

The crystal structure of aramayoite $\text{Ag}(\text{Sb}, \text{Bi})\text{S}_2$ *

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Auszug

Die Kristallstruktur von Aramayoit, mit der idealen Zusammensetzung $\text{Ag}(\text{Sb}, \text{Bi})\text{S}_2$, wurde mittels nicht-integrierter photographischer Daten bestimmt. Die Gitterkonstanten sind: $a = 7,76 \pm 0,02 \text{ \AA}$, $b = 8,85 \pm 0,02 \text{ \AA}$, $c = 8,23 \pm 0,02 \text{ \AA}$, $\alpha = 100^\circ 11' \pm 15'$, $\beta = 90^\circ 43' \pm 15'$, $\gamma = 103^\circ 50' \pm 15'$; die Raumgruppe ist $P1$. Der R -Wert für 418 beobachtete Reflexe ergab sich zu 11,9%.

Aramayoit weist eine Superstruktur auf; die Substruktur ist vom Steinsalztypus. Die Struktur hat statistischen Charakter, indem Wismut die Antimonlagen partiell oder vollständig ersetzen kann. Der Inhalt der Elementarzelle entspricht der Formeleinheit $\text{Ag}_5\text{Sb}_{3,75}\text{Bi}_2\text{S}_{12}$ (Valenzregel ist nicht erfüllt). Es gibt in der Struktur drei Schichttypen: eine Antimon-Wismut-Schicht, eine Silberschicht und eine gemischte Schicht mit allen drei Typen von Metallatomen.

Die mittleren Bindungsabstände sind 2,55(8) Å für Ag–S, 2,66(8) Å für Sb–S und 2,77(7) Å für Bi–S.

Aramayoit weist eine gewisse Ähnlichkeit mit Matildit, AgBiS_2 , auf. Beides sind Schichtstrukturen mit ausgesprochener Spaltbarkeit. Aber im Falle von Matildit sind die Ebenen abwechselungsweise Ag-, Bi-, S-Ebenen, mit Metallschichten zwischen den Schwefelschichten. Beide haben eine Substruktur von deformiertem Steinsalztypus mit statistischen Superstrukturen.

Abstract

The crystal structure of aramayoite of the ideal composition $\text{Ag}(\text{Sb}, \text{Bi})\text{S}_2$ was determined using non-integrated photographic data. The cell dimensions are: $a = 7.76 \pm 0.02 \text{ \AA}$, $b = 8.85 \pm 0.02 \text{ \AA}$, $c = 8.23 \pm 0.02 \text{ \AA}$, $\alpha = 100^\circ 11' \pm 15'$, $\beta = 90^\circ 43' \pm 15'$, $\gamma = 103^\circ 50' \pm 15'$. The space group is $P1$. The final R value was 11.9% for 418 observed reflections.

Aramayoite has a superstructure, and the substructure has a rocksalt-type arrangement. The structure is statistical, with partial and complete substitution of antimony atomic sites by bismuth. The unit-cell content is found to correspond

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with the formula unit $\text{Ag}_5\text{Sb}_{3.75}\text{Bi}_2\text{S}_{12}$ (valence rule is not fulfilled). There are three types of layers in the unit cell, an antimony-bismuth layer, a silver layer, and a mixed layer consisting of all three types of metal atoms.

The mean bond distances are 2.55(8) Å for Ag—S, 2.66(8) Å for Sb—S and 2.77(7) Å for Bi—S.

Aramayoite has a certain similarity with matildite, AgBiS_2 . Both are layer structures with pronounced cleavages. But in the case of matildite, the layers are alternate Ag, Bi, S, with metal layers in between sulfur layers. Both have distorted rocksalt-type substructures with statistical superstructures.

Introduction

Aramayoite, ideal composition $\text{Ag}(\text{Sb},\text{Bi})\text{S}_2$, is a black mineral found in Bolivia. Crystals exhibit a very marked cleavage parallel (010). It was first investigated in 1926 by YARDLEY¹, who determined cell dimensions. BERMAN and WOLFE² demonstrated that YARDLEY's cell was not correct in that it did not satisfy all the crystal habits found. They determined a new set of cell dimensions and reported the space group as $P\bar{1}$.

