The Crystal Structure of Aikinite, PbCuBiS₃

By Iwao Kohatsu and B. J. Wuensch

Department of Metallurgy and Materials Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, *U.S.A.*

Aikinite, $PbCuBiS_3$, is orthorhombic, space group *Pnma*, with $a=11\cdot608$ (1), $b=4\cdot0279$ (3), $c=11\cdot275$ (2) Å. $D_m=7\cdot07$ (1) g.cm^{-3} and $D_x=7\cdot25$ g.cm^{-3} for $Z=4$. Diffraction data were recorded with an equi-inclination diffractometer equipped with a proportional counter as detector. Least-squares refinement reduced the disagreement index for a structure proposed by Wickman from 23% to 9·6% and permitted distinction between Pb and Bi on the basis of bond distances. The asymmetric unit of the structure contains Pb, Cu, Bi and 3S. The Pb atom is coordinated by five S atoms at distances ranging from 2·84 to 2·98 Å in locations close to an octahedral environment; two additional S neighbors are located at 3·24 Å. The Bi atom has three S neighbors at 2·66 and 2·73 Å, three more distant S atoms at 2·97 to 3·12 Å, and a seventh S neighbor at 3·53 Å. The copper atom has a distorted tetrahedral coordination, and all three types of S atoms have octahedral coordination. Aikinite is a stuffed derivative of the stibnite structure type; Pb occupies the interior (5-coordinated) positions of the stibnite quadruple chain, while Cu is added to a tetrahedral interstice. These substitutions cause no major distortions of the stibnite arrangement and the atomic positions in aikinite are remarkably similar to these in bismuthinite, Bi_2S_3.

Introduction

Bismuth compounds constitute roughly one-fifth of the known sulfosalts, but have received much less study than other minerals of this group. Only four structures have been completely determined. These include galeno-bismutite, $PbBi_2S_4$, studied by Wickman (1951) and subsequently refined by Iitaka & Nowacki (1962); cosalite, $Pb_2Bi_2S_5$ (Weitz & Hellner, 1960); $PbCu_4Bi_5S_{11}$ (Kupčík & Makovický, 1968) and emplectite, $CuBiS_2$ (Kupčík, 1965; Jenkins, 1969). The structure of aikinite was partially determined by Wickman (1953). Only approximate corrections for severe absorption effects were made. The metal atoms were readily located, but accurate coordinates could not be obtained for sulfur. Bi and Pb have essentially identical scattering power and may be distinguished only through relatively slight differences in bond lengths. Wickman was accordingly unable to distinguish among the heavy atoms.

Aikinite has recently assumed increased importance toward an understanding of the crystal chemistry of the Bi sulfosalts. Three complex minerals – gladite, $PbCuBi_5S_9$; hammarite, $Pb_2Cu_2Bi_4S_9$ and $Pb_3Cu_3Bi_7S_{15}$ – have recently been described and appear to be superstructures based upon aikinite (Welin, 1966). On the basis of this apparent relationship, an extensive series of hypothetical aikinite derivatives has been proposed (Moore, 1967). The present reinvestigation of aikinite was undertaken to determine the role of Pb and Bi in the aikinite structure, and to permit comparison with the related minerals seligmannite, $PbCuAsS_3$, and bournonite, $PbCuSbS_3$ (Hellner & Leineweber, 1956; Leineweber, 1956; Takéuchi & Haga, 1969).

Experimental

Well-formed prismatic crystals from Beresovsk, USSR (Harvard Museum Catalogue No. 82490) were selected for study. Chemical analyses of material from this locality (Palache, Berman & Frondel, 1944) provide results close to the ideal composition. Precession photographs indicated orthorhombic symmetry and systematic absences for $0kl$ reflections with $k+l\neq2n$ and $hk0$ reflections with $h\neq2n$. The diffraction symbol is thus $mmmPn-a$ which permits $Pn2_1a$ (C^9_{2v}) and *Pnma* (D^{16}_{2h}) as possible space groups. The latter was employed by Wickman and was subsequently found to be satisfactory for the present structure determination.

A back-reflection Weissenberg camera with diameter of 114·592 mm was used to determine precise lattice constants. Using b and c as rotation axes, spacings for 56 $h0l$ and 29 $hk0$ reflections were obtained. The least-squares program *LCLSQ* (Burnham, 1961) was employed to correct for film shrinkage, specimen absorption and eccentricity. The lattice constants obtained (Table 1) are similar to the values obtained by Wickman (1953) and Peacock (1942) for material from the same locality. The present lattice constants provide a density of 7·25 g.cm^{-3}; the observed value is $7\cdot07\pm0\cdot01$ g.cm^{-3} (Palache *et al.*, 1944).

Integrated intensities were recorded with an ω-scan (rotating crystal, stationary counter) performed with the aid of an equi-inclination diffractometer equipped with a proportional counter as detector. The Cu $K\alpha$ sphere contained 580 independent reflections of which 548 were accessible with the diffractometer which was employed.

Aikinite has a very high linear absorption coefficient (1380 cm^{-1} for Cu $K\alpha$). It proved necessary to record three sets of intensities before a satisfactory refinement of the structure could be achieved. A first set of data was obtained from a thin (0.102×0.036 mm diameter) prismatic fragment in an attempt to obtain high transmission factors while maintaining maximum specimen volume in the X-ray beam. Small-scale irregularities in the crystal shape, which would have been negligible for a less-absorbing material, limited the accuracy of absorption correction. Refinement employing this set of data did not proceed beyond 18·2%.

