Zeitschrift für Kristallographie, Bd. 132, S. 71–86 (1970)

A redetermination of the crystal structure of aikinite $[BiS_2|S|Cu^{IV}Pb^{VII}]$*

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(Received 13 January 1970)

Auszug

Die Kristallstruktur von Aikinit, $CuPbBiS_3$, wurde neu bestimmt, um die strukturellen Beziehungen zu Seligmannit ($CuPbAsS_3$) und Bournonit ($CuPbSbS_3$) aufzuklären. Gitterkonstanten und Raumgruppe sind: $a = 11{,}638 \pm 0{,}003$ Å, $b = 4{,}039 \pm 0{,}001$ Å, $c = 11{,}319 \pm 0{,}002$ Å, D_{2h}^{16}–$Pnma$. Die Struktur wurde mittels neuer 3d-Intensitätsdaten nach der Methode der kleinsten Quadrate verfeinert ($R = 6{,}4\,^0/_0$ für alle 573 Reflexe). Die Bi- konnten von den Pb-Atomen durch ihre Koordinationen unterschieden werden.

Sechs S-Atome um ein Pb bilden ein trigonales Prisma. Diese Prismen liegen in einer Linie parallel *b*. $CuBiS_3$-Doppelketten parallel *b* werden durch unendliche Cu-Tetraeder- und Bi-Pyramiden-Ketten gebildet. Die langen (Bi–S)-Bindungen von 2,95 Å Länge halten diese $CuBiS_3$-Doppelketten zusammen, so daß $CuBiS_3$-Schichten senkrecht zu [001] entstehen.

Die Atome der einen Hälfte jeder Aikinitzelle gehen durch 2_1-Achsen parallel *b* mit einer Translation von 2 Å in diejenigen der anderen Hälfte über. Die Atomanordnung in jedem Zellteil ist derjenigen von Bournonit und Seligmannit ähnlich. Jedoch existiert in diesen Strukturen kein Symmetrieelement, welches die Atome der einen Hälfte in diejenigen der anderen überführte. Dieser strukturelle Unterschied kann wohl durch die Differenz in der Größe der SbS_3-Pyramiden mit der Pb-S-Anordnung [nicht aufeinander passende (S–S)-Abstände] erklärt werden.

Die strukturelle Formel von Aikinit ist $[BiS_2|S|Cu^{IV}Pb^{VII}]$, Typ II.$a_2$, im Gegensatz zu Seligmannit $[(AsS_3)_2|Cu^{IV}Pb^{VII}Pb^{VIII}]$ und Bournonit $[(SbS_3)_2|Cu^{IV}Pb^{VII}Pb^{VIII}]$, Typ II,$a_1$. Aikinit ist daher mit diesen letzteren Strukturen nicht isotyp; hingegen besteht eine große Ähnlichkeit mit Wismutglanz (Bi_2S_3) und Antimonglanz (Sb_2S_3).

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* Contribution No. 204, Part 56 on sulfides and sulfosalts.

Abstract

The crystal structure of aikinite, $CuPbBiS_3$, has been reexamined to elucidate the structural relations among this mineral and bournonite ($CuPbSbS_3$) and seligmannite ($CuPbAsS_3$). The cell dimensions and space group are: $a = 11.638 \pm 0.003$, $b = 4.039 \pm 0.001$, $c = 11.319 \pm 0.002$ Å, D_{2h}^{16}–*Pnma*. The structure was refined by a three-dimensional least-squares method with newly determined intensity data ($R = 6.4\,{}^0/_0$ for all 573 reflections). Bi atoms could be distinguished from Pb atoms by the comparison of their coordinations.

Six S atoms around the Pb atom make a trigonal prism. These prisms lie in a line parallel to the b axis. $CuBiS_3$ composite chains along the b axis are formed by infinite chains of Cu tetrahedra and Bi pyramids. The longer bonds of Bi (= 2.95 Å) bind the $CuBiS_3$ chains together and form $CuBiS_3$ sheets perpendicular to [001].

In aikinite, the atoms in one half of the cell are related to the atoms in the other half by 2_1 axes parallel to b and are shifted by 2 Å along this direction. The configuration of atoms in each part is similar to that of bournonite and seligmannite. However, there is no symmetry element in bournonite to shift the atoms along the corresponding direction. This structural difference may result from the misfit of the size of the SbS_3 pyramids to the lead array.

The structural formula of aikinite is $[BiS_2|S|Cu^{IV}Pb^{VII}]$, type II.$a_2$, in contrast to seligmannite $[(AsS_3)_2|Cu^{IV}Pb^{VII}Pb^{VIII}]$ and bournonite $[SbS_3)_2|Cu^{IV}Pb^{VII}Pb^{VIII}]$, type II.$a_1$. So aikinite is not isotypical with these latter structures, but shows a great relationship to stibnite (Sb_2S_3) and bismuthinite (Bi_2S_3).

Introduction

Aikinite was first investigated roentgenographically by PEACOCK (1942). He determined lattice constants $a_P = 11.30$, $b_P = 11.64$, $c_P = 4.00$ Å, space group *Pnam* (or *Pna*2_1) and cell content $4[CuPbBiS_3]$ and pointed out that aikinite is not isostructural with bournonite or seligmannite, but has a close relation to bismuthinite.

The crystal structure of aikinite was proposed by WICKMAN in 1953. Though he could directly locate the heavy atoms from the Patterson diagram, it was impossible to find the positions of the remaining light atoms from it. WICKMAN used the trial and error method to place the Cu atoms and crystal-chemical considerations to place the S atoms. Distinction between Bi and Pb atoms was impossible because of the small difference in their scattering powers and because of the relatively inaccurate coordinates of the S atoms.

The composition of aikinite, $CuPbBiS_3$, is similar to that of bournonite, $CuPbSbS_3$, and seligmannite, $CuPbAsS_3$. HELLNER and LEINEWEBER (1956) determined both structures and proved that they are isotypical. They pointed out the analogy of their structures with the structure of aikinite, that is, the face-diagonal directions [110] of bournonite and seligmannite corresponding to the *a* and the *c* axis of aikinite. Recently, the structures of bournonite and seligmannite were refined by EDENHARTER *et al.* (1970).

The present investigation was undertaken in order to reexamine the structure of aikinite and to elucidate the structural relationship of aikinite with seligmannite and bournonite.

