20	30	35
h 10 2		
1*	61	-63
2	112	-105
6	391	475
7	168	-184
8*	29	8
9	224	289
10	195	-239
12	134	-183
13	197	224
14	66	72
15	152	166
16	40	-47
17	109	-115
18	73	74
19	29	38
h 11 2		
1	114	-116
2	117	-131
3	154	168
5*	17	-20
7*	29	48
8*	20	-70
10	203	-245
11*	15	10
13	64	81
16	202	220
17	164	-173
18	54	-64
19	162	181
h 12 2		
0	182	193
10	53	68
11	126	156
12	255	-319
13	83	95
14	158	176
16	145	-161
17	92	113
18	208	220
19	24	24
h 13 2		
1	386	-387
5	101	128
13	140	-166
14	141	-157
15	193	215
16*	21	29
17*	28	-30
18	95	107
h 14 2		
1	286	265
3	114	132
4	147	163
7*	20	-37
12	48	35
13	55	63
14	68	83
15	78	88
16	105	114
17	100	-116
18	130	137
h 15 2		
3	68	71
4	102	-113
5*	34	-54
9*	25	-55
10*	40	-53
12	161	-208
13	210	-269
14*	16	21
15	121	-133
16	29	-23
17*	8	3
h 16 2		
0	99	-125
4	108	137
5	80	-92
9	55	75
11*	41	31
13*	12	-21
14	38	48
15*	27	-44
16	138	151
h 17 2		
2	211	204
4	264	318
6*	24	-18
7	158	196
10	100	128
12*	22	26
13	40	35
15	55	54
16*	12	-18
h 18 2		
0*	9	18
1	101	-99
2*	31	-10
3	169	178
5*	17	-22
6	135	-178
14	99	112
15	120	120
h 19 2		
2	181	184
5*	24	-54
6	175	217
7	135	-161
10	111	138
11	96	-118
14	71	74
h 20 2		
0	93	-120
1	70	65
4	108	127
5	151	-183
6	144	180
7	140	-179
8	225	-281
9	271	-333
10	37	-41
11	64	-80
12	112	-134
h 21 2		
1	60	42
3	110	-140
5	74	89
6	127	149
7	110	-132
8	267	-325
9*	10	38
11	97	117
12	96	-116
13	33	60
h 22 2		
1*	30	-84
2	178	230
4	45	-56
5*	33	19
6	52	54
7	78	-97
8	82	103
9	45	-51
10	35	54
11	47	-63
h 23 2		
2	152	197
3	120	129
4	42	44
5	68	81
7	94	113
8	105	-118
9	78	90
10	109	120
h 24 2		
0	177	-204
2	198	249
3	185	203
4	52	43
5	73	84
6	38	42
7	32	37
8*	11	25
9	71	-77
h 25 2		
3	124	-143
4*	15	-24
5	130	-146
7	116	-130
h 26 2		
0	39	-45
1*	23	63
2	47	-67
3	39	57
4	100	-121
h 0 3		
3	253	-208
5*	51	-42
7	680	-659
9	254	-194
13	466	-429
15*	34	-15
17	264	-317
h 1 3		
6	136	90
9	68	52
10*	53	40
11	164	135
12	78	-66
13	357	275
14	404	-367
15	118	-108
18	124	-120
h 2 3		
5*	25	-12
11	100	-85
13	138	-154
16	67	-71
17	160	156
18	188	123
h 3 3		
1	139	-142
2	160	130
5	134	-121
6	171	-120
11	124	103
13	197	-171
15	155	132
17	147	173
18	222	251
h 4 3		
6	94	-76
7	98	104
8	357	-282
9	348	262
11	62	62
13	200	167
16	184	-191
17	78	93
18	78	-74
h 5 3		
1	343	-349
4	145	-133
6*	28	-46
7	110	-97
8	452	362
9	216	-169
10	61	-52
11	143	124
13	118	-102
14	115	-105
15	273	264
16	87	-82
17	80	70
18	77	86
h 6 3		
0	303	303
1	226	-203
4	234	221
5*	40	43
7	105	-100
8	80	84
9	124	126
10*	13	-42
11	72	-48
12	541	-471
13	188	-168
14	113	116
15	55	-64
16	38	47
17	212	-224
h 7 3		
2	94	66
4	283	-273
5	93	-92
6	203	-201
7	97	99
8	247	-245
10	101	88
11	68	54
12	126	-112
13	60	47
14	211	-207
15	80	84
16	61	-67
17	237	-237
h 8 3		
0*	52	44
4	416	393
7	428	452
8	100	97
9	70	85
10	62	-56
11	106	85
12	96	74
13	233	-214
14	182	168
15	135	-127
16	226	-225
17	66	72
h 9 3		
1*	13	22
2*	59	-76
3	268	233
4	512	-478
5	166	160
6	359	359
8*	19	-7
9	116	-134
10	58	58
11	66	-65
13	262	-245
14	48	-33
15	74	79
16	78	80
h 10 3		
0*	59	-74
1*	20	49
4	134	-125
7	101	118
8*	26	2
9	130	140
10	59	-66
11	287	258
12	101	98
13	250	222
14	37	-34
15	37	-32
16	185	194
h 11 3		
1*	58	-74
3*	33	-21
4*	31	11
6*	28	-15
7*	50	-63
8	101	121
9	286	-310
10	261	264
11	68	63
12	286	-262
13	87	-80
15	55	-49
16	106	-116
h 12 3		
0	404	-390
1	492	-443
2	247	-230
3*	34	-39
4*	22	-12
5	127	-110
6*	25	54
7*	48	71
8	64	45
9	150	172
10	144	-146
11	301	-295
12	160	-159
13	171	-159
14	116	105
15	64	-76
h 13 3		
2	92	90
3	53	58
4*	33	1
6	63	-82
7	75	89
8	148	-171
9	136	149
10	87	92
11	355	-340
12	237	-219
13	71	-71
14*	20	5
h 14 3		
0*	17	-7
2*	33	18
4	151	146
5	254	-249
6	55	58
8	43	30
9	194	-202
10	137	148
11*	32	-7
12*	15	5
13	81	-75
14	114	112
h 15 3		
1*	16	-2
2	39	-61
3*	37	51
4	307	-288
5	399	395
6	509	504
7	58	61
8	188	216
10	177	169
11	112	-114
12	30	22
13	26	-17
14	53	-47
h 16 3		
0*	34	-57
2*	30	-17
3	49	-36
4	68	-80
6	329	332
7	45	52
8*	11	10
9	87	-64
10	87	-82
11	114	112
12	173	-165
13	64	64
h 17 3		
2	93	105
3	149	-138
6*	24	32
7	60	-68
8	51	-48
h 18 3		
0	458	-464
1	201	-190
2	114	117
3	133	-137
4*	34	-24
5	60	-54
6*	10	17
7*	14	-2
8	61	-67
10	266	-246
11	116	-100
h 19 3		
1	274	-281
2	202	-188
5*	14	14
6	46	-53
7	65	69
8	39	39
10	159	-148
h 20 3		
1	136	122
2	247	233
3	84	79
4*	28	32
5	49	-48
6	111	119
7	70	-78
8	64	59
9	124	-116
h 21 3		
1	46	41
2*	24	-22
3*	5	-21
4	88	-86
5	230	232
6	78	-72
7	52	-49
h 22 3		
1*	14	26
2	58	-66
3	70	-80
4	141	134
5	133	136
h 23 3		
1	39	-48
h 0 4		
10	456	374
12	79	-69
h 1 4		
3*	43	-46
4*	16	-41
6*	23	8
7*	45	-33
8*	26	22
11	261	229
13*	9	-5
h 2 4		
3	102	115
4	142	142
5	173	174
6	194	-184
7	99	92
8	68	-73
9	94	76
11	90	93
12*	20	39
h 3 4		
5	527	-571
6	248	236
7*	19	-26
9*	21	31
10*	33	4
11	152	150
12	59	-53
h 4 4		
0*	26	14
5	83	-98
6	302	-340
7	210	217
8	108	104
9*	12	26
11	63	53
12	139	130
h 5 4		
5	152	153
11	83	78
12	213	-209
h 6 4		
2*	33	27
7*	31	71
8	44	-40
10	290	277
11	145	-142
h 7 4		
6*	34	-25
7	85	-105
8	72	76
9	215	233
10	326	323
11	145	143
h 8 4		
4*	19	55
5*	30	-48
6*	14	-14
7	62	57
8*	30	-62
9	236	243
10	35	72
11	155	165
h 9 4		
2*	5	54
5*	19	-55
8	48	-66
9	58	57
10	101	120
h 10 4		
0*	20	14
7	85	106
8*	21	-14
9	116	-146
10	114	131
h 11 4		
5*	9	9
7*	19	-45
8*	23	31
9*	19	-30
h 12 4		
3*	29	-54
5*	24	-51
h 13 4		
3*	19	17
5*	16	-61
6*	26	4
7*	28	-56
h 15 4		
3*	22	-42
4*	30	66