A second set of data was recorded with a sample ground to 0·060 mm radius ($\mu_l r = 8.33$) which was spherical to within 0·003 mm in all radial directions. Although an accurate correction for absorption could be evaluated, the small crystal volume combined with low transmission factors produced weak intensities with very poor counting statistics when the diffractometer was operated under normal conditions. This set of data also failed to provide a satisfactory refinement. However, a satisfactory set of data was eventually obtained with the spherical specimen by increasing the number of counts recorded. Background intensity was recorded for 50 sec at $\pm 4°$ in φ from the diffraction maximum and the total number of counts accumulated as the crystal was rotated through 8° in φ at a slow scanning rate ($\frac{3}{4}°$ φ/min).

The integrated intensities were corrected for Lorentz, polarization and absorption factors with modified versions of the programs *FINTE* and *GNABS* (Onken, 1964). No correction for extinction was made. An intensity was considered to be below the minimum detectable value when $B + 0.6745$ σ_B exceeded $E - 0.6745$ σ_E, where B is the integrated background,

E is the total number of counts accumulated, and 0·6745 σ is the probable error computed from counting statistics. Of the 548 accessible reflections, 47 were unobservable and were assigned values equal to $\frac{1}{3}$ the minimum detectable intensity. This provided 14 observations per parameter in subsequent refinement incorporating anisotropic thermal motion. The reliability of the data was tested by evaluating the deviation of individual structure factor measurements from an average of four symmetry-equivalent values. The mean deviation in such comparisons for 20 different $\{hk3\}$ structure factors was 3·5%. (This deviation is compared with the final agreement between F_{obs} and
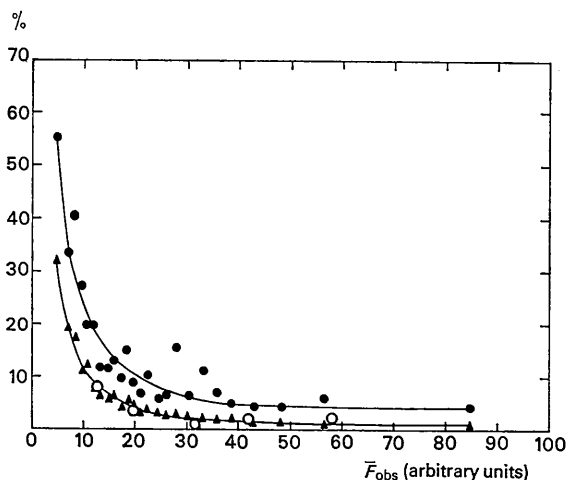

Fig. 1. Plot of σ/F_{obs}, $|\bar{F}_{obs} - F_i|/\bar{F}_{obs}$ for symmetry-equivalent reflections and $||F_{obs}| - |F_{cal}||/|F_{obs}|$ as a function of $|F_{obs}|$. ▲ σ/F_{obs} (groups of 20 reflections). ○ $|\bar{F}_{obs} - F_i|/\bar{F}_{obs}$ (groups of 16 reflections). ● $||F_{obs}| - |F_{cal}||/|F_{obs}|$ (groups of 20 reflections).

Table 1. *Crystallographic data and atomic positions for aikinite and bismuthinite*

(y parameter for all atoms is $\frac{1}{4}$; estimated standard deviations in parentheses).

		Aikinite, CuPbBiS₃ Wickman (1953)		Present work (λCu $K\alpha_1 =$ 1·54051 Å)	Departure from bismuthinite arrangement	Bismuthinite, Bi₂S₃ (Kupčik & Veselá, 1965)
a		11·65 Å		11·6083 (10) Å		11·28 (2) Å
b		4·00		4·0279 (3)		3·97 (1)
c		11·30		11·2754 (17)		11·11 (2)
Space group		*Pnma*		*Pnma*		*Pnma*
M(1)	x	A	0·017	Bi 0·0185 (2)	+0·0017	Bi(1) 0·0168
	z		0·685	0·6812 (2)	+0·0071	0·6741
M(2)	x	B	0·332	Pb 0·3332 (2)	−0·0075	Bi(2) 0·3407
	z		0·487	0·4880 (3)	+0·0020	0·4660
Cu	x		0·240	0·2320 (8)		
	z		0·210	0·2081 (9)		
S(1)	x		0·060	0·0454 (9)	−0·0032	0·0486
	z		0·135	0·1373 (11)	+0·0071	0·1300
S(2)	x		0·370	0·3795 (9)	+0·0010	0·3785
	z		0·045	0·0553 (11)	−0·0023	0·0576
S(3)	x		0·230	0·2146 (9)	−0·0023	0·2169
	z		0·810	0·8036 (9)	−0·0026	0·8062

F_{cal} in Fig. 1, below.) The mean reproducibility of a structure factor measurement, as determined by re-measurement of a number of reflections, was 2·5%.

Refinement of the structure

The full-matrix least-squares program *SFLS* 5 (Prewitt, 1962) was used for structure factor calculation and refinement. Neutral-atom form factors obtained from Table 3.3.1 of *International Tables for X-ray Crystallography*, Vol. III (1962) were employed. Corrections for anomalous scattering were employed for all atoms. A weighting scheme based on the standard deviation of F_{obs} (as derived from counting statistics) was used in the initial stages of refinement. In the final cycles this scheme was modified by an empirical function of F_{obs} which was selected to keep the value of $w(|F_{obs}| - |F_{cal}|)^2$ constant and independent of $|F_{obs}|$ for all values of F_{obs}.