Experimental

Some massive crystals (W 50) from Beresowsk, Ural, were available for the present study. They were too brittle to prepare a spherical specimen, and a small platy fragment with dimensions 0.141 × 0.063 × 0.021 mm was used for the measurement of the cell dimensions and intensities. Electron microprobe analyses yielded the values given in Table 1.

Table 1. *Microprobe analyses of aikinite samples*

Analysis No.	139	140a	350	Theor.
Pb	36.4	36.4	35.5	36.0%
Cu	7	7.1	10.0	11.0
Bi	40.4	40.1	39.1	36.3
S	16.4	16.3	15.9	16.7
Σ	100.2	99.9	100.5	100.0%

Analysis No. 139 : Aikinite 134-61, Gladhammar, Småland, Sweden.
140a: do., other grain [with PbS needles (Analysis No. 140b) enclosed].
350 : Aikinite (W 50), Beresowsk, Ural (this paper).
Theor.: $CuPbBiS_3$.
Analyses: G. BURRI (nos. 139, 140a, 140b), H. RUDOLF (no. 350).

The lattice constants were determined from back-reflection Weissenberg photographs on which diffraction patterns of silicon powder were recorded to calibrate the effect of film shrinkage. A least-squares best fit of the lattice parameters was calculated with the aid of an IBM-1620 programme written by N. D. JONES (unpublished). The results are

	Present study	WICKMAN (1953)	PEACOCK (1942)
a	11.638 ± 0.003 Å	11.65 Å	11.64 Å
b	4.039 ± 0.001	4.00	4.00
c	11.319 ± 0.002	11.30	11.30

The unit cell contains four formula units. The diffraction symbol for aikinite is *mmmPn-a*. This permits *Pnma* and $Pn2_1a$ as possible space groups. Since a piezoelectric test did not show an acentric feature, *Pnma* was assumed to be the correct space group.

Three-dimensional 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. Corrections for absorption were also made because of the high linear-absorption coefficient of the material ($\mu = 1380$ cm^{-1} for Cu$K\alpha$).

All these calculations were done with the aid of a local version of the programme ACACA (WUENSCH and PREWITT, 1965).

Refinement of the structure

The Patterson functions $P(xz)$ and $P_1(xz)$ were evaluated with $h0l$ and $h1l$ reflections respectively. The x and z coordinates of the two independent heavy atoms in WICKMAN's model were confirmed by the minimum function and the y coordinates from $P_1(xz)$.

Then structure amplitudes were calculated with the coordinates of the heavy atoms given by WICKMAN and with the atomic scattering amplitude of Pb. The discrepancy index R for all 573 reflections was about 30⁰/₀. The signs obtained from these calculations were used for three-dimensional Fourier and difference Fourier syntheses. The positions of Cu and S atoms proposed by WICKMAN were confirmed from these syntheses. Several cycles of three-dimensional least-squares refinements, in which all atoms were included, and in which isotropic temperature factors were varied, reduced R to 12⁰/₀. At this stage, the interatomic distances among heavy atoms and sulfur atoms were calculated and marked differences were found for the coordination of two independent heavy atoms. One of them was regarded as Bi and the other as Pb (see following chapter).

Further refinements by a least-squares method were made with individual atomic-scattering factors for Bi and Pb. Neutral-atom form amplitudes given by THOMAS, UMEDA and KING were used for Pb and Bi. Those given by FREEMAN and WATSON and by DAWSON were employed for Cu and S respectively[1].