and later anisotropically. There was no other peak in the difference Fourier, which was almost flat.

The final R value at the end of the anisotropic refinement for all the atoms was $9.6^0/_0$ for the observed 1217 reflections ($10.8^0/_0$ for all the 1432 reflections). Reflections with $I < 2.33\,\sigma(I)$ were assigned as unobserved reflections.

In the course of these calculations, individual weights were calculated by the modified formula of GABE (1966) and these were assigned for the reflections

$$w = \frac{1}{\sigma^2(F)} = 4F_o^2 \Big/ \sum_{i=1}^{4} \left(\frac{\partial F_o^2}{\partial q_i}\right)^2 \sigma^2(q_i)\,,$$

where q_1 = peak count, q_2 = background count, $q_3 = (LP)^{-1}$ and q_4 = transmission. The effect of anomalous dispersion was taken into consideration, but no significant difference was found between the enantiomorphs.

A block-diagonal least-squares program written by ENGEL (1968) for the BullGamma30S was used in the earlier stages of the analysis and in the later stages, a program of the same author for IBM 370/155 was used (ENGEL, 1972).

A list of the final observed and calculated structure amplitudes is given in Table 4.

Description of the structure

The final atomic coordinates are given in Table 5(a) and the anisotropic temperature factors in Table 5(b). The root-mean-square displacement of the atoms along the principal axes of the vibration ellipsoids are given in Table 6. The atomic arrangement projected down the c axis is shown in Fig. 1. The structure proposed by WEITZ and HELLNER is essentially correct, as can be seen from Table 5(a). The average shift in the coordinates of the heavy atoms from the model of WEITZ and HELLNER is 0.012 Å (0.008 Å in the a direction and 0.017 in the b direction), and in that of the sulfur atoms is 0.024 Å (0.021 in the a direction and 0.026 Å in the b direction). The largest shift in a heavy-atom coordinate is 0.03 Å and in that of a sulfur atom is 0.05 Å. WEITZ and HELLNER did not find any statistical copper in their structure.

The interatomic distances and angles are tabulated in Tables 7a and 7b. A distinction of Pb from Bi is impossible by x-ray measurements, as the difference in their atomic scattering amplitudes is only unity. However, a study of their coordinations permits one to make a distinction between them. As can be seen from Table 7a, four metal atoms [Pb(1), Pb(2), Bi(1), Bi(2)] have three nearest sulfur atoms in the range of 2.57 to 2.84 Å, whereas the remaining four metal atoms have no sulfur atom at a distance shorter than 2.72 Å. The former are therefore regarded as bismuth atoms and the latter as lead atoms. These values are in good agreement with those found in other bismuth-lead sulfides, as aikinite and galenobismutite, as can be seen from Table 8.

Cosalite has four independent lead and bismuth atoms in the structure. Six sulfur atoms around Pb(1) make a distorted octahedron. The octahedron is built up by S(3′), S(8), S(8′), S(5′), S(5″) and S(7). Pb(2) also has a distorted octahedral configuration with S(3′), S(3″), S(3‴), S(4), S(1′) and S(1″). The octahedron around Pb(1) is a little more distorted than the one around Pb(2). These octahedra are arranged parallel to the *c* axis. These Pb—S distances are in the range 2.72 to 3.02 Å and are in good agreement with the value found in galena (2.97 Å). The mean standard deviation in Pb—S distances is 0.01 Å. Similar coordination for the lead atom is also found in marrite

Table 5a. *The final atomic coordinates of cosalite, their standard deviations and occupancy factors.* In brackets: atomic coordinates given by WEITZ and HELLNER (1960)