Experimental

Crystal data: $a = 7.76 \pm 0.02$ Å, $b = 8.85 \pm 0.02$ Å, $c = 8.23 \pm 0.02$ Å, $\alpha = 100^\circ 11' \pm 15'$, $\beta = 90^\circ 43' \pm 15'$, $\gamma = 103^\circ 50' \pm 15'$, Space group: $P\bar{1}$, $Z = 6$ [units of $\text{Ag}(\text{Sb},\text{Bi})\text{S}_2$], $V = 539.5$ Å³, $d = 5.69$, $\lambda(\text{CuK}\alpha) = 1.54178$, $\mu(\text{CuK}\alpha) = 1119.5$ cm⁻¹, $F_{000} = 812.0$, cell weight, $M = 1796$.

Aramayoite shows a pronounced (010) cleavage and a lesser (100) cleavage. The crystal of aramayoite selected for x-ray investigation was an extremely small, long, flat, plate-like needle of dimensions $0.005 \times 0.014 \times 0.110$ mm. The necessity for so small a crystal despite the disadvantages in terms of reduced intensities, arises not only because of the high absorption coefficient, but also because it was not possible to select a larger crystal which was sufficiently undamaged by the severe cleavage (010). This cleavage yields fine, foil-like cleavage plates, and many attempts had to be made before a suitable crystal was found. Even so, the best crystal selected showed elongation of upper layer spots characteristic of cleavage, and this effect rendered the crystal unsatisfactory for use on a Weissenberg diffractometer. The very small size of the crystal, giving rise as it did to reduced inten-

¹ K. YARDLEY, X-ray examination of aramayoite. *Min. Mag.* **21** (1926—1928) 163—169.

² H. BERMAN and C. W. WOLFE, Crystallography of aramayoite. *Min. Mag.* **25** (1938—1940) 466—474.

sities, made it impractical to collect integrated photographic data even with long exposures. Data was collected (non-integrated) on a Nonius Weissenberg camera. A total of 418 reflections was collected from the above-mentioned crystal mounted along the needle (*c*) direction (layers *hk0*—*hk6*). A multiple-film method (4 films) was used to record the reflection data for $\text{CuK}\alpha$ filtered radiation.

There were no systematic absences in the diffraction pattern, and the space group was therefore assigned as triclinic ($P\bar{1}$ or $P1$).

Cell dimensions were determined from *h0l*, *0kl* and *hk0* Weissenberg photographs, a second crystal being selected for the *h0l* and *0kl* orientations to avoid remounting the crystal used for data collection. The cell dimensions were found to be in agreement with those of BERMAN and WOLFE².

The intensities were estimated visually with reference to a calibrated intensity strip made from a strong characteristically shaped aramayoite reflection. Lorentz and polarisation corrections were applied to the intensity data. Absorption corrections for an irregularly shaped crystal were also applied using the programme of PREWITT and WUENSCH³ on an IBM 360 machine. Layer scaling was carried out on the basis of exposure times, since it was not possible to obtain suitable cross-level data, particularly for the weak levels with $l = 2n + 1$.

Structure determination and refinement

The x-ray films showed the intensity distribution characteristic of a superstructure with substructure halving in the *a* and *c* directions. Intensities with $h = 2n + 1$ and $l = 2n + 1$ were generally weak or very weak, and those with $h = 2n$ and $l = 2n$ generally strong. (Since data had to be collected about the *c* axis, the very weak layers with $l = 2n + 1$ required rather long exposure times to record even the stronger reflections in these layers.)

The space group was initially assumed to be $P\bar{1}$ since the centrosymmetric space group was reported by BERMAN and WOLFE², probably derived from morphological considerations.

The Patterson map for the substructure (using only reflections with $h = 2n$, $l = 2n$) was computed and solved. Attempts to refine this model by a least-squares method were not successful. Models with shifts of origin were also tried, but without success. A calculation of the Wilson statistics for the substructure data was made and this

³ B. J. WUENSCH and C. T. PREWITT, Corrections for x-ray absorption by a crystal of arbitrary shape. *Z. Kristallogr.* **122** (1965) 24–59.

Table 1. *Wilson statistics for substructure data of aramayoite*

	Experimental, aramayoite	Centrosymmetric*	Non- centrosymmetric*
$\langle E ^2 \rangle$	1.005	1.000	1.000
$\langle E^2 - 1 \rangle$	0.592	0.968	0.736
$\langle E \rangle$	0.929	0.798	0.886
$E > 1$	42.0	32.0	36.8 %
$E > 2$	0.5	5.0	1.8 %
$E > 3$	0.0	0.3	0.01 %

* G. H. STOUT and L. H. JENSEN, *X-ray structure determination*. MacMillan, London, p. 321 (1968).

showed the space group to be unambiguously non-centrosymmetric ($P1$). The results of the Wilson statistics for the substructure data are given in Table 1.