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

Table 2. *Observed and calculated structure amplitudes for aikinite*

h	k	l	$\|F_o\|$	F_c
0	2	0	590.1	-609.1
	4		254.1	267.9
0	1	1	136.6	140.9
	3		82.4	-91.0
0	0	2	8.5*	-9.0
	2		6.4*	5.5
	4		5.1*	-4.7
0	1	3	149.6	-150.9
	3		80.7	87.7
0	0	4	218.5	237.5
	2		148.6	-164.6
	4		57.9	66.2
0	1	5	191.6	-203.4
	3		101.5	114.7
0	0	6	344.0	375.6
	2		236.1	-279.5
	4		117.2	133.8
0	1	7	85.1	92.8
	3		54.0	-62.8
0	0	8	74.7	-79.8
	2		54.2	65.3
0	1	9	183.2	-195.9
	3		145.0	126.7
0	0	10	153.2	157.4
	2		130.4	-120.4
0	1	11	46.2	-40.9
0	0	12	53.0	42.6
	2		38.9	-33.7
0	1	13	34.8	36.8
1	0	1	32.9	29.4
	1		178.4	172.0
	2		20.1	-15.8
	3		80.0	-92.1
	4		22.7	2.0
1	0	2	43.8	-53.0
	1		241.8	-242.7
	2		27.8	32.5
	3		143.2	132.1
	4		12.6	-11.3
1	0	3	325.7	329.7
	1		262.1	274.1
	2		236.0	-240.5
	3		123.6	-137.8
	4		99.0	109.2
1	0	4	86.9	95.4
	1		239.5	245.0
	2		59.4	-65.9
	3		142.1	-142.0
	4		21.0	20.0
1	0	5	76.2	-85.4
	1		95.8	102.5
	2		68.1	67.3
	3		55.0	-61.3
	4		35.2	-37.8
1	0	6	22.1	7.0
	1		92.8	-104.1
	2		20.5	-10.1
	3		50.0	59.2
	4		14.4	10.4
1	0	7	133.2	144.5
	1		169.9	196.2
	2		101.9	-110.6
	3		100.7	-110.6
	4		55.6	55.2
1	0	8	66.9	76.6
	1		73.1	-81.5
	2		46.6	-53.3
	3		48.8	50.7
1	0	9	151.2	161.0
	1		64.3	63.6
	2		119.6	-125.8
	3		43.3	-40.1
1	0	10	64.4	57.0
	1		51.0	55.5
	2		49.4	-45.1
	3		39.0	-36.7
1	0	11	82.7	-78.4
	1		89.7	80.0
	2		68.3	63.8
1	0	12	70.1	60.9
	1		112.7	-100.3
	2		55.0	-48.3
1	0	13	85.7	78.0
	1		47.0	41.2
2	0	0	58.9	40.0
	1		165.1	150.8
	2		54.5	-39.8
	3		79.7	-76.1
	4		34.6	33.2
2	0	1	93.9	80.2
	1		249.2	268.2
	2		61.5	-55.0
	3		142.7	-141.0
	4		27.6	28.2
2	0	2	232.8	-215.7
	1		324.4	330.7
	2		171.0	160.2
	3		178.7	-172.2
	4		86.9	-78.3
2	0	3	63.9	56.9
2	1	3	101.5	-101.0
	2		42.3	-37.1
	3		57.5	51.0
	4		16.2	15.3
2	0	4	222.7	-231.8
	1		194.4	204.4
	2		167.8	161.3
	3		125.0	-112.6
	4		84.1	-71.9
2	0	5	90.6	81.8
	1		34.5	-31.8
	2		66.7	-59.3
	3		26.4	22.0
	4		32.7	29.7
2	0	6	77.3	78.2
	1		77.7	77.7
	2		63.2	-61.9
	3		43.6	-40.0
	4		34.0	34.6
2	0	7	142.3	132.5
	1		191.6	198.5
	2		109.0	-101.9
	3		118.7	-119.0
	4		46.3	50.9
2	0	8	170.3	-163.1
	1		118.6	118.2
	2		127.2	126.8
	3		66.1	-68.1
2	0	9	24.4	18.2
	1		85.2	-88.6
	2		8.5*	-11.5
	3		48.9	54.4
2	0	10	47.3	-42.8
	1		34.6	34.1
	2		34.1	31.8
	3		20.7	-18.6
2	0	11	52.3	46.7
	1		42.3	42.6
	2		39.8	-36.3
2	0	12	25.9	26.7
	1		44.7	39.5
	2		20.0	-21.2
2	0	13	49.2	46.0
	1		80.8	75.1
3	0	1	337.0	-353.8
	1		18.0	15.6
	2		246.5	249.6
	3		7.2*	-8.1
	4		114.9	-108.0
3	0	2	114.9	-110.3
	1		175.7	-190.8
	2		77.4	76.7
	3		100.3	110.3
	4		43.1	-43.6
3	0	3	21.7	16.0
	1		140.6	-146.0
	2		20.8	-16.1
	3		79.1	77.9
	4		16.9	15.7
3	0	4	45.7	31.9
	1		257.1	249.1
	2		36.8	-29.6
	3		159.4	-147.5
	4		24.4	22.0
3	0	5	421.5	-423.6
	1		157.1	151.9
	2		326.6	312.5
	3		91.4	-84.8
	4		157.3	-148.4
3	0	6	12.5*	-7.1
	1		37.5	-33.2
	2		17.9	11.1
	3		26.3	26.5
	4		11.7	-12.8
3	0	7	95.6	-86.2
	1		77.3	-73.0
	2		67.8	63.7
	3		42.0	41.0
	4		26.2	-27.6
3	0	8	54.1	-55.2
	1		31.4	16.7
	2		38.4	40.2
	3		6.5*	-8.7
3	0	9	52.9	-46.8
	1		9.4	11.8
	2		35.7	34.0
	3		5.8*	-5.7
3	0	10	46.2	47.0
	1		143.6	154.7
	2		35.8	-36.3
	3		96.6	-96.9
3	0	11	168.6	-181.0
	1		50.6	54.0
	2		138.2	144.2
3	0	12	18.8	-17.9
	1		13.4	-14.1
	2		14.5	14.4
3	0	13	18.2	20.4
	1		36.1	-31.8
4	0	0	198.2	194.4
4	1	0	290.6	-289.1
	2		147.7	-137.6
	3		173.3	161.9
	4		70.6	63.5
4	0	1	67.8	66.1
	1		180.2	160.3
	2		52.0	-50.0
	3		109.1	-102.0
	4		21.5	19.3
4	0	2	390.2	-393.1
	1		152.7	-162.0
	2		292.1	276.5
	3		74.1	83.1
	4		121.2	-126.1
4	0	3	91.0	-92.9
	1		21.3	16.9
	2		65.5	65.8
	3		7.7*	-2.8
	4		31.7	-28.4
4	0	4	111.2	-104.2
	1		103.7	-107.6
	2		80.5	78.6
	3		58.1	57.9
	4		43.9	-39.0
4	0	5	64.0	-67.5
	1		29.5	-34.9
	2		48.1	50.4
	3		19.8	19.4
	4		25.4	-22.6
4	0	6	90.5	84.8
	1		200.0	-201.2
	2		70.3	-68.5
	3		122.3	118.9
	4		37.5	39.3
4	0	7	10.6*	11.8
	1		190.4	185.0
	2		8.1*	-10.1
	3		119.9	-117.4
4	0	8	180.1	-186.3
	1		72.2	-68.2
	2		135.3	143.4
	3		39.9	39.7
4	0	9	112.5	-114.6
	1		56.9	-59.2
	2		81.9	88.7
	3		35.9	42.9
4	0	10	49.3	52.3
	1		53.3	-52.4
	2		39.9	-41.9
	3		32.1	31.0
4	0	11	45.8	-46.1
	1		18.3	15.1
	2		34.2	36.7
4	0	12	15.7	-14.1
	1		59.3	-60.5
	2		11.4	9.7
4	0	13	9.7	-4.7
	1		64.0	59.8
5	0	1	99.4	85.7
	1		164.1	-150.9
	2		65.8	-58.4
	3		84.8	79.3
	4		23.8	25.2
5	0	2	170.1	-164.3
	1		163.9	-165.3
	2		117.6	118.8
	3		86.3	95.0
	4		58.1	-54.8
5	0	3	231.6	242.6
	1		172.4	-185.7
	2		169.8	-182.0
	3		104.7	108.0
	4		94.7	88.2
5	0	4	124.0	135.1
	1		103.3	111.9
	2		92.5	-99.5
	3		64.4	-63.9
	4		51.2	47.4
5	0	5	20.6	-2.3
	1		88.7	-97.9
	2		7.6*	6.2
	3		47.1	49.1
	4		10.8	-8.0
5	0	6	98.0	-101.7
	1		115.8	-120.1
	2		73.7	71.9
	3		68.3	70.0
5	0	7	41.1	40.9
	1		111.6	-109.6
	2		32.1	-31.0
	3		69.0	69.9
5	0	8	65.5	-62.2
	1		60.6	-59.1
	2		49.9	50.6
	3		37.2	39.0
5	0	9	104.2	106.6
	1		132.1	-139.5
	2		78.2	-82.5
	3		84.5	85.2
5	0	10	24.2	-19.9
5	1	10	43.5	44.1
	2		16.5	14.1
5	0	11	48.9	-53.5
	1		14.7	10.5
	2		37.4	43.9
5	0	12	70.9	-71.0
	1		53.9	-61.8
5	0	13	49.5	44.9
6	0	0	299.6	298.5
	1		271.7	-254.5
	2		238.8	-225.0
	3		161.4	151.3
	4		101.4	109.3
6	0	1	96.4	87.1
	1		186.2	170.3
	2		74.6	-69.7
	3		102.9	-96.2
	4		35.1	39.1
6	0	2	139.1	142.6
	1		124.3	122.7
	2		92.2	-98.7
	3		67.1	-70.7
	4		38.7	37.7
6	0	3	81.5	-71.8
	1		91.6	-97.8
	2		62.2	57.7
	3		53.7	53.5
	4		34.5	-34.4
6	0	4	123.8	131.9
	1		19.3	15.1
	2		92.9	-99.4
	3		17.3	-11.7
	4		46.7	46.3
6	0	5	68.9	-67.7
	1		101.7	-104.6
	2		52.8	52.2
	3		63.3	64.6
	4		28.1	-26.4
6	0	6	216.5	228.7
	1		82.0	-86.7
	2		166.2	-175.6
	3		54.3	55.2
6	0	7	87.8	91.4
	1		50.7	50.5
	2		69.2	-72.9
	3		35.4	-33.4
6	0	8	20.7	19.2
	1		107.3	106.9
	2		17.5	-11.6
	3		64.4	-68.8
6	0	9	87.7	-82.4
	1		115.8	-119.6
	2		67.4	68.0
	3		74.0	73.3
6	0	10	83.8	85.2
	1		22.4	-25.5
	2		61.5	-67.8
6	0	11	22.4	21.6
	1		33.2	-33.8
	2		16.9	-18.8
6	0	12	72.8	75.3
	1		16.1	11.0
7	0	1	26.2	-11.6
	1		226.4	215.3
	2		9.6*	10.8
	3		120.2	-124.9
	4		14.6	-9.5
7	0	2	80.4	-75.2
	1		82.0	-76.3
	2		60.7	60.9
	3		51.0	49.0
	4		33.8	-34.4
7	0	3	233.0	242.3
	1		23.5	16.8
	2		170.3	-184.8
	3		7.1	-9.3
	4		91.7	90.6
7	0	4	154.4	159.5
	1		94.5	98.7
	2		123.8	-127.7
	3		66.5	-68.2
7	0	5	72.9	-69.9
	1		218.6	236.2
	2		57.2	55.2
	3		140.6	-140.2
7	0	6	40.6	40.5
	1		73.1	-70.4
	2		31.9	-28.8
	3		49.1	47.8
7	0	7	99.1	102.0
	1		17.2	17.3
	2		75.8	-78.6
	3		13.7	-8.8
7	0	8	7.4*	1.3
	1		40.0	-35.4
	2		6.0*	-1.2
	3		22.4	19.2
7	0	9	73.8	74.9
	1		18.1	14.3
	2		55.0	-60.0