The atomic parameters of Wickman (1953) provided a value of $R = \Sigma||F_{obs}| - |F_{cal}||/\Sigma|F_{obs}|$ of 23·2% with Pb placed in both heavy atom positions, and with all atoms arbitrarily assigned an isotropic temperature factor of 1·0 Å². Refinement of the positional param-

Fig. 2. Electron density section $\varrho(x\frac{1}{4}z)$ for aikinite. This section passes through the center of all atoms in the asymmetric unit. Contour intervals at 13·0 $e.Å^{-3}$; zero contour dotted.

eters and the temperature factors of the metal atoms reduced the disagreement index to 14·5%. Wickman's description of the structure thus proved to be correct. Metal–sulfur bond lengths were computed at this stage to determine the species occupying the two heavy metal sites (designated A and B by Wickman). The shortest A–S and B–S separations were found to be 2·68 and 2·84 Å, respectively. The distance of closest approach between Pb and S seldom falls below 2·8 Å (Nowacki, 1969), while in the four Bi sulfosalts for which structures are known, minimum Bi–S contacts ranging from 2·54 to 2·63 Å have been observed. The atom designated as A by Wickman was thus identified as Bi. A difference map was also prepared at this stage and revealed anisotropic thermal motion, particularly for Pb and Cu. Subsequent cycles of refinement in which anisotropic temperature factors were introduced for these two atoms reduced R to 11·6%. Further improvement was attained by allowing all atoms to acquire anisotropic temperature factors, and R converged to 9·8%.

The agreement between F_{obs} and F_{cal} was compared with the agreement between measurements of symmetry-equivalent F_{obs}, and the standard deviation of the measurements. Fig. 1 compares plots, as a function of $|F_{obs}|$, of

(1) $||F_{obs}| - |F_{cal}||/\Sigma|F_{obs}|$

(2) $\sigma/|F_{obs}|$, where σ is the standard deviation evaluated from counting statistics, and

(3) $\frac{1}{4}\Sigma|\bar{F} - F_i|/\bar{F}$, where $\bar{F}$ is the average of 4 symmetry-equivalent reflections, and F_i represents the individual observations.

Each quantity has been averaged over a group of reflections of similar magnitude to reduce scatter. The plot of the mean difference among measurements of equivalent F_{obs} is essentially the same as that for σ as a function of F_{obs}. Discrepancies in the former comparison therefore reflect counting statistics rather than inaccuracies in the correction for absorption. The standard deviation is an increasingly large fraction of F_{obs} for the smaller structure factors. Observations for which $||F_{obs}| - |F_{cal}|| > 0·25|F_{obs}|$ were therefore excluded from the evaluation of parameter shifts in a few final cycles of refinement. The final value of R for 501 observable structure factors was 9·6% and the 'weighted' R, $\{\Sigma w(|F_{obs}| - |F_{cal}|)^2/\Sigma w F_{obs}^2\}^{1/2}$, was 9·0%. When the 47 unobservable reflections were included, R and the weighted R were 10·6% and 9·6%, respectively. Final values of $||F_{obs}| - |F_{cal}||/F_{obs}$ are also plotted as a function of F_{obs} in Fig. 1. For the small structure factors with large standard deviations, ΔF is approximately 2σ. For the larger structure factors (approximately $\frac{2}{3}$ of the data) $\Delta F/F_{obs}$ is parallel to the plot of σ/F_{obs} and is 3% larger.

Results of the refinement

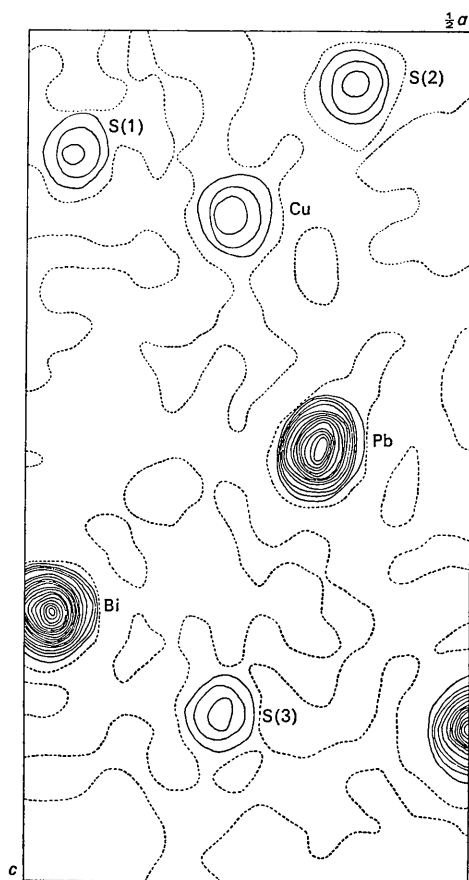The asymmetric unit of aikinite contains three metal atoms: Pb, Cu and Bi, and three sulfur atoms. All are

located at special position 4(c)m. The atomic coordinates are compared with the parameters reported by Wickman (1953) in Table 1. The metal atom locations remain essentially the same. The S atom coordinates have shifted by as much as 0·015 (0·17 Å), and the present parameters permitted distinction between Pb and Bi on the basis of bond lengths. Anisotropic temperature-factor coefficients are given in Table 2 along with equivalent isotropic temperature factors. The observed structure factors are compared in Table 3 with values computed for the parameters of Tables 1 and 2. All atoms in the asymmetric unit are located at $y = \frac{1}{4}$. The electron density in this section is presented in Fig. 2. Anisotropy of thermal vibration is clearly evident for Pb.