Atom	x	y	z	Occupancy factor
Bi(1)	0.98212(9) [−0.018]	0.15503(9) [0.155]	0.25 [0.25]	
Bi(2)	0.09276(10) [0.093]	0.30330(10) [0.302]	0.25 [0.25]	
Pb(1)	0.27415(10) [0.274]	0.04064(10) [0.040]	0.25 [0.25]	
Pb(2)	0.03437(15) [0.035]	0.43512(13) [0.433]	0.75 [0.75]	
Bi(3)	0.08994(11) [0.091]	0.01082(10) [0.011]	0.75 [0.75]	
Bi(4)	0.18547(10) [0.186]	0.17157(9) [0.171]	0.75 [0.75]	
Pb(3)	0.38270(13) [0.383]	0.20591(12) [0.206]	0.25 [0.25]	
Pb(4)	0.29262(11) [0.293]	0.37318(12) [0.374]	0.25 [0.25]	0.50
S(1)	0.4766(6) [0.476]	0.1384(6) [0.138]	0.75 [0.75]	
S(2)	0.0292(6) [0.029]	0.2286(8) [0.230]	0.75 [0.75]	
S(3)	0.4141(8) [0.413]	0.9987(8) [0.002]	0.25 [0.25]	
S(4)	0.1518(7) [0.152]	0.3623(6) [0.364]	0.75 [0.75]	
S(5)	0.2823(7) [0.285]	0.4646(8) [0.465]	0.75 [0.75]	
S(6)	0.2279(6) [0.228]	0.2376(6) [0.235]	0.25 [0.25]	
S(7)	0.1278(6) [0.131]	0.0884(6) [0.088]	0.25 [0.25]	
S(8)	0.3066(6) [0.306]	0.1244(7) [0.125]	0.75 [0.75]	
S(9)	0.3622(8) [0.360]	0.2959(7) [0.296]	0.75 [0.75]	0.50
S(10)	0.4346(7) [0.434]	0.4152(7) [0.418]	0.25 [0.25]	0.50
Cu(1)	0.386(3)	0.057(3)	0.75	0.12

Table 5b. *The final anisotropic temperature-factor coefficients for cosalite*
The values are the coefficients in the expression
$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Bi(1)	0.00055(4)	0.00105(3)	0.025(2)	0.00000(5)	0	0
Bi(2)	68(4)	105(3)	30(2)	0(5)		
Pb(1)	89(4)	126(4)	27(3)	7(6)		
Pb(2)	184(7)	154(5)	45(3)	− 13(8)		
Bi(3)	91(4)	121(4)	23(2)	− 2(6)		
Bi(4)	64(4)	112(3)	32(2)	7(6)		
Pb(3)	134(5)	140(4)	33(3)	3(7)		
Pb(4)	93(5)	162(5)	34(3)	− 1(7)		
S(1)	0.0004(2)	0.0009(2)	0.024(14)	−0.0003(3)		
S(2)	4(3)	17(3)	14(14)	− 2(4)		
S(3)	11(3)	13(3)	28(16)	13(4)		
S(4)	8(3)	9(2)	41(17)	− 1(4)		
S(5)	9(3)	16(3)	18(16)	− 0(4)		
S(6)	2(2)	11(2)	35(15)	− 3(3)		
S(7)	4(3)	9(2)	48(16)	9(4)		
S(8)	4(3)	13(2)	8(13)	1(3)		
S(9)	13(3)	13(3)	9(14)	− 4(4)		
S(10)	7(3)	12(2)	11(13)	3(4)		
Cu(1)	27(12)	22(10)	0.08(7)	12(17)		

Table 6. *The root-mean-squared displacement of the atoms of cosalite along the principal axes of the vibration ellipsoids and direction cosines of these axes with respect to the crystallographic axes*

Atom	B_{isotrop}	Axes	B	$\sqrt{\bar{u}^2}$	$\cos\alpha_1$	$\cos\alpha_2$	$\cos\alpha_3$
Bi(1)	1.62 Å^2	1	0.80 Å^2	0.101 Å	1	0	0
		2	2.40	0.174	0	1	0
		3	1.67	0.145	0	0	1
Bi(2)	1.79	1	0.99	0.112	1	0	0
		2	2.40	0.174	0	1	0
		3	1.97	0.158	0	0	1
Pb(1)	1.98	1	1.30	0.128	0.999	− 0.040	0
		2	2.88	0.191	0.040	0.999	0
		3	1.78	0.150	0	0	1
Pb(2)	3.05	1	2.67	0.184	0.990	0.139	0
		2	3.53	0.212	− 0.139	0.990	0
		3	2.95	0.193	0	0	1

Table 6. *(Continued)*

Atom	B_{isotrop}	Axes	B	$\sqrt{\bar{u}^2}$	$\cos\alpha_1$	$\cos\alpha_2$	$\cos\alpha_3$
Bi(3)	1.87 Å^2	1	1.33 Å^2	0.130 Å	1	0.013	0
		2	2.76	0.187	− 0.013	1	0
		3	1.53	0.139	0	0	1
Bi(4)	1.87	1	0.93	0.109	0.999	− 0.039	0
		2	2.56	0.180	0.039	0.999	0
		3	2.11	0.164	0	0	1
Pb(3)	2.45	1	1.95	0.157	1	− 0.022	0
		2	3.20	0.201	0.022	1	0
		3	2.19	0.167	0	0	1
Pb(4)	2.43	1	1.36	0.131	1	0.004	0
		2	3.70	0.216	− 0.004	1.000	0
		3	2.23	0.168	0	0	1
S(1)	1.36	1	0.48	0.078	0.989	0.149	0
		2	2.02	0.160	− 0.149	0.989	0
		3	1.58	0.142	0	0	1
S(2)	1.81	1	0.61	0.088	0.998	0.066	0
		2	3.92	0.223	− 0.066	0.998	0
		3	0.91	0.107	0	0	1
S(3)	2.14	1	0.89	0.106	0.862	− 0.507	0
		2	3.69	0.216	0.507	0.862	0
		3	1.85	0.153	0	0	1
S(4)	2.00	1	1.19	0.123	0.996	0.088	0
		2	2.13	0.164	− 0.088	0.996	0
		3	2.68	0.184	0	0	1
S(5)	2.03	1	1.36	0.131	1	0.012	0
		2	3.56	0.212	− 0.012	1	0
		3	1.18	0.122	0	0	1
S(6)	1.69	1	0.25	0.056	0.994	0.109	0
		2	2.52	0.178	− 0.109	0.994	0
		3	2.30	0.171	0	0	1
S(7)	1.92	1	0.25	0.056	0.901	− 0.433	0
		2	2.33	0.172	0.433	0.901	0
		3	3.17	0.200	0	0	1

Table 6. *(Continued)*

Atom	B_{isotrop}	Axes	B	$\sqrt{\bar{u}^2}$	$\cos\alpha_1$	$\cos\alpha_2$	$\cos\alpha_3$
S(8)	1.33 Å^2	1	0.56 Å^2	0.085 Å	0.999	— 0.044	0
		2	2.86	0.190	0.044	0.999	0
		3	0.55	0.084	0	0	1
S(9)	1.80	1	1.77	0.150	0.996	0.257	0
		2	3.05	0.197	— 0.257	0.996	0
		3	0.59	0.087	0	0	1
S(10)	1.53	1	1.01	0.113	0.988	— 0.153	0
		2	2.87	0.191	0.153	0.988	0
		3	0.70	0.094	0	0	1
Cu(1)	4.83	1	3.25	0.203	0.852	— 0.524	0
		2	5.82	0.272	0.524	0.852	0
		3	5.42	0.262	0	0	1