Table 2. *(Continued)*

h	k	l	$\lvert F_o \rvert$	F_c
7	0	10	88.9	94.6
	1		33.1	37.5
	2		69.3	-74.6
7	0	11	21.4	-20.9
	1		93.4	95.2
7	0	12	14.5	-13.0
8	0	0	61.7	53.7
	1		30.4	29.5
	2		46.8	-41.2
	3		8.1*	-9.1
8	0	1	143.8	128.6
	1		71.8	63.1
	2		97.9	-95.4
	3		40.4	-43.2
8	0	2	141.0	-144.3
	1		149.6	160.0
	2		99.9	107.1
	3		93.1	-97.3
8	0	3	38.4	-33.0
	1		9.8*	-3.6
	2		29.1	24.2
	3		6.6*	6.0
8	0	4	49.5	-47.8
	1		141.7	152.0
	2		36.3	36.5
	3		89.7	-90.5
8	0	5	8.5*	-4.8
	1		62.5	-59.6
	2		6.8*	5.1
	3		42.0	39.6
8	0	6	8.1*	-12.0
	1		7.3*	2.9
	2		6.5*	8.5
	3		9.9	1.8
8	0	7	128.1	126.0
	1		61.4	67.2
	2		99.4	-98.6
	3		38.3	-42.5
8	0	8	133.8	-130.3
	1		111.4	112.9
	2		99.8	103.1
8	0	9	27.9	-27.1
	1		7.1*	1.8
	2		20.7	21.9
8	0	10	6.7*	-3.5
	1		42.5	44.6
8	0	11	36.9	35.6
	1		14.4	17.5
9	0	1	188.1	-179.4
	1		33.6	25.4
	2		145.5	138.8
	3		18.8	-16.3
9	0	2	135.2	-132.2
	1		10.8*	-4.5
	2		102.2	103.9
	3		6.7*	-0.4
9	0	3	82.1	-87.5
	1		105.0	-104.5
	2		58.5	64.3
	3		65.9	68.5
9	0	4	135.5	130.8
	1		100.9	99.4
	2		105.0	-102.4
	3		61.6	-58.9
9	0	5	100.5	-105.0
	1		81.9	82.1
	2		77.6	81.7
	3		55.3	-55.7
9	0	6	81.6	-82.2
	1		7.0*	3.2
	2		63.0	64.6
	3		3.8*	-3.7
9	0	7	105.6	-104.8
	1		17.0	-10.5
	2		77.6	80.7
9	0	8	14.3	-16.1
	1		44.1	43.7
	2		11.0	13.9
9	0	9	12.6	-8.0
	1		42.5	-41.2
	2		7.1*	5.2
9	0	10	52.7	52.0
	1		55.4	60.8
10	0	0	14.0*	-27.8
	1		223.2	-236.8
	2		24.0	19.0
	3		133.5	144.6
10	0	1	101.8	99.4
10	1	1	85.6	83.3
	2		74.2	-82.4
	3		48.9	-52.5
10	0	2	71.9	-73.5
	1		39.8	31.3
	2		54.2	58.4
	3		24.9	-23.1
10	0	3	28.7	-30.6
	1		8.4*	-12.7
	2		22.9	25.4
	3		4.5*	7.5
10	0	4	39.2	-38.1
	1		72.9	-76.5
	2		26.2	27.9
	3		40.7	44.5
10	0	5	61.8	-64.9
	1		25.1	-21.9
	2		46.6	50.1
10	0	6	7.0*	-12.9
	1		151.0	-152.9
	2		13.5	9.4
10	0	7	74.4	68.8
	1		55.3	51.5
	2		57.1	-57.3
10	0	8	73.6	-72.6
	1		24.6	24.3
	2		56.9	58.8
10	0	9	87.0	-90.0
	1		8.4	-5.3
11	0	1	29.6	27.6
	1		42.3	-48.5
	2		18.6	-20.9
	3		25.1	29.0
11	0	2	89.5	-85.3
	1		8.5*	-14.1
	2		64.8	68.3
	3		8.0	10.3
11	0	3	119.7	118.2
	1		156.5	-167.9
	2		88.9	-92.9
11	0	4	45.3	44.7
	1		7.0*	-4.6
	2		35.7	-36.4
11	0	5	7.7*	-6.3
11	1	5	19.1	12.5
	2		9.1	5.2
11	0	6	70.4	-66.0
	1		35.0	-40.8
	2		50.6	53.3
11	0	7	36.7	36.1
	1		47.0	-49.0
11	0	8	54.5	-54.2
	1		18.0	-17.5
12	0	0	52.9	57.6
	1		49.8	-54.1
	2		36.8	-42.3
12	0	1	104.5	101.8
	1		8.0*	4.0
	2		77.7	-80.3
12	0	2	58.5	65.9
	1		41.7	41.6
	2		42.2	-51.5
12	0	3	32.0	-28.0
	1		13.3	12.3
	2		22.7	21.5
12	0	4	73.1	77.0
	1		19.3	17.3
	2		53.4	-60.2
12	0	5	40.5	-39.3
	1		26.5	-25.6
12	0	6	60.1	61.3
	1		52.4	-53.1
12	0	7	67.4	68.0
13	0	1	36.2	39.7
	1		94.3	102.7
13	0	2	52.0	-49.4
	1		9.7	-5.8
13	0	3	28.1	31.1
	1		33.4	-30.7
13	0	4	98.6	106.3
	1		11.3	-12.8
13	0	5	35.7	39.6
14	0	0	34.9	-34.5
14	0	1	57.6	60.0
14	0	2	32.0	-33.4