The model obtained from the Patterson map was subsequently refined in the space group $P1$ to an R value of 16%. This level of refinement was considered to be sufficient for a starting model for the solution of the superstructure. No attempts were made to distinguish between silver and antimony at this stage.

It was not possible to achieve a successful refinement of the substructure to the complete structure by least squares, starting with the substructure model and using all the data in the refinement. This is not common with superstructures.

The partial or "odd" Patterson map was computed. This is a Patterson map based only on superstructure reflections. Because of the relatively high symmetry of the structure there was considerable overlapping of peaks in this map, and it was not possible to interpret it successfully. The "odd" Patterson method was applied successfully perhaps for the first time by MARUMO⁴ in the case of nowackiite and was later described in some detail by TAKÉUCHI⁵.

A trial and error method based on minimization of the residual R , which has been developed and programmed by ITO⁶, was next used. This method, in its application to aramayoite, was beset by the

⁴ F. MARUMO, The crystal structure of nowackiite, $\text{Cu}_6\text{Zn}_3\text{As}_4\text{S}_{12}$. *Z. Kristallogr.* **124** (1967) 352–368.

⁵ Y. TAKÉUCHI, The investigation of superstructures by means of partial Patterson functions. *Z. Kristallogr.* **135** (1972) 120–136.

⁶ T. ITO, On the application of a minimum residual method to the structure determination of superstructures. *Z. Kristallogr.* **137** (1973) 399–411.

problem of having several possible structures all of which refined to about 18–19%. The starting coordinates were those obtained for the substructure. Distinguishing the correct structure was therefore more difficult, and this is probably due to the limitations both in quality and quantity of the intensity data. Only after several trials with the above method did a model emerge which refined by least-squares from the 18% which was the lower limit of the “minimum residual” method.

The contributions to the superstructure come from both changes in the multiplicities at atomic sites as well as from small shifts in the atomic positions. Least-squares refinement to improve the positional and thermal parameters reduced the R value from 18% to 14%. Up to this stage of the refinement, data which had not been corrected for absorption ($\mu R \approx 1.6$) were used. When absorption-corrected data

Table 2. *Positional and thermal parameters of aramayoite*
(estimated standard deviations in brackets)

Atom	x	y	z	B	Site occupancy
Ag(1)	0.305(4)	0.306(5)	0.340(4)	3.9(7) Å ²	
Ag(2)	0.472(9)	0.014(9)	0.009(9)	3.8(1.2)	0.50
Ag(3)	0.554(6)	0.028(7)	0.479(7)	2.3(1.0)	0.50
Ag(4)	0.325(5)	0.301(6)	0.891(6)	6.0(9)	
Ag(5)	0.802(4)	0.331(5)	0.351(5)	4.5(7)	
Ag(6)	0.814(3)	0.335(4)	0.839(4)	2.8(5)	
Sb(1)	0.051(2)	0.994(3)	0.514(3)	1.4(3)	
Sb(2)	0.174(3)	0.661(3)	0.151(3)	1.0(3)	
Sb(3)	0.175(2)	0.649(3)	0.658(3)	1.1(2)	($\frac{1}{2}$ Sb + $\frac{1}{2}$ Bi)
Sb(4)	0.668(2)	0.637(3)	0.158(3)	1.7(3)	($\frac{1}{2}$ Sb + $\frac{1}{2}$ Bi)
Sb(5)	0.676(4)	0.642(5)	0.647(4)	1.8(5)	0.75
Bi(1)	0.988(2)	0.986(2)	0.002(2)	0.8(1)	
S(1)	0.202(7)	0.990(8)	0.239(8)	1.0(1.1)	
S(2)	0.687(11)	0.926(13)	0.219(13)	2.6(1.8)	
S(3)	0.299(8)	0.954(9)	0.709(9)	1.0(1.1)	
S(4)	0.831(8)	0.938(10)	0.725(10)	1.0(1.1)	
S(5)	0.066(10)	0.337(11)	0.154(11)	1.5(1.4)	
S(6)	0.522(10)	0.325(12)	0.208(11)	1.8(1.5)	
S(7)	0.136(8)	0.354(9)	0.632(9)	1.0(1.1)	
S(8)	0.565(12)	0.303(15)	0.654(14)	2.9(1.9)	
S(9)	0.416(12)	0.552(14)	0.415(13)	2.8(1.8)	
S(10)	0.895(9)	0.634(11)	0.421(12)	0.6(1.1)	
S(11)	0.377(7)	0.616(9)	0.942(9)	1.0(1.1)	
S(12)	0.925(10)	0.693(12)	0.873(11)	2.0(1.6)	

were substituted, the R value dropped to 12.6%. Further adjustments to the atomic-site occupancies gave a final R value of 11.9%.