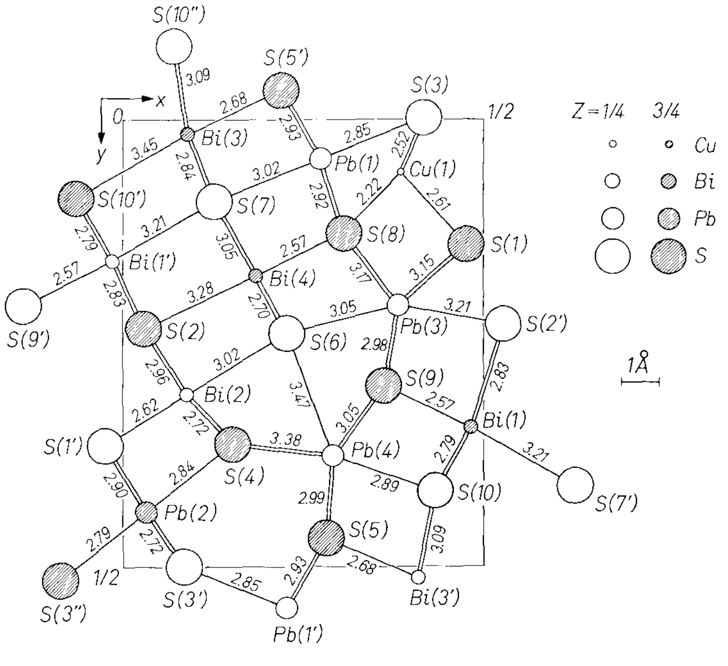

Fig. 1. A projection of the structure of cosalite ‖ c

Table 7a. *Interatomic distances in cosalite*

Pb(1)–S(3′)	2.854(15) Å	
S(8)	2.915(11)	(2×]
S(5′)	2.929(13)	[2×]
S(7)	3.020(12)	
Mean	2.927	
Pb(2)–S(3′)	2.719(12) Å	[2×]
S(3′′′)	2.789(16)	
S(4)	2.838(14)	
S(1′)	2.902(9)	[2×]
Mean	2.812	
Pb(3)–S(9)	2.982(13) Å	[2×]
S(6)	3.051(11)	
S(1)	3.151(10)	[2×]
S(8)	3.166(11)	[2×]
S(2′)	3.205(14)	
Mean	3.107	
Pb(4)–S(10)	2.891(13) Å	
S(5)	2.987(14)	[2×]
S(9)	3.047(12)	[2×]
S(4)	3.379(10)	[2×]
S(6)	3.466(14)	
Mean	3.148	
S(1)–S(8)	3.265(16) Å	
S(3′)	3.88(2)	
S(2′)	3.900(19)	[2×]
S(4′)	3.913(15)	[2×]
S(3′′)	4.085(19)	[2×]
S(9)	4.35(2)	
S(2)–S(9′)	3.825(17) Å	[2×]
S(10′)	3.88(2)	
S(4)	3.96(2)	
S(6)	4.309(14)	[2×]
S(7)	4.346(19)	[2×]
S(3)–S(3′)	3.859(17) Å	[2×]
S(4)	4.039(20)	
Cu(1′′′)	4.04(6)	
S(8′)	4.165(19)	[2×]
S(5)	4.341(18)	[2×]
S(4)–S(5)	3.49(2) Å	
S(6)	3.886(17)	[2×]
S(9)	4.32(2)	
S(5)–S(10)	3.737(17) Å	[2×]
Cu(1′)	3.89(6)	
S(7)	3.976(19)	[2×]
S(8′)	4.18(2)	
S(9)	4.31(3)	
S(6)–S(9)	3.554(16) Å	[2×]
S(8)	3.700(17)	[2×]
S(7)	4.046(19)	
S(7)–S(8)	4.064(14) Å	[2×]
S(10′)	4.211(15)	
S(10′′)	4.31(2)	[2×]
S(8)–S(9)	4.23(2) Å	
S(9)–S(10)	3.761(19) Å	[2×]
Bi(1)–S(9′)	2.572(16) Å	
S(10)	2.785(11)	[2×]
S(2′)	2.831(12)	[2×]
S(7′)	3.205(12)	
Mean	2.835	
Bi(2)–S(1′)	2.619(12) Å	
S(4)	2.715(10)	[2×]
S(2)	2.962(12)	[2×]
S(6)	3.021(12)	
Mean	2.832	
Bi(3)–S(5′)	2.678(15) Å	
S(7)	2.841(10)	[2×]
S(10′)	3.090(12)	[2×]
S(10′′′)	3.453(14)	
Mean	2.999	
Bi(4)–S(8)	2.573(12) Å	
S(6)	2.695(9)	[2×]
S(7)	3.046(10)	[2×]
S(2)	3.281(13)	
Mean	2.889	
Cu(1)–S(8)	2.22(6) Å	
S(3′)	2.52(4)	[2×]
S(1)	2.61(6)	
Mean	2.464	