A block-diagonal least-squares programme written by D. van der Helm (Philadelphia) for IBM 1620 and a programme written by P. Engel (Bern) for Bull Gamma 30S were used for there finements. Least-squares weights were calculated by the following formula:

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

where p_1 = scale factor, p_2 = total integrated peak count, p_3 = background count and $p_4 = 1/LP$ respectively (Gabe, 1966).

The final discrepancy index R is $6.4\,^0/_0$ for all 573 reflections. The observed and the final calculated structure amplitudes are shown in Table 2.

Discussion of the structure

The values obtained for the atomic positions and temperature factors are given in Table 3. The electron density and the atomic arrangement projected along the b axis are illustrated in Fig. 1. The model which was proposed by Wickman is essentially correct as is shown in Table 3. The average shift of the heavy atoms from Wickman's result is 0.03 Å, that of Cu 0.08 Å and that of S 0.16 Å.

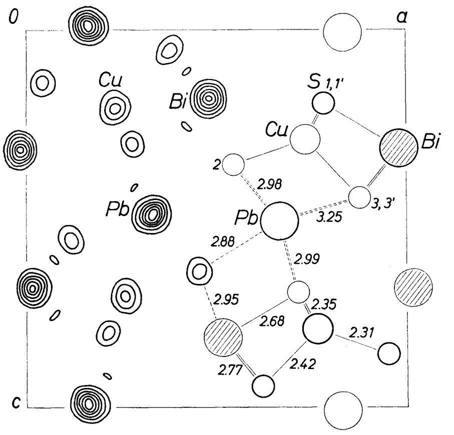

Fig. 1

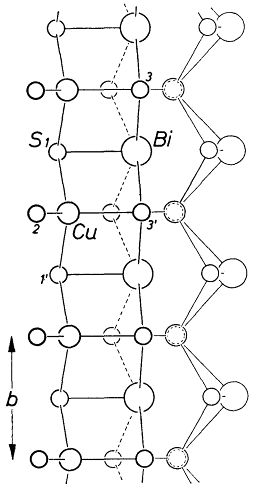

Fig. 2

Fig. 1. Projection of the electron density and of the atomic arrangement parallel to *b* in aikinite

Fig. 2. Composite chain $BiS_{2/2}SCuS = CuBiS_3$

The interatomic distances and bond angles are tabulated in Table 4.

The difference of the atomic-scattering amplitudes being too small, it is impossible to distinguish Bi from Pb by x-ray diffraction meas-

Table 3. *Atomic parameters of aikinite*

	Wickman (1953)			present determination			
	x	y	z	x	y	z	B
Bi	0.017	$\frac{1}{4}$	0.685	0.0189 ± 0.0001	$\frac{1}{4}$	0.6827 ± 0.0001	2.53 Å ± 0.04
Pb	0.832	$\frac{1}{4}$	0.013	0.8329 ± 0.0001	$\frac{1}{4}$	0.0105 ± 0.0001	3.13 ± 0.04
Cu	0.240	$\frac{1}{4}$	0.210	0.2338 ± 0.0004	$\frac{1}{4}$	0.2085 ± 0.0004	3.75 ± 0.08
S(1)	0.730	$\frac{1}{4}$	0.690	0.7160 ± 0.0005	$\frac{1}{4}$	0.6986 ± 0.0005	1.87 ± 0.09
S(2)	0.060	$\frac{1}{4}$	0.135	0.0467 ± 0.0005	$\frac{1}{4}$	0.1400 ± 0.0005	2.11 ± 0.10
S(3)	0.370	$\frac{1}{4}$	0.045	0.3775 ± 0.0005	$\frac{1}{4}$	0.0559 ± 0.0005	2.10 ± 0.09

Table 4. *Interatomic distances and bond angles in aikinite*

	S(1)	S(2)	S(3)	Pb	Cu
Bi	2.658 ± 0.006 Å 3.530 ± 0.006 Å	2.948 ± 0.004 Å (2)	2.755 ± 0.004 Å (2) 3.163 ± 0.006 Å		
Pb	2.989 ± 0.004 Å (2)	2.888 ± 0.006 Å 2.991 ± 0.004 Å (2)	3.261 ± 0.005 Å (2)		3.291 ± 0.004 Å (2) 3.382 ± 0.005 Å
Cu	2.350 ± 0.004 Å (2)	2.312 ± 0.008 Å	2.404 ± 0.007 Å	3.291 ± 0.004 Å (2) 3.382 ± 0.005Å	