Table 2. *Anisotropic temperature factor coefficients*

$\beta_{12} = \beta_{23} = 0$ for all atoms and $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hl\beta_{13})]$

Atom	β_{ij}		Equivalent isotropic temperature factor
Pb	$\beta_{11} =$	0·0120 (3)	2·70 (6) Å²
	$\beta_{22} =$	0·0034 (1)	
	$\beta_{33} =$	0·0284 (14)	
	$\beta_{13} =$	$-0·0087$ (3)	
Bi	$\beta_{11} =$	0·0016 (1)	1·43 (4)
	$\beta_{22} =$	0·0182 (11)	
	$\beta_{33} =$	0·0044 (1)	
	$\beta_{13} =$	0·0002 (1)	
Cu	$\beta_{11} =$	0·0032 (5)	2·69 (18)
	$\beta_{22} =$	0·0478 (63)	
	$\beta_{33} =$	0·064 (10)	
	$\beta_{13} =$	$-0·0001$ (5)	
S(1)	$\beta_{11} =$	0·0026 (8)	1·52 (19)
	$\beta_{22} =$	0·0255 (72)	
	$\beta_{33} =$	0·0029 (8)	
	$\beta_{13} =$	0·0009 (6)	
S(2)	$\beta_{11} =$	0·0013 (6)	1·30 (17)
	$\beta_{22} =$	0·0096 (53)	
	$\beta_{33} =$	0·0051 (9)	
	$\beta_{13} =$	0·0007 (6)	

Table 2 (*cont.*)

S(3)	$\beta_{11} =$	0·0027 (7)	0·84 (19)
	$\beta_{22} =$	0·0083 (59)	
	$\beta_{33} =$	0·0011 (7)	
	$\beta_{13} =$	0·0002 (5)	

Discussion of the structure

Interatomic distances in aikinite are presented in Table 4. The coordination polyhedra, along with the orientation of the principal axes of the thermal-vibration ellipsoid of the central atom, are shown in Fig. 3. The Pb atom has seven sulfur neighbors at distances ranging from 2·84 to 3·28 Å. These distances are in good agreement with values found in other lead sulfosalts (Nowacki, 1969). The five closest neighbors (2·84 to 2·98 Å) form a square pyramid about Pb with locations close to octahedral positions. The Pb atom, however, is displaced from the base of the pyramid and all bond angles are much less than 90°. The remaining two sulfur atoms at greater distance (3·24 Å) constitute a 'split vertex' for an octahedral-like coordination.

The Bi atom also has seven neighbors. Bond lengths range from 2·66 to 3·53 Å. The seventh neighbor, however, is nearly 0·5 Å more distant than the other six and is not considered to be part of the nearest-neighbor configuration. The coordination scheme is quite distinct from that of the Pb polyhedron. Three S are close to Bi (2·66 and 2·73 Å) while the remaining three are at larger distances (2·97 and 3·12 Å). The closest three neighbors constitute a BiS₃ trigonal pyramid which is characteristic of group V metals with p^3 electron configuration. When the sulfur at intermediate distances are included, the coordination polyhedron becomes a severely distorted octahedron. The Bi atom is displaced from the plane of the square formed by the close (2·73 Å) and intermediate (2·97 Å) S atoms.

Copper has a tetrahedral coordination with neighbors located at 2·31 to 2·43 Å. These distances are again normal for copper-containing sulfosalts. The tetrahedron, however, is distorted. Bond angles

Table 3. *Comparison of observed and calculated structure factors*

(Unobservable values indicated by asterisk)

(Table 5) range from 97·9° to 116·7°, compared with the 109·47° angle which would occur in a regular polyhedron. The distortion is more severe than in seligmannite, as mentioned later. S(1) and S(2) are 6-coordinated; S(3) has only five neighbors, but the long Bi–S(3) separation constitutes a sixth, but more distant

Table 4. *Interatomic distances*

Estimated standard deviations in parentheses; closest second-nearest atom in brackets.

		Pb			Bi			Cu	
Metal atom	S(1ᵛ)	2·839 (12) Å		S(3)	2·663 (11) Å		S(1)	2·308 (14) Å	
polyhedra	S(3′)	2·948 (8)	2×	S(2′)	2·734 (8)	2×	S(3′)	2·366 (7)	2×
	S(1′)	2·978 (8)	2×	S(1‴)	2·966 (9)	2×	S(2)	2·428 (14)	
	S(2′)	3·275 (9)	2×	S(2‴)	3·117 (13)		[S(1‴)	4·035 (14)]	
	[S(3)	3·815 (11)]		[S(3ⁱᵛ)	3·531 (11)]				