Table 7b. *Bond angles in cosalite*

S(3′)—Pb(1)—S(5′)	97.3(4)°*
S(7)	178.4(5)
S(8)	92.4(3)*
S(5′)—Pb(1)—S(5″)	87.7(3)
S(7)	83.9(4)*
S(8)—Pb(1)—S(5′)	91.2(3)*
S(5″)	170.3(4)*
S(7)	86.4(3)*
S(8′)	88.2(3)
S(1′)—Pb(2)—S(1″)	88.7(3)
S(3′)—Pb(2)—S(1′)	87.4(3)*
S(1″)	176.1(4)*
S(3″)	96.5(4)
S(3‴)	88.9(4)*
S(4)	93.2(4)*
S(3‴)—Pb(2)—S(1′)	91.7(4)*
S(4)	176.7(5)
S(4)—Pb(2)—S(1′)	85.9(3)*
S(1)—Pb(3)—S(1′)	80.2(2)
S(2′)	75.7(3)*
S(8)	62.2(3)*
S(8′)	111.0(3)*
S(6)—Pb(3)—S(1)	132.7(2)*
S(2′)	136.4(4)
S(8)	73.0(3)*
S(8)—Pb(3)—S(2′)	134.5(2)*
S(8′)	79.7(2)
S(9)—Pb(3)—S(1)	90.3(3)*
S(1′)	151.8(4)*
S(2′)	76.3(4)*
S(6)	72.2(4)*
S(8)	87.0(3)*
S(8′)	145.0(4)*
S(9′)	85.7(3)
S(4)—Pb(4)—S(4′)	73.8(2)
S(6)	69.2(3)*
S(5)—Pb(4)—S(4)	66.2(4)°*
S(4′)	114.3(3)*
S(5)	85.5(4)
S(6)	131.3(3)*
S(9)	91.1(3)*
S(9′)	157.5(4)*
S(9)—Pb(4)—S(4)	84.3(3)*
S(4′)	134.4(4)*
S(6)	65.8(3)*
S(9′)	83.5(3)
S(10)—Pb(4)—S(4)	140.6(2)*
S(5)	78.9(4)*
S(6)	131.2(4)
S(9)	78.6(4)*
S(2′)—Bi(1)—S(2″)	91.5(4)
S(7′)	91.9(3)*
S(9′)—Bi(1)—S(2′)	90.0(4)
S(7′)	177.3(5)
S(10)	89.1(4)*
S(10)—Bi(1)—S(2′)	178.7(4)*
S(2″)	87.5(3)*
S(7′)	89.1(3)*
S(10′)	93.5(3)
S(1′)—Bi(2)—S(4)	94.4(4)*
S(2)	88.4(3)*
S(6)	179.2(4)
S(2)—Bi(2)—S(2′)	86.5(3)
S(6)	92.2(3)*
S(4)—Bi(2)—S(2)	88.3(3)*
S(2′)	174.0(4)*
S(4′)	96.7(3)
S(6)	85.1(3)*
S(5′)—Bi(3)—S(7′)	92.2(4)*
S(10′)	80.4(4)*
S(10‴)	173.6(5)

Table 7b. *(Continued)*

S(7)—Bi(3)—S(7′)	91.1(3)°
S(10′)	93.0(3)*
S(10″)	171.6(3)*
S(10‴)	83.4(3)*
S(10′)—Bi(3)—S(10″)	82.1(3)
S(10‴)	104.4(3)*
S(6)—Bi(4)—S(2)	91.7(3)*
S(6′)	97.6(3)
S(7)	89.4(3)*
S(7′)	172.8(3)*
S(7)—Bi(4)—S(2)	86.7(3)*
S(7′)	83.5(2)
S(8)—Bi(4)—S(2)	178.6(5)
S(6)	89.2(3)*
S(7)	92.3(3)*
S(3′)—Cu(1)—S(1)	105.7(1.5)*
S(3″)	108.0(2)
S(8)—Cu(1)—S(1)	85.0(2)
S(3′)	123.3(1.2)*
Cu(1)—S(1)—Bi(2′)	163.7(1.4)
Pb(2′)	78.4(1.0)*
Pb(3)	90.3(1.0)*
Bi(2′)—S(1)—Pb(2′)	90.0(3)*
Pb(3)	102.1(4)*
Pb(2′)—S(1)—Pb(2″)	88.7(4)
Pb(3)	167.5(4)*
Pb(3′)	94.36(0.08)*
Pb(3′)—S(1)—Pb(3)	80.2(3)
Bi(1′)—S(2)—Bi(1″)	91.5(5)
Bi(2)	174.3(5)*
Bi(2′)	90.77(0.05)*
Bi(4)	91.8(4)*
Pb(3′)	91.5(3)*
Bi(2)—S(2)—Bi(2′)	86.5(4)
Bi(4)	83.0(3)*
Pb(3′)	93.7(4)*
Pb(3′)—S(2)—Bi(4)	175.4(6)
Cu(1′)—S(3)—Cu(1″)	107.6(1.8)°
Pb(1′)	66.8(1.2)*
Pb(2)	170.8(1.3)*
Pb(2′)	77.5(1.2)*
Pb(2″)	82.2(1.4)*
Pb(1′)—S(3)—Pb(2″)	124.9(7)
Pb(2)—S(3)—Pb(1′)	122.4(4)*
Pb(2′)	96.5(5)
Pb(2″)	91.1(4)*
Bi(2)—S(4)—Bi(2′)	96.7(5)
Pb(2)	89.4(3)*
Pb(4)	85.5(2)*
Pb(4′)	145.0(5)*
S(5)	131.3(2)*
Pb(2)—S(4)—Pb(4)	125.6(4)*
S(5)	97.8(5)
Pb(4)—S(4)—Pb(4′)	73.8(3)
S(5)	51.5(3)*
Bi(3′)—S(5)—Pb(1)	94.6(5)*
Pb(4)	104.0(4)*
S(4)	159.9(7)
Pb(1)—S(5)—Pb(1′)	87.7(5)
Pb(4)	90.4(1)*
Pb(4′)	161.5(6)*
S(4)	99.9(4)
Pb(4)—S(5)—Pb(4′)	85.5(5)
S(4)	62.3(3)*
Bi(2)—S(6)—Pb(3)	163.1(5)
Pb(4)	79.6(3)
S(9)	114.4(4)
Bi(4)—S(6)—Bi(2)	92.7(3)*
Bi(4′)	97.7(5)
Pb(3)	98.4(3)*
Pb(4)	130 9(2)*
S(9)	91.0(2)
Bi(4′)—S(6)—S(9)	151.2(5)
Pb(3)—S(6)—Pb(4)	83.5(3)
S(9)	53.0(3)

Table 7b. *(Continued)*

Pb(4)–S(6)–S(9)	51.4(3)°
Bi(3)–S(7)–Bi(1′)	95.9(3)*
Bi(3′)	91.1(4)
Bi(4)	92.40(0.05)*
Bi(4′)	173.2(4)*
Pb(1)	89.4(3)*
Bi(4)–S(7)–Bi(4′)	83.5(3)
Bi(4′)–S(7)–Bi(1′)	89.4(3)*
Pb(1)–S(7)–Bi(1′)	172.4(5)
Bi(4)	84.9(3)*
Cu(1)–S(8)–Bi(4)	159.1(1.7)
Pb(1)	69.2(1.1)*
Pb(3)	97.8(1.2)*
Bi(4)–S(8)–Pb(1)	96.3(3)*
Pb(3)	98.2(4)*
Pb(1)–S(8)–Pb(1′)	88.2(4)
Pb(3)	94.23(0.08)*
Pb(3′)	164.9(4)*
Pb(3)–S(8)–Pb(3′)	79.7(3)
Bi(1′)–S(9)–Pb(3)	102.2(4)°*
Pb(4)	96.5(4)*
S(6′)	145.2(2)
Pb(3)–S(9)–Pb(3′)	85.7(4)
Pb(4)	92.35(0.11)*
Pb(4′)	161.2(6)*
S(6′)	101.6(5)
Pb(3′)–S(9)–S(6′)	54.8(3)
Pb(4)–S(9)–S(6′)	107.6(5)
Pb(4′)–S(9)–Pb(4)	83.5(4)
S(6′)	62.8(3)
Bi(1)–S(10)–Bi(1′)	93.5(5)
Bi(3)	90.95(0.09)*
Bi(3′)	166.6(5)*
Bi(3″)	91.6(3)*
Pb(4)	95.5(4)*
Bi(3)–S(10)–Bi(3′)	82.1(4)
Bi(3″)	75.7(3)*
Pb(4)–S(10)–Bi(3)	96.6(3)*
Bi(3″)	169.6(6)

* = [2×]

(Wuensch and Nowacki, 1967) and dufrenoysite (Ribár, Nicca and Nowacki, 1969).