S(1)–Bi–S(2)	83.07°	± 0.15°	S(1)–Pb–S(1)′	85.00°	± 0.10°	S(1)–Cu–S(1)′	118.47°	± 0.24°
S(1)–Bi–S(3)	83.43	0.15	S(2)–Pb–S(2)′	84.94	0.11	S(1)–Cu–S(2)	112.59	0.19
S(2)–Bi–S(2)′	86.46	0.11	S(3)–Pb–S(3)′	76.52	0.09	S(1)–Cu–S(3)	98.54	0.20
S(2)–Bi–S(3)	88.05	0.12	S(1)–Pb–S(2)″	78.62	0.14	S(1)′–Cu–S(2)	112.59	0.19
S(3)–Bi–S(3)′	94.27	0.13	S(2)–Pb–S(2)″	83.40	0.15	S(1)′–Cu–S(3)	98.54	0.20
			S(1)–Pb–S(3)	66.62	0.13	S(2)–Cu–S(3)	114.44	0.27
			S(1)–Pb–S(2)	92.22	0.11			
			S(2)–Pb–S(3)	78.60	0.13			

Table 5. *Coordinations of Bi and Pb in cosalite, galenobismutite and aikinite*
(Numbers in parentheses indicate the number of distinct vectors of this length)

Bi—S	Pb—S	Bi—S	Pb—S
Cosalite		Galenobismutite	
2.62 (1) Å	2.84 (1) Å	2.63 (1) Å	2.85 (1) Å
2.83 (2)	2.93 (2)	2.73 (2)	2.98 (2)
2.85 (2)	2.93 (2)	2.99 (2)	3.01 (2)
3.25 (1)	2.97 (1)	3.12 (1)	3.21 (2)
2.64 (1)	2.74 (2)	2.78 (2)	
2.74 (2)	2.82 (1)	2.79 (1)	
2.94 (2)	2.83 (1)	3.00 (1)	
3.05 (1)	2.89 (2)	3.02 (2)	
		3.10 (1)	
2.62 (1)	2.99 (2)		
2.85 (2)	3.03 (1)	Aikinite	
3.04 (2)	3.15 (2)	2.66 (1)	2.89 (1)
3.44 (1)	3.18 (1)	2.76 (2)	2.99 (2)
	3.18 (2)	2.95 (2)	2.99 (2)
		3.16 (1)	3.26 (2)
2.54 (1)	2.90 (1)		
2.66 (2)	2.99 (2)		
3.04 (2)	3.03 (2)		
3.31 (1)	3.38 (2)		
	3.54 (1)		

urements. However, the first heavy atom which was denoted as *A* by WICKMAN has three nearest S atoms at about 2.7 Å, while the second one, *B*, has no shorter distance than 2.88 Å. The former consequently is considered to be Bi and the latter Pb. These values are in good agreement with those of cosalite and galenobismutite (Table 5).

Six S atoms around the Pb atom make an ordinary trigonal prism and one S atom is located in the direction perpendicular to one of the three faces of the prism. These prisms lie in a line along the *b* axis. Cu atoms are inserted within tetrahedral groups of S atoms. Each Bi atom forms a flat trigonal pyramid with three S atoms which is similar to the pyramids of Sb and As atoms in various sulfosalts (NOWACKI, 1969). BiS_3 pyramids form an infinite chain along the *b* axis sharing their corners, and tetrahedra of Cu atoms make also such a chain along the same direction. These two kinds of chains are combined with each other and yield a $CuBiS_3$ composite chain (Fig. 2). The longer Bi—S bonds (2.95 Å) link these composite chains to build a sheet parallel to (001). The Pb atoms are sandwiched between these sheets (Fig. 3).

The structure of aikinite, as Wickman has pointed out, is quite similar to that of stibnite, Sb_2S_3, or bismuthinite, Bi_2S_3, one half of its Bi atoms [the Bi(2)] being replaced by Pb. There are tetrahedral holes in the bismuthinite structure, these positions being occupied by Cu atoms in aikinite. Therefore the perfect cleavage parallel to (010) observed in bismuthinite disappears in the structure of aikinite.

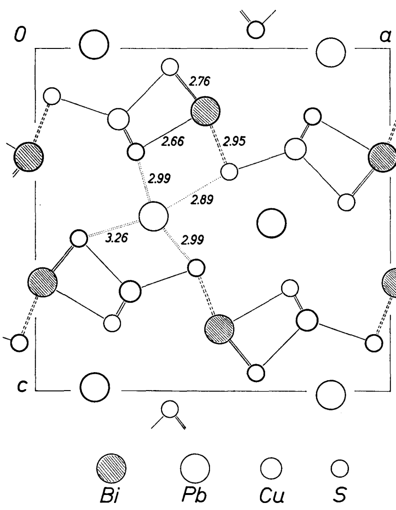

Fig. 3. Projection of the aikinite structure parallel to *b*, showing the composite chains $CuBiS_3$ parallel to *b*, hold together by Bi—S = 2.95 Å bonds to form sheets parallel to (001) between which the Pb atoms are sandwiched

Recently, Welin (1966) showed that several sulfosalts with aikinite-like structures exist and he could predict the composition of other hypothetical members of this group. It was observed that intermediate compositions between Bi_2S_3 and $CuPbBiS_3$ are nearly stoichiometric and correspond to superstructures with integral multiples Z of the a translation of aikinite in the orientation *Pbnm*.

The general structure-cell formula of aikinite derivatives is $Cu_xPb_xBi_{8Z-x}S_{12Z}$. Moore (1967) derived the inequality $4Z > x$ and gave a classification according to Z^n with $n = x/4$ = number of Pb(Cu) atoms in the asymmetric unit $< Z$ (aikinite: $Z = 1$, $x = 4$, $n = 1$). Gladite, hammarite and Welin's new compound RM 24,100:3 for example may be described as 3^1, 3^2 and 5^3 aikinite with the formula

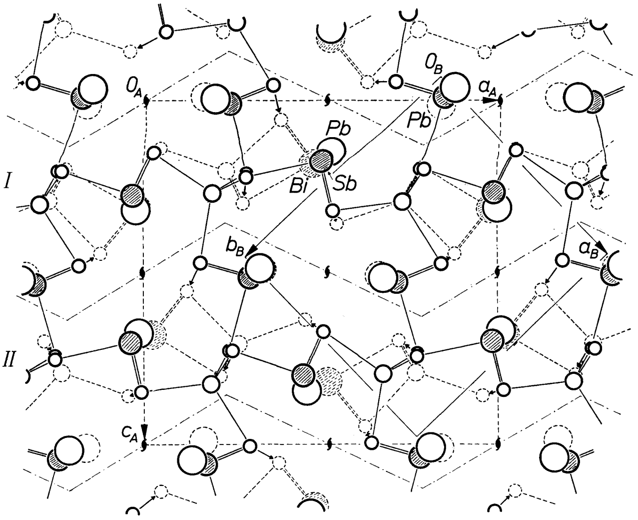

Fig. 4*a*. Projection of the structures both of bournonite (solid lines) parallel to *c* and of aikinite (broken lines) parallel to *b*