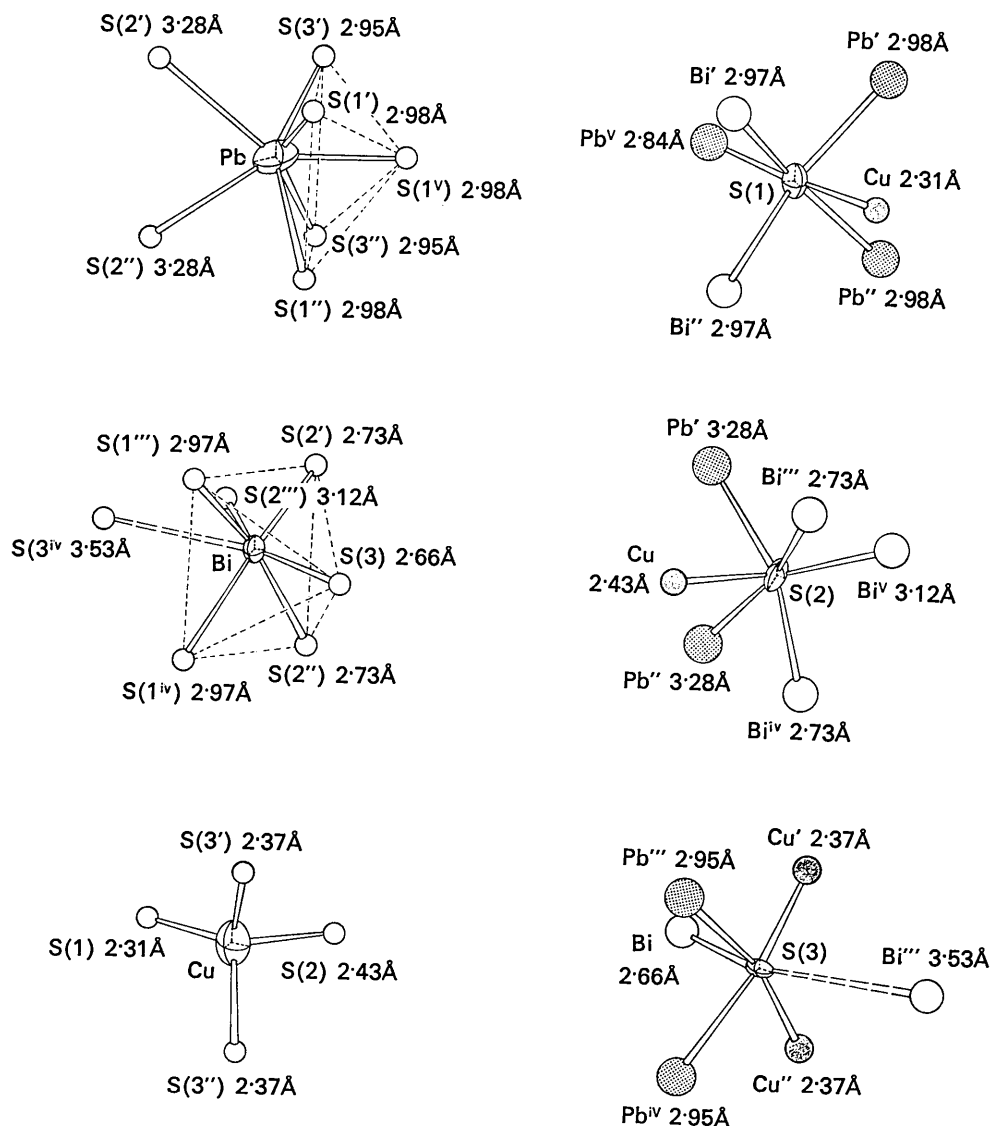|		S(1)			S(2)			S(3)	
Sulfur atom	Cu	2·308 (14) Å		Cu	2·428 (14) Å		Cu′	2·366 (7) Å	2×
polyhedra	Pbᵛ	2·839 (19)		Bi‴	2·734 (8)	2×	Bi	2·663 (11)	
	Bi′	2·966 (9)	2×	Biᵛ	3·117 (12)		Pb‴	2·948 (8)	2×
	Pb′	2·978 (8)	2×	Pb′	3·275 (9)	2×	[Bi‴	3·531 (11)]	
	[Cu‴	4·035 (14)]		[Pb	4·908 (10)]				

Fig. 3. Coordination polyhedra and orientation of thermal-vibration ellipsoid of central atom.

neighbor, for this atom as well. The S–S contacts in each metal polyhedron (Table 6) vary from 3·42 to 4·25 Å. All values are within 15% of Pauling's van der Waals separation of 3·7 Å.

The principal axes and orientation of the thermal-vibration ellipsoids for the atoms are given in Table 7. For most atoms the primary vibration directions are directed towards the midpoint of faces of the coordina-

Table 5. *Bond angles (standard deviations in parentheses)*

	Pb			Bi			Cu		
Metal-atom polyhedra	S(2')–Pb–S(3')	66·5° (3) 2×	S(3ⁱᵛ)–Bi–S(2''')	61·6° (3)		S(2)–Cu–S(3')	97·9° (4) 2×	
	S(2')–Pb–S(2'')	75·9° (3)	S(3ⁱᵛ)–Bi–S(1''')	73·6° (3) 2×		S(1)–Cu–S(3')	113·8° (4) 2×	
	S(2')–Pb–S(1')	79·0° (3) 2×	S(2''')–Bi–S(2')	77·3° (3) 2×		S(1)–Cu–S(2)	114·6° (6)	
	S(1ᵛ)–Pb–S(3')	79·2° (3) 2×	S(3)–Bi–S(1''')	81·7° (3) 2×		S(3')–Cu–S(3'')	116·7° (6)	
	S(1ᵛ)–Pb–S(1')	82·6° (3) 2×	S(3)–Bi–S(2')	84·2° (3) 2×*				
	S(1'')–Pb–S(1')	85·1° (3)	S(1''')–Bi–S(2')	88·1° (2) 2×				
	S(3')–Pb–S(3'')	86·2° (3)	S(2')–Bi–S(2'')	94·9° (4)*				
	S(1')–Pb–S(3')	91·3° (2) 2×	S(3ⁱᵛ)–Bi–S(2''')	117·3° (2) 2×				
	S(2')–Pb–S(3')	116·2° (3) 2×	S(3ⁱᵛ)–Bi–S(1')	117·5° (3) 2×				
	S(2'')–Pb–S(1')	129·9° (3) 2×	* for 3 shortest bonds					