The Pb(3) and Pb(4) atoms have a coordination of eight, which could be described as a trigonal prism || c, and additional two S atoms. For Pb(3), the trigonal prism is formed by S(9), S(9′), S(1), S(1′), S(8) and S(8′). Almost perpendicular to the face formed by S(8), S(8′), S(9), S(9′) lies the S(6) at a distance of 3.05 Å and almost perpendicular to the face formed by S(1), S(1′), S(9), S(9′) lies S(2′) at a distance of 3.21 Å. The atoms S(5), S(5′), S(9), S(9′), S(4) and S(4′) form the trigonal prism around Pb(4) and almost normal to the faces formed by S(9), S(9′), S(4), S(4′) and S(9), S(9′), S(5), S(5′) lie S(6) and S(10) at distances of 3.47 and 2.89 Å respectively. These Pb—S distances are in the range 2.89 to 3.47 Å and have a mean standard deviation of 0.01 Å. Similar coordination for the lead atom is also found in bournonite and seligmannite (Edenharter, Nowacki and Takéuchi, 1970), in hatchite

Table 8. *Coordination of Bi and Pb in cosalite, aikinite and galenobismutite*

Bi—S		Pb—S		Bi—S		Pb—S	
Cosalite				*Galenobismutite*			
2.57 Å	(1)	2.85 Å	(1)	2.63 Å	(1)	2.85 Å	(1)
2.79	(2)	2.92	(2)	2.73	(2)	2.98	(2)
2.83	(2)	2.93	(2)	2.99	(2)	3.01	(2)
3.21	(1)	3.02	(1)	3.12	(1)	3.21	(2)
2.62	(1)	2.72	(2)	2.78	(2)		
2.72	(2)	2.79	(1)	2.79	(1)		
2.96	(2)	2.84	(1)	3.00	(1)		
3.02	(1)	2.90	(2)	3.02	(2)		
				3.10	(1)		
2.68	(1)	2.98	(2)				
2.84	(2)	3.05	(1)	*Aikinite*			
3.09	(2)	3.15	(2)	2.66	(1)	2.89	(1)
3.45	(1)	3.17	(2)	2.76	(2)	2.99	(2)
		3.21	(1)	2.95	(2)	2.99	(2)
2.57	(1)			3.16	(1)	3.26	(2)
2.70	(2)	2.89	(1)				
3.05	(2)	2.99	(2)				
3.28	(1)	3.05	(2)				
		3.38	(2)				
		3.47	(1)				

Number in parenthesis indicate the number of vectors of this length.

(Marumo and Nowacki, 1967) and wallisite (Takéuchi, Ohmasa and Nowacki, 1968).

There are four independent bismuth atoms in the structure. Five sulfur atoms, S(10), S(10′), S(2′), S(2″) and S(9) around the Bi(1) at distances of 2.79 (×2), 2.83 (×2) and 2.57 Å form a square pyramid and in addition there is another S atom, S(7′), at a distance of 3.21 Å from the Bi. Such square pyramidal coordination has also been observed in $CuBi_5S_8$ (Ohmasa and Nowacki, 1972). The other three Bi atoms have a coordination of six, forming a distorted octahedron. The octahedron around Bi(3) is a little more distorted than that around Bi(2) and Bi(4). The shorter of these Bi—S distances are in the range 2.57 to 2.84 Å and the longer three are in the range 2.96 to 3.45 Å. The mean standard deviation in the Bi—S distances is 0.01 Å. Similar coordination for bismuth atom are also observed in galenobismutite

Table 9. *Metal—metal distances in cosalite*

Pb(1)—Cu(1)	2.97(4) Å	[2×]
Bi(4)	4.095(3)	[2×]
Bi(3)	4.123(2)	[2×]
Pb(4′)	4.199(4)	
Pb(3)	4.459(4)	
Pb(2′)	4.883(3)	
Pb(2)—Cu(1′)	3.28(6)	
Cu(1″)	3.49(5)	[2×]
Bi(2)	3.908(3)	[2×]
Pb(2′)	3.931(4)	[2×]
Pb(3′)	4.443(4)	
Pb(1′)	4.883(3)	[2×]
Pb(3)—Cu(1)	4.10(6)	[2×]
Bi(1′)	4.331(3)	[2×]
Pb(4)	4.351(4)	
Bi(4)	4.356(4)	[2×]
Pb(2′)	4.443(4)	
Pb(1)	4.459(4)	
Bi(2′)	4.501(3)	[2×]
Pb(4)—Bi(2)	4.166(3)	
Pb(1′)	4.199(4)	
Bi(1′)	4.203(2)	[2×]
Pb(3)	4.351(4)	
Bi(3′)	4.468(3)	[2×]
Bi(1)—Bi(2′)	4.125(3)	
Bi(3′)	4.194(3)	
Pb(4′)	4.203(2)	[2×]
Pb(3′)	4.331(3)	[2×]
Bi(4′)	4.399(2)	[2×]
Bi(3″)	4.497(3)	[2×]
Bi(2)—Pb(2)	3.908(3) Å	[2×]
Bi(1′)	4.125(3)	
Bi(4)	4.142(3)	[2×]
Pb(4)	4.166(3)	
Pb(3′)	4.501(3)	[2×]
Bi(3)—Bi(3′)	4.023(2)	[2×]
Pb(1′)	4.123(2)	[2×]
Bi(1′)	4.194(3)	
Bi(4)	4.252(3)	
Pb(4′)	4.468(3)	[2×]
Bi(1″)	4.497(3)	[2×]
Bi(4)—Pb(1)	4.095(3)	[2×]
Bi(2)	4.142(3)	[2×]
Bi(3)	4.252(3)	
Pb(3)	4.356(3)	[2×]
Bi(1′)	4.399(2)	[2×]
Cu(1)	4.71(6)	
Cu(1)—Pb(1)	2.97(4)	[2×]
Pb(2′)	3.28(6)	
Pb(2″)	3.49(5)	[2×]
Pb(3)	4.10(6)	[2×]
Bi(4)	4.71(6)	

Sums of metallic radii:

Pb—Pb	3.408 Å	Pb—Bi	3.480 Å
Pb—Cu	2.980	Bi—Cu	3.052
Bi—Bi	3.552	Cu—Cu	2.552

(Iitaka and Nowacki, 1962), CuBi$_5$S$_8$ (Ohmasa and Nowacki, 1972) and hodrushite (Kupčík and Makovický, 1968).