It was noticed towards the end of the refinement that certain sulfur-atom isotropic-temperature factors became very low. These were kept fixed at the value for the overall temperature factor obtained from Wilson statistics.

Table 3. *Interatomic distances and angles in aramayoite*;
estimated standard deviations in brackets

(a) Interatomic distances

Ag(1)—S(6)	2.05(8) Å	Sb(3)—S(3)	2.59(7) Å
Ag(1)—S(9)	2.11(10)	Sb(3)—S(12)	2.69(8)
Ag(1)—S(5)	2.54(8)	Sb(3)—S(10)	2.87(7)
Ag(1)—S(1)	2.70(7)	Sb(3)—S(11)	2.89(6)
Ag(1)—S(7)	2.70(7)	Sb(3)—S(9)	2.91(9)
Ag(1)—S(8)	3.21(10)	* Sb(4)—S(2)	2.49(10)
Ag(2)—S(3)	2.70(9)	Sb(4)—S(10)	2.78(8)
Ag(2)—S(2)	2.72(11)	Sb(4)—S(11)	2.80(6)
Ag(2)—S(1)	2.83(8)	Sb(4)—S(6)	2.83(8)
Ag(2)—S(6)	2.88(10)	Sb(4)—S(9)	2.97(9)
Ag(3)—S(2)	2.50(10)	Sb(4)—S(12)	3.13(8)
Ag(3)—S(8)	2.58(11)	Sb(5)—S(10)	2.54(8)
Ag(3)—S(3)	2.80(7)	Sb(5)—S(12)	2.56(8)
Ag(4)—S(11)	2.67(7)	Sb(5)—S(4)	2.57(8)
Ag(4)—S(8)	2.72(10)	Sb(5)—S(9)	2.64(9)
Ag(4)—S(7)	2.74(7)	Sb(5)—S(8)	2.93(11)
Ag(5)—S(6)	2.44(8)	Sb(5)—S(11)	3.38(6)
Ag(5)—S(10)	2.56(9)	Bi(1)—S(4)	2.49(6)
Ag(5)—S(5)	2.63(8)	Bi(1)—S(1)	2.54(5)
Ag(6)—S(8)	2.38(10)	Bi(1)—S(12)	2.55(8)
Ag(6)—S(7)	3.03(7)	Bi(1)—S(2)	2.97(9)
Ag(6)—S(12)	3.04(9)	Bi(1)—S(5)	3.05(8)
Sb(1)—S(4)	2.48(6)	Bi(1)—S(3)	3.46(6)
Sb(1)—S(1)	2.56(6)	Ag(1)—Sb(1)	3.48(4)
Sb(1)—S(3)	2.62(6)	Ag(2)—Ag(4)	3.31(8)
Sb(1)—S(7)	3.07(7)	Ag(3)—Ag(5)	3.25(6)
Sb(1)—S(10)	3.08(8)	Ag(4)—Bi(1)	3.59(4)
Sb(2)—S(11)	2.39(6)	Ag(5)—Sb(5)	3.67(5)
Sb(2)—S(5)	2.79(8)	S(1)—S(6)	3.43(10)
Sb(2)—S(1)	2.83(6)	S(3)—S(8)	3.39(12)
Sb(2)—S(12)	3.08(8)	S(4)—S(12)	2.90(10)
Sb(2)—S(10)	3.13(8)	S(5)—S(9)	3.40(12)
Sb(2)—S(9)	3.27(9)	S(7)—S(9)	3.22(11)
* Sb(3)—S(7)	2.52(7)		

* Sb(3), Sb(4) = ($\frac{1}{2}$ Sb + $\frac{1}{2}$ Bi).