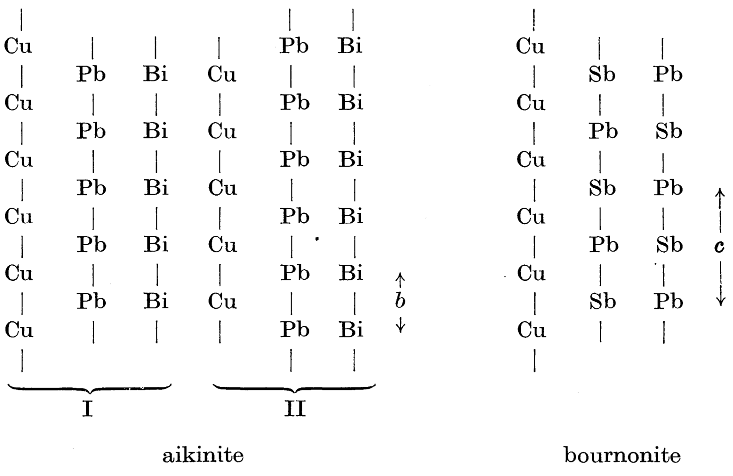

Fig. 4*b*. Sequences of metal and semimetal atoms parallel to *b* or *c* in aikinite and bournonite respectively

(in the asymmetric unit) $CuPbBi_5S_9$, $Cu_8Pb_8Bi_{16}S_{36}$ and $Cu_{12}Pb_{12}Bi_{28}S_{60}$ and the space group *Pbnm*, *Pbnm* and *Pbmm* (OHMASA and NOWACKI, 1970) respectively.

The structure of bournonite[2] projected along the *c* axis and that of aikinite along the *b* axis are given simultaneously in Fig. 4*a*. The former is drawn in solid lines and superposed on the latter, drawn in broken lines. The *a* and *b* axes of bournonite are nearly parallel to [101] and [$10\bar{1}$] directions of aikinite. In the figure, the relative positions of the Bi and the Pb atoms in aikinite agree well with those of Sb and Pb in bournonite. The locations of the S atoms in both projected structures (as shown by arrows in the drawing) are also rather contiguous. But this resemblance of both projected structures is not maintained in three dimensions, because the relative positions along the projection axes are not the same through the unit cell. In aikinite we have 2_1 axes parallel to *b* and therefore the *y* coordinates of the atoms in the upper half of the cell differ by one-half (= 2 Å) from those in the lower half in such a way that region I is transformed into region II (Fig. 4*a*); while in bournonite there is no such relation between the two regions. This difference is clear from Table 6, in which the coordinates of atoms in bournonite are transformed into the cell of aikinite and are compared with the coordinates of the corresponding atoms in aikinite. The sequences of metal and semimetal atoms along the projection axes are shown schematically in Fig. 4*b*. These differences in their structures may be attributed mainly to the short Me—S distances in the Sb pyramid by reasons discussed below.

Table 7 shows S—S distances of MeS_3 pyramids in various sulfosalts. The average value of the S—S distances in Sb and Bi pyramids is 3.63 Å, 3.83 Å respectively. The period of an array of Pb prisms which share their basal planes with each other is in the range of 4.0 Å—4.2 Å. Therefore the misfit of the size may be much larger for Sb than for Bi pyramids and therefore it becomes impossible to have both *infinite* chains of Sb and Pb in one and the same structure. The misfit of AsS_3 pyramids with a Pb-S array has been pointed out already by IITAKA and NOWACKI (1962). No example is known to us in which with certainty infinite Sb chains exist together with infinite Pb arrays.

The array of Sb and Pb in bournonite does not fit to the structure of aikinite. Otherwise, Sb pyramids should share their edges each other and form Sb_2S_4 groups. They should also share some edges with

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[2] The results of the refinement by EDENHARTER *et al.* (1970) were used for the atomic positions of bournonite.

Table 6. *Coordinates of atoms in aikinite* (A) *and bournonite* (B) [transformed to the cell of (A)]