	S(1)			S(2)			S(3)		
Sulfur-atom polyhedra	Cu–S(1)–Pb'	75·6° (3) 2×	Cu–S(2)–Pb'	68·5° (3) 2×	Pbⁱᵛ–S(3)–Cu'	77·8° (2)	2×
	Pb'–S(1)–Pb''	85·1° (1)	Pb'–S(2)–Pb''	75·9° (3)	Pb'''–S(3)–Pbⁱᵛ	86·2° (3)	
	Bi'–S(1)–Bi''	85·5° (3)	Cu–S(2)–Bi'''	86·4° (3) 2×	Bi–S(3)–Cu'	89·3° (3)	2×
	Cu–S(1)–Bi'	89·8° (4) 2×	Pb''–S(2)–Biⁱᵛ	89·7° (1) 2×	Bi–S(3)–Pb'''	101·8° (3)	2×
	Bi'–S(1)–Pb'	92·8° (1) 2×	Biⁱᵛ–S(2)–Biᵛ	94·9° (4)	Cu'–S(3)–Cu''	116·7° (6)	
	Pbᵛ–S(1)–Bi'	97·3° (3) 2×	Biᵛ–S(2)–Pb'	101·1° (3) 2×			
	Pbᵛ–S(1)–Pb'	97·4° (3) 2×	Biᵛ–S(2)–Bi'''	102·7° (3) 2×			

Table 6. *Sulfur–sulfur separations*

Presence of a metal atom following the separation indicates that the edge is shared with that coordination polyhedra

	Pb				Bi				Cu			
S(2')–S(3')	3·423 (16) Å	2×	Bi	S(2''')–S(3ⁱᵛ)	3·423 (16) Å		Pb	S(2)–S(3')	3·617 (13) Å	2×	Bi
S(1ᵛ)–S(3')	3·689 (12)	2×	Bi	S(3)–S(2')	3·617 (12)	2×	Cu*	S(1)–S(3')	3·916 (14)	2×	Bi
S(1ᵛ)–S(1')	3·839 (19)	2×	Pb	S(2''')–S(2')	3·667 (18)	2×	Bi	S(1)–S(2)	3·986 (16)		Pb
S(1')–S(2')	3·986 (16)	2×	Cu	S(3)–S(1''')	3·689 (12)		Pb	S(3')–S(3'')	4·028 (0)	= b	Pb
S(1')–S(1'') ⎫			Bi	[S(1''')–S(3ⁱᵛ)	3·916 (14)	2×]	Cu				
S(2')–S(2'') ⎬	4·028 (0) = b		Bi	S(1''')–S(1ⁱᵛ) ⎫	4·028 (0)	= b	Pb*				
S(3)–S(3'') ⎭			Bi	S(2')–S(2'') ⎭							
			Cu								
S(1')–S(3') ⎰	4·245 (17)	2×									

* Edges spanning 2 short Bi bonds

Table 7. *Principal axes and orientations of thermal vibration ellipsoids*

	Principal axes	R.m.s. Amplitude	Orientation with respect to		
			a	*b*	*c*
Pb	1	0·128 (4) Å	22·6° (1·1)	90°	67·4° (1·1)
	2	0·153 (4)	90°	180°	90°
	3	0·251 (4)	157·4° (1·1)	90°	22·6° (1·1)
Bi	1	0·105 (3)	176·3° (2·6)	90°	86·3° (2·6)
	2	0·122 (4)	90°	180°	90°
	3	0·168 (3)	86·3° (2·6)	90°	3·8° (2·6)
Cu	1	0·146 (13)	1·5° (10·2)	90°	88·5° (10·2)
	2	0·198 (13)	90°	180°	90°
	3	0·203 (15)	91·6° (10·0)	90°	1·6° (10·0)
S(1)	1	0·111 (20)	137·6° (19·7)	90°	47·6° (19·7)
	2	0·145 (21)	90°	180°	90°
	3	0·156 (17)	47·6° (19·7)	90°	42·5° (19·7)
S(2)	1	0·089 (20)	90°	0°	90°
	2	0·089 (20)	10·9° (8·6)	90°	100·9° (8·6)
	3	0·183 (20)	79·1° (8·6)	90°	10·9° (8·6)
S(3)	1	0·082 (30)	97·2° (13·9)	90°	7·2° (13·9)
	2	0·082 (30)	90°	180°	90°
	3	0·136 (20)	7·2° (13·9)	90°	82·8° (13·9)

tion polyhedra. Copper, however, has large vibration amplitudes in two directions which are in a plane normal to the symmetry plane of the structure. The smallest principal axis is the direction of the Pb atom, and this may represent a repulsive interaction.
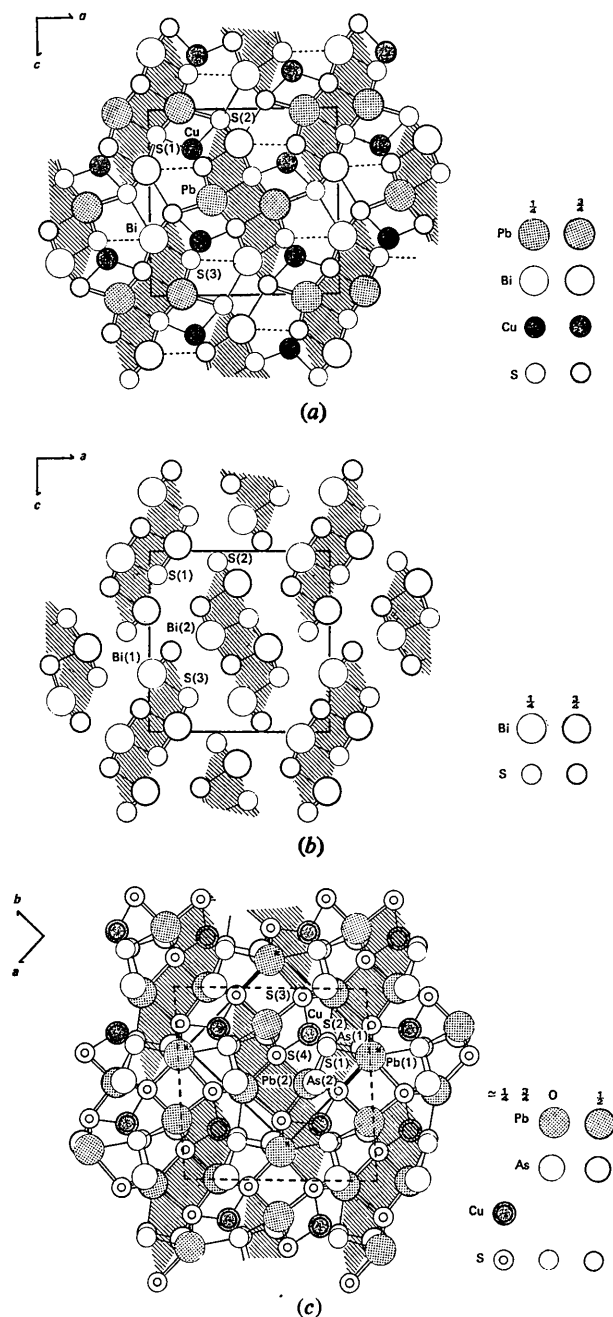