There is a statistical copper atom in the structure. Four sulfur atoms S(8), S(3′), S(3″) and S(1) surround the copper tetrahedrally at distances of 2.22, 2.52 (×2), and 2.61 Å respectively. This tetrahedron is a little distorted in the a direction. The copper has an occupancy factor of 0.12 and the mean standard deviation in Cu—S distance is 0.05 Å, very much larger than the Pb—S and Bi—S distances in the structure. Similar tetrahedral coordination for copper is also found in aikinite (Ohmasa and Nowacki, 1970), CuBi$_5$S$_8$ (Ohmasa and Nowacki,

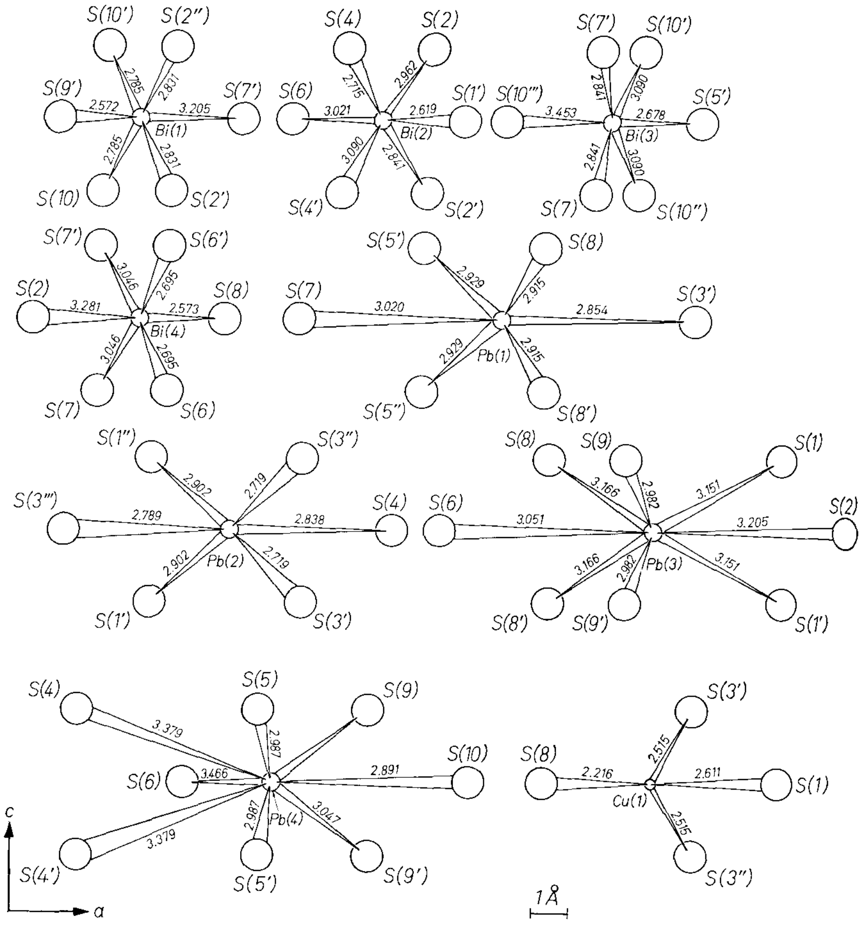

Fig. 2a. Coordination of Pb, Bi and Cu atoms in cosalite

1972) and also in bournonite and seligmanite (Edenharter, Nowacki and Takéuchi, 1970).

The coordination around the metal atoms and that around the sulfur atoms are shown in Fig. 2a and Fig. 2b, projected down the *b* axis. The coordination polyhedra of the sulfur atoms S(1), S(2), S(3), S(7), S(8), and S(10) have the form of a distorted octahedron, with six metal atoms around them. The remaining sulfur atoms S(4), S(5), S(6) and S(9) have five metal atoms surrounding them.

The metal-metal distances are given in Table 9. All the distances are generally much larger than the sum of the metallic radii of the