Region I				Region II			
Atom	x	y	z	Atom	x	y	z
$\mathrm{Bi_A}$	0.9811	0.75	0.3173	$\mathrm{Bi_A}$	0.0189	0.25	0.6827
$\mathrm{Pb(2)_B}$	0.995	0.75	0.317	$\mathrm{Pb(1)_B}$	0.000	0.75	0.673
$\mathrm{Sb(2)_B}$	0.986	1.75	0.276	$\mathrm{Sb(1)_B}$	− 0.025	1.75	0.701
$\mathrm{Bi_A}$	0.4811	0.75	0.1827	$\mathrm{Bi_A}$	0.5189	0.25	0.8173
$\mathrm{Pb(1)_B}$	0.534	0.75	0.151	$\mathrm{Pb(2)_B}$	0.460	0.75	0.839
$\mathrm{Sb(1)_B}$	0.508	1.75	0.179	$\mathrm{Sb(2)_B}$	0.451	1.75	0.798
$\mathrm{Pb_A}$	0.1671	0.75	0.9895	$\mathrm{Pb_A}$	0.8329	0.25	0.0105
$\mathrm{Sb(2)_B}$	0.178	0.75	1.052	$\mathrm{Sb(1)_B}$	0.841	0.75	− 0.007
$\mathrm{Pb(2)_B}$	0.140	1.75	1.040	$\mathrm{Pb(1)_B}$	0.870	1.75	− 0.032
$\mathrm{Pb_A}$	0.6671	0.75	0.5105	$\mathrm{Pb_A}$	0.3329	0.25	0.4895
$\mathrm{Sb(2)_B}$	0.713	0.75	0.530	$\mathrm{Sb(1)_B}$	0.307	0.75	0.514
$\mathrm{Pb(2)_B}$	0.674	1.75	0.518	$\mathrm{Pb(1)_B}$	0.335	1.75	0.489
$\mathrm{Cu_A}$	0.2338	0.25	0.2085	$\mathrm{Cu_A}$	0.7662	0.75	0.7915
$\mathrm{Cu_B}$	0.209	0.262	0.271	$\mathrm{Cu_B}$	0.674	0.262	0.793
$\mathrm{Cu_B}$	0.209	1.238	0.271	$\mathrm{Cu_B}$	0.674	1.238	0.793
$\mathrm{Cu_A}$	0.7338	0.25	0.2915	$\mathrm{Cu_A}$	0.2662	0.75	0.7085
$\mathrm{Cu_B}$	0.733	0.238	0.298	$\mathrm{Cu_B}$	0.198	0.237	0.820
$\mathrm{Cu_B}$	0.733	1.262	0.298	$\mathrm{Cu_B}$	0.198	1.262	0.820
$\mathrm{S(1)_A}$	0.2840	0.75	0.3014	$\mathrm{S(1)_A}$	0.7160	0.25	0.6986
$\mathrm{S(1)_B}$	0.302	0.75	0.215	$\mathrm{S(1)_B}$	0.767	0.75	0.737
$\mathrm{S(2)_B}$	0.301	1.75	0.224	$\mathrm{S(2)_B}$	0.766	1.75	0.746
$\mathrm{S(1)_A}$	0.7840	0.75	0.1986	$\mathrm{S(1)_A}$	0.2160	0.25	0.8014
$\mathrm{S(2)_B}$	0.784	0.75	0.205	$\mathrm{S(2)_B}$	0.249	0.75	0.727
$\mathrm{S(1)_B}$	0.793	1.75	0.205	$\mathrm{S(1)_B}$	0.258	1.75	0.726
$\mathrm{S(2)_A}$	0.0467	0.25	0.1394	$\mathrm{S(2)_A}$	0.9533	0.75	0.8606
$\mathrm{S(4)_B}$	0.043	0.213	0.152	$\mathrm{S(3)_B}$	1.003	0.225	0.844
$\mathrm{S(4)_B}$	0.043	1.287	0.152	$\mathrm{S(3)_B}$	1.003	1.275	0.844
$\mathrm{S(2)_A}$	0.5467	0.25	0.3606	$\mathrm{S(2)_A}$	0.4533	0.75	0.6394
$\mathrm{S(3)_B}$	0.538	0.225	0.322	$\mathrm{S(4)_B}$	0.509	0.213	0.674
$\mathrm{S(3)_B}$	0.538	1.275	0.322	$\mathrm{S(4)_B}$	0.509	1.287	0.674
$\mathrm{S(3)_A}$	0.3775	0.25	0.0559	$\mathrm{S(3)_A}$	0.6213	0.75	0.9441
$\mathrm{S(4)_B}$	0.370	0.287	− 0.042	$\mathrm{S(3)_B}$	0.637	0.275	0.995
$\mathrm{S(4)_B}$	0.370	1.213	− 0.042	$\mathrm{S(3)_B}$	0.637	1.225	0.995
$\mathrm{S(3)_A}$	0.8775	0.25	0.4441	$\mathrm{S(3)_A}$	0.1213	0.75	0.5559
$\mathrm{S(4)_B}$	0.835	0.287	0.479	$\mathrm{S(3)_B}$	0.172	0.275	0.473
$\mathrm{S(4)_B}$	0.835	1.213	0.479	$\mathrm{S(3)_B}$	0.172	1.225	0.473

Table 7. S–S *distances in* MeS$_3$ *pyramids in various sulfosalts*

AsS$_3$ pyramids		
binnite	3.40 Å	(Wuensch *et al.*, 1966)
gratonite	3.47	(Ribár and Nowacki, 1969a)
hutchinsonite	3.44	(Takéuchi *et al.*, 1965)
marrite	3.43	(Wuensch and Nowacki, 1967)
nowackiite	3.49	(Marumo, 1967)
rathite-I	3.45	(Marumo and Nowacki, 1965)
seligmannite	3.43	(Edenharter *et al.*, 1970)
trechmannite	3.36	(Matsumoto and Nowacki, 1969)
mean	3.43 Å	
SbS$_3$ pyramids		
berthierite	3.56 Å	(Buerger and Hahn, 1954)
bournonite	3.59	(Edenharter *et al.*, 1970)
jamesonite	3.68	(Niizeki and Buerger, 1957a)
livingstonite	3.60	(Niizeki and Buerger, 1957b)
miargyrite	3.75	(Knowles, 1964)
stephanite	3.62	(Ribár and Nowacki, 1969b)
stibnite	3.64	(Ščavničar, 1960)
tetrahedrite	3.61	(Wuensch, 1964)
mean	3.63 Å	
BiS$_3$ pyramids		
aikinite	3.72 Å	(present study)
cosalite	3.89	(Weitz and Hellner, 1960)
galenobismutite	3.87	(Iitaka and Nowacki, 1962)
mean	3.83 Å	

Cu tetrahedra. These configurations would be unusual and have up to date not been found in sulfosalts.

Since As pyramids have still smaller dimensions than Sb pyramids, seligmannite can not have the structure of aikinite.

In this way it can be understood why the structure of aikinite is different from that of seligmannite and bournonite.

This difference appears also in the structural formulae of these crystal species (Nowacki, 1969): seligmannite (bournonite) = $\{[\mathrm{As(Sb)S_3}]_2|\mathrm{Cu_2^{IV}Pb^{VII}Pb^{VIII}}\}$ versus aikinite = $[\mathrm{BiS_2}|\mathrm{S}|\mathrm{Cu^{IV}Pb^{VII}}]$. Whereas in the former isolated MeS$_3$ pyramids (Me = As, Sb) occur, i.e. the BS$_3$ pyramids do not have common S atoms, in the latter these pyramids are combined to infinite chains $BiS_{2/2}S = BiS_2$ and additional S atoms are bonded only to Cu and Pb, not to Bi. Therefore seligmannite (bournonite) belongs to the structure type II.a_1 and aikinite to the type II.a_2, according to the classification given by Nowacki (1969).

Acknowledgment

The authors are grateful to Dr. P. Engel for his kind help. They are also indebted to the Rechenzentrum der Universität Bern (Prof. W. Nef and Dr. R. R. Hüsser) for the use of the Bull Gamma 30S computer, to the International Business Machines, Extension Suisse for the opportunity to perform the data reduction by the IBM 360/65 computer in Basel, to Mr. H. Bruggesser for his great help and to the Schweizerischer Nationalfonds (Project No. 3508—2.17.68) Kommission zur Förderung der wissenschaftlichen Forschung (Projects nos. 384/386) and Stiftung Entwicklungsfonds Seltene Metalle for financial help.

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