(a)

(b)

(c)

Fig. 4. Projections of the structures of aikinite, bismuthinite, and seligmannite, with regions corresponding to the stibnite quadruple chain indicated by shading. (*a*) Aikinite, $PbCuBiS_3$. (*b*) Bismuthinite, Bi_2S_3 (Kupčík & Veselá, 1965) (Only bonds within chains are indicated for clarity. Interchain bonds are of comparable length, as in aikinite). (*c*) Seligmannite, $PbCuAsS_3$ (Takéuchi & Haga, 1969).

Since relatively little information is available, it is of interest to compare the coordination of Bi in aikinite with that observed in other bismuth sulfosalts. Three short, nearly orthogonal bonds may be identified in all structures. With but a few exceptions [*e.g.* Bi(2) in galenobismutite (Iitaka & Nowacki, 1962)] a fourth and fifth sulfur neighbor are present at somewhat greater distances to complete a square pyramid about the Bi atom. The apical Bi–S bond is usually shortest. There is variation in the arrangement of the more distant neighbors. Three general types of coordination have been observed. In emplectite (Jenkins, 1969) and for Bi(1) through Bi(3) in $PbCu_4Bi_5S_{11}$ (Kupčík & Makovický, 1968), no additional sulfur atom is closer than about 3·5 Å. For Bi(2) in bismuthinite (Kupčík & Veselá, 1965) and Bi(4) in $PbCu_4Bi_5S_{11}$, two neighbors are present at 3·33 Å which constitute a 'split' vertex for an octahedral-like coordination. For Bi in aikinite, Bi(1) in galenobismutite and Bi(5) in $PbCu_4Bi_5S_{11}$, only a single additional neighbor is present, and it is located at a closer distance (3·08 to 3·12 Å). There is close correspondence between all bond distances observed for such octahedral coordination:

aikinite	2·66 (1 ×) 2·73 (2 ×) 2·97 (2 ×) 3·12 (1 ×) Å
Bi(1),galenobismutite	2·63 (1 ×) 2·73 (2 ×) 2·99 (2 ×) 3·12 (1 ×)
$Bi(5)PbCu_4Bi_5S_{11}$	2·65 (1 ×) 2·74 (2 ×) 2·97 (1 ×) 3·08 (2 ×)

Similar octahedral coordination exists about the four independent Bi atoms in cosalite (Weitz & Hellner, 1960), but this structure has been less well refined ($R = 24·5\%$).

Aikinite, as noted by Wickman (1953), is a 'stuffed' derivative of the structure of stibnite, Sb_2S_3 (Ščavničar, 1960) or bismuthinite, Bi_2S_3 (Kupčík & Veselá, 1965). A projection of the structure is given in Fig. 4(*a*), in which the quadruple chains of the stibnite structure are indicated by shading. The Pb and Bi atoms in aikinite substitute in ordered fashion for Sb(2) and Sb(1), respectively, in the stibnite structure type. The latter atoms represent the [1+2+2] and [1+2] coordinated atoms at the interior and edge of the stibnite quadruple chain, respectively. The Cu atom in aikinite is added to a tetrahedral interstice which is unoccupied in the stibnite structure.

It is of interest to examine the effect of the addition of the interstitial Cu and the substitution of Pb for Bi on the relative atomic arrangements in aikinite and bismuthinite (Kupčík & Veselá, 1965). A projection of the bismuthinite structure* is presented in Fig. 4(*b*). The lattice of aikinite is expanded by 2·9% along **a**, and 1·5% along **b** and **c** relative to bismuthinite (Table 1). Surprisingly, the atomic positions in the two structures are nearly identical in spite of the addition of

---

* The original space group settings of Wickman (1953) and Hellner & Leineweber (1956) have been maintained for aikinite and seligmannite, respectively, throughout this paper. Kupčík & Veselá's (1965) description of bismuthinite has been changed to correspond to the present description of aikinite.

the interstitial Cu atom. Aikinite differs little from a homogeneously expanded version of the bismuthinite structure. One significant distortion of the structure (Table 1) is the z coordinate of Pb. This parameter determines the component of the Pb–Cu separation in (010), and the shift represents a repulsive interaction with Cu. Interatomic distances in aikinite are consequently very similar to those observed in bismuthinite. In the latter structure the bond lengths for Bi(1) which correspond to those reported for Bi in Table 4 are 2·69, 2·65, 3·04, 3·02 and 3·39 Å, respectively. The principal difference is in the most distant sulfur, S(2'), which, in bismuthinite, is 0·14 Å closer to Bi. The Bi(2) atom in the bismuthinite structure is replaced by Pb in aikinite. Bond lengths of nearest neighbors are accordingly appreciably larger in aikinite: 2·84 and 2·95 Å *versus* 2·57 and 2·74 Å for S(1) and S(3), respectively. Interestingly, the four more distant neighbors are located at virtually identical distances in the two structures.