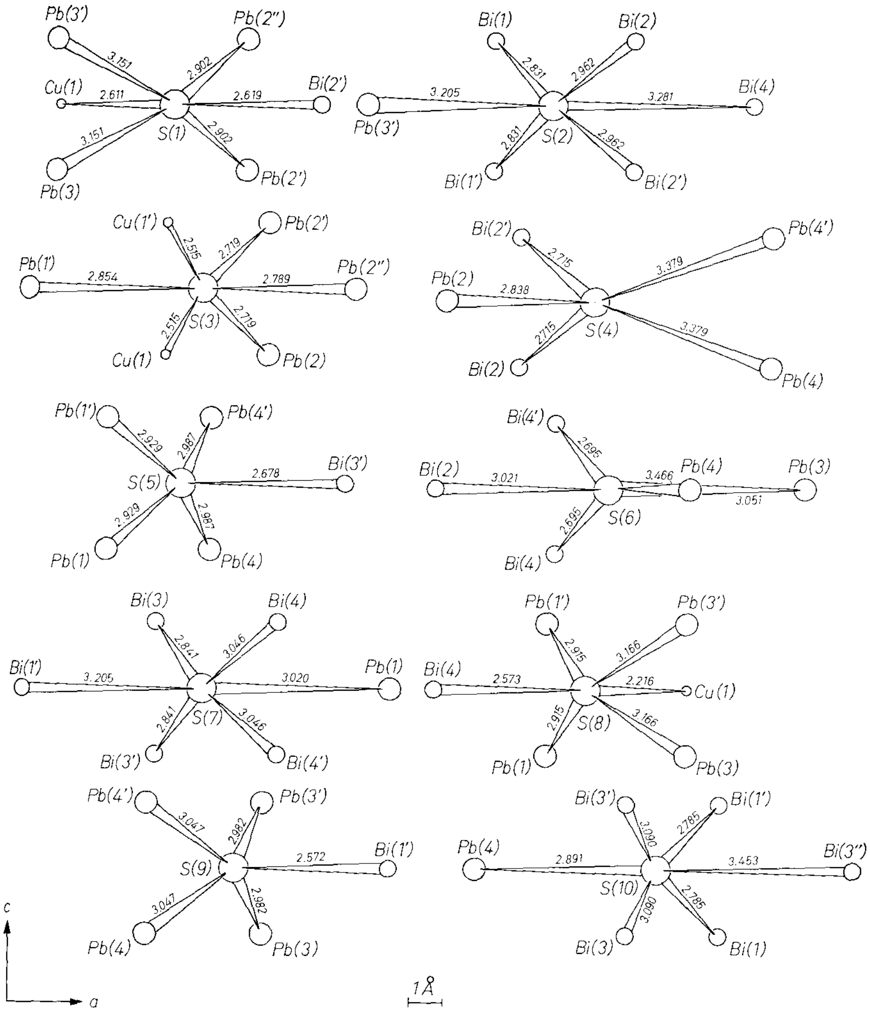

Fig. 2b. Coordination of the sulfur atoms in cosalite

corresponding metal atoms. There is only one exception. It is a Pb(1)—Cu(1) distance of 2.97 Å, which is of the same order of magnitude as the sum of the metallic radii, 2.98 Å. But the standard deviation in this bond length, which involves the statistical copper, is rather higher (0.04 Å) and hence this deviation is well within the limits of the standard deviation. The S—S distances are given in Table 7b. A projection of the structure down the c axis is given in Fig. 3. The c axis of cosalite

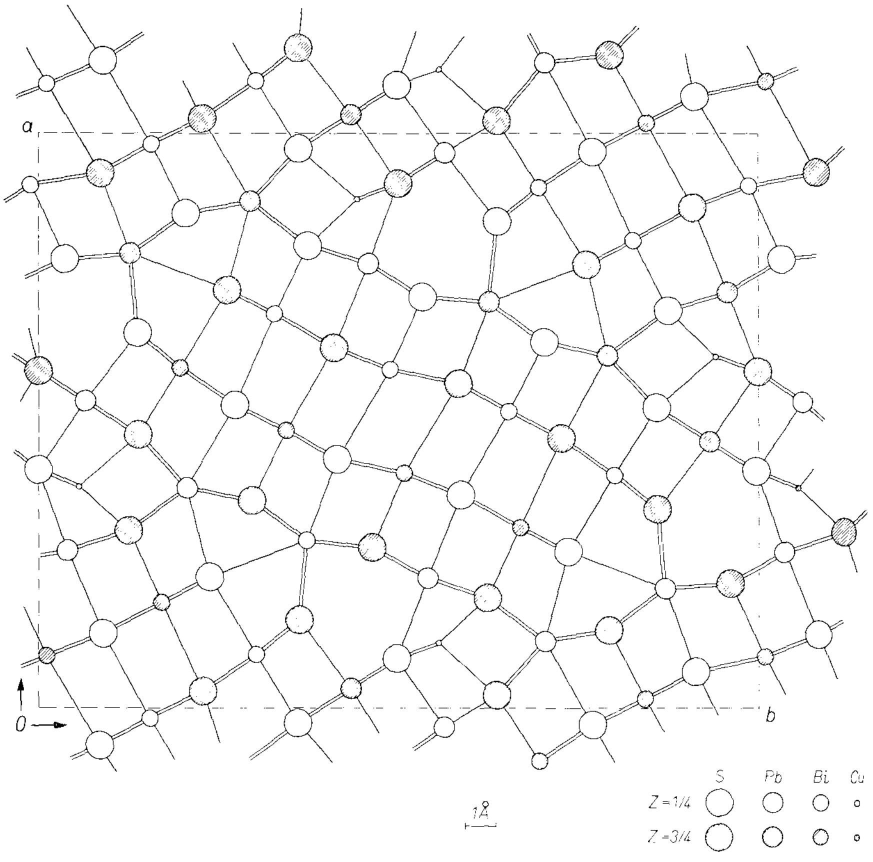

Fig. 3. Structure of cosalite projected ∥ [001]

is the d_{110} of galena. Hence the structure of cosalite could be described as a deformed galena-like structure.

In cosalite, the factor φ, the metal-to-sulfur ratio is 2.5 and hence it comes under the Type III in the classification of Nowacki (1969). A schematic diagram of the Bi—S linkages down (001) is given in Fig. 4. If we consider the three short Bi—S bonds, we can see, that each bismuth shares one sulfur with its translated one and thus forms an infinite chain of the composition $BiS_{2/2}S = BiS_2$. All the four chains of bismuth run parallel to (001). There are two additional sulfur atoms which are not connected by short bonds to bismuth, S(2) and S(3). The Pb atoms are introduced in the interstices and are connected to the main chains by bonds through the sulfur atoms. Thus the composition

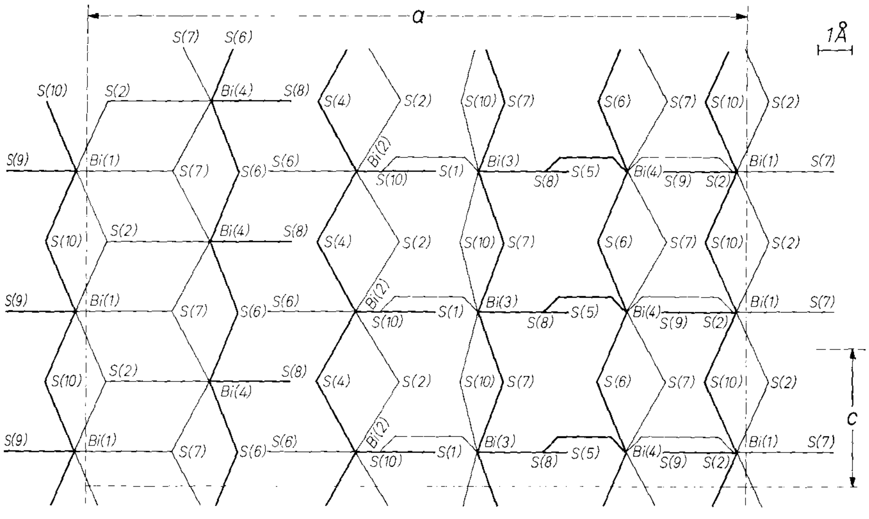

Fig. 4. A schematic representation of the Bi–S bonds within single sheets running along the c axis. Each sheet is linked to the neighbouring ones through the Pb atoms;

—— Bi–S bonds of length 2.57 to 2.84 Å
- - - - Bi–S bonds of length 2.83 to 3.21 Å

of cosalite could be written as $(BiS_2)_4S_2Pb_4 = Pb_4Bi_4S_{10}$. The structural formula could be written as $[BiS_2|S|Pb^{VI}Pb^{VIII}]$ and it belongs to the type III.a$_3$ in the classification of Nowacki (1969).

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