The lattice constants of seligmannite and bournonite are closely related to those of aikinite and bismuthinite, with [a, b, c] of seligmannite and bournonite approximately equal to $[-\frac{1}{2}0\frac{1}{2}/-\frac{1}{2}0-\frac{1}{2}/0-20]$ [a, b, c] of aikinite and bismuthinite.* As noted by Hellner & Leineweber (1956), projections of the seligmannite and bournonite structures bear a striking similarity to a projection of aikinite. A projection of seligmannite (Takéuchi & Haga, 1969) is compared with aikinite in Fig. 4(c). It is indeed possible to define a stibnite-like region in a portion of the seligmannite projection but, even so, the structure differs from that of aikinite in two important respects. The ordering schemes of Pb and the group V metal are quite distinct. The Pb and As atoms alternate along the stibnite-like chain in seligmannite, while this is not the case in aikinite. This is the feature which causes the **c** translation in seligmannite to be twice the period of the stibnite chain and hence double the **b** translation in aikinite. Secondly, and more importantly, atoms on opposing surfaces of a stibnite-like chain are staggered by one-half of the period of the chain. Corresponding atoms in seligmannite are opposite one another – that is, they have the same z coordinate. The similarity between aikinite and seligmannite therefore occurs *only* in projection; the two structures are quite distinct. Takéuchi & Haga (1969) note that the Cu tetrahedron in seligmannite is quite regular. They prefer to describe the structure as a network of Cu tetrahedra and AsS₃ pyramids, with Pb occupying cavities in the framework. Takéuchi & Haga therefore group seligmannite with other copper sulfosalts and point out that seligmannite contains layers which are similar to those present in enargite, Cu_3AsS_4, and cubanite, $CuFe_2S_3$. The present work shows that the Cu tetrahedron in aikinite is much more distorted than in seligmannite, while the $PbBiS_3$ chain is virtually identical to the Bi_2S_3 quadruple chain in bismuthinite. Thus seligmannite may be considered a copper sulfosalt in spite of its superficial resemblance to aikinite in

projection, while aikinite is a true stuffed derivative of bismuthinite.

Note added in proof: — A full report of the structure of bismuthinite has appeared (Kupčik & Veselá-Nováková, 1970) The temperature factors for the atoms in bismuthinite [not avaliable in Kupčík & Veselá (1965)] bear close resemblance to those found in aikinite:

	Pb,Bi(2)	Bi,Bi(1)	S(1)	S(2)	S(3)
Aikinite	2·70	1·43	1·52	1·30	0·84Å²
Bismuthinite	0·95	0·94	0·96	0·92	0·76

The difference in temperature-factor magnitudes between the two studies may reflect systematic error. With the exception of Pb, however, the correspondence of relative values within the two structures is striking.

References

BURNHAM, C. W. (1961). *Carnegie Inst. Washington Year Book*, **61**, 133.
HELLNER, E. & LEINEWEBER, G. (1956). *Z. Kristallogr.* **107**, 150.
IITAKA, Y. & NOWACKI, W. (1962). *Acta Cryst.* **15**, 691.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
JENKINS, J. K. (1969). S. B. Thesis. Massachusetts Inst. of Technology.
KUPČÍK, V. (1965). Program and Abstracts for Meeting of the Crystallographic Section of the German Mineralogical Soc., Oct. 13–16, 1965, Marburg; p. 16.
KUPČÍK, V. & MAKOVICKÝ, E. (1968). *N. Jb. Miner. Mh.* **7**, 236.
KUPČÍK, V. & VESELÁ, L. (1965). Program and Abstracts for Meeting of the Crystallographic Section of the German Mineralogical Soc., Oct. 13–16, 1965, Marburg; p. 18.
KUPČÍK V. & VESELÁ-NOVÁKOVÁ, L. (1970). *Tschermaks min. petrogr. Mitt.* **14**, 55.
LEINEWEBER, G. (1956). *Z. Kristallogr.* **108**, 161.
MOORE, P. B. (1967). *Amer. Min.* **52**, 1874.
NOWACKI, W. (1969). *Schweiz. min. petrogr. Mitt.* **49**, 109.
ONKEN, H. H. (1964). *Manual for Some Computer Programs for X-ray Analysis.* Crystallographic Laboratory, Massachusetts Inst. of Technology.
PALACHE, C., BERMAN, H. & FRONDEL, C. (1944). *The System of Mineralogy.* Vol. 1, 7th ed. p. 412. New York: John Wiley.
PEACOCK, M. A. (1942). *Univ. Toronto Studies, Geol. Ser.,* **47**, 63.
PREWITT, C. T. (1962). Ph. D. Thesis, Massachusetts Inst. of Technology.
ŠĆAVNIČAR, S. (1960). *Z. Kristallogr.* **114**, 85.
TAKÉUCHI, Y. & HAGA, N. (1969). *Z. Kristallogr.* **130**, 254.
WEITZ, G. & HELLNER, E. (1960). *Z. Kristallogr.* **113**, 385.
WELIN, E. (1966). *Ark. Min. Geol.* **4**, 377.
WICKMAN, F. E. (1951). *Ark. Min. Geol.* **1**, 219.
WICKMAN, F. E. (1953). *Ark. Min. Geol.* **1**, 501.