Table 3. (Continued)
(b) Interatomic angles

S(6) —Ag(1)—S(9)	81(4)°	S(2) —Sb(4)—S(10)	97(3)°
S(6) —Ag(1)—S(5)	103(3)	S(2) —Sb(4)—S(11)	86(3)
S(6) —Ag(1)—S(1)	91(3)	S(2) —Sb(4)—S(6)	151(5)
S(9) —Ag(1)—S(5)	94(3)	S(2) —Sb(4)—S(9)	96(3)
S(9) —Ag(1)—S(7)	83(3)	S(2) —Sb(4)—S(12)	89(3)
S(5) —Ag(1)—S(1)	88(2)	S(10) —Sb(4)—S(11)	167(6)
S(5) —Ag(1)—S(7)	97(3)	S(10) —Sb(4)—S(6)	81(2)
S(1) —Ag(1)—S(7)	105(2)	S(10) —Sb(4)—S(9)	78(3)
S(3) —Ag(2)—S(2)	148(4)	S(10) —Sb(4)—S(12)	103(2)
S(3) —Ag(2)—S(1)	106(3)	S(11) —Sb(4)—S(6)	91(2)
S(3) —Ag(2)—S(6)	119(3)	S(11) —Sb(4)—S(9)	89(2)
S(2) —Ag(2)—S(1)	90(3)	S(11) —Sb(4)—S(12)	90(2)
S(2) —Ag(2)—S(6)	92(3)	S(10) —Sb(5)—S(12)	92(3)
S(1) —Ag(2)—S(6)	74(3)	S(10) —Sb(5)—S(4)	86(2)
S(2) —Ag(3)—S(8)	136(4)	S(10) —Sb(5)—S(9)	89(3)
S(2) —Ag(3)—S(3)	146(3)	S(10) —Sb(5)—S(8)	99(3)
S(8) —Ag(3)—S(3)	78(3)	S(12) —Sb(5)—S(8)	93(3)
S(11) —Ag(4)—S(8)	92(3)	S(12) —Sb(5)—S(11)	89(2)
S(11) —Ag(4)—S(7)	76(2)	S(4) —Sb(5)—S(11)	100(2)
S(8) —Ag(4)—S(7)	79(3)	S(9) —Sb(5)—S(8)	80(3)
S(6) —Ag(5)—S(10)	94(3)	S(9) —Sb(5)—S(11)	90(2)
S(6) —Ag(5)—S(5)	113(2)	S(8) —Sb(5)—S(11)	76(3)
S(10) —Ag(5)—S(5)	89(3)	S(4) —Bi(1)—S(1)	164(4)
S(8) —Ag(6)—S(7)	107(2)	S(4) —Bi(1)—S(12)	70(2)
S(8) —Ag(6)—S(12)	95(3)	S(4) —Bi(1)—S(2)	102(2)
S(7) —Ag(6)—S(12)	82(2)	S(4) —Bi(1)—S(5)	110(2)
S(4) —Sb(1)—S(1)	162(5)	S(1) —Bi(5)—S(12)	100(2)
S(4) —Sb(1)—S(3)	90(2)	S(1) —Bi(1)—S(2)	90(2)
S(1) —Sb(1)—S(3)	102(2)	S(1) —Bi(1)—S(5)	81(2)
S(11) —Sb(2)—S(5)	91(2)	S(12) —Bi(1)—S(2)	92(3)
S(11) —Sb(2)—S(1)	109(2)	S(2) —Bi(1)—S(5)	90(2)
S(5) —Sb(2)—S(1)	160(4)	Sb(1) —S(1) —Bi(1)	112(2)
S(7) —Sb(3)—S(3)	165(6)	Sb(1) —S(1) —Ag(1)	83(2)
S(7) —Sb(3)—S(12)	100(2)	Bi(1) —S(1) —Ag(1)	100(2)
S(7) —Sb(3)—S(10)	97(2)	Ag(3) —S(2) —Sb(4)	117(3)
S(7) —Sb(3)—S(11)	76(2)	Ag(3) —S(2) —Ag(2)	96(3)
S(7) —Sb(3)—S(9)	72(2)	Ag(2) —S(2) —Sb(4)	113(4)
S(3) —Sb(3)—S(12)	88(2)	Sb(1) —S(3) —Sb(3)	93(2)
S(3) —Sb(3)—S(10)	97(2)	Sb(1) —S(3) —Ag(2)	150(4)
S(3) —Sb(3)—S(11)	93(2)	Sb(1) —S(3) —Ag(3)	91(2)
S(3) —Sb(3)—S(9)	100(2)	Sb(3) —S(3) —Ag(2)	103(2)
S(12) —Sb(3)—S(10)	82(2)	Sb(3) —S(3) —Ag(3)	109(3)
S(12) —Sb(3)—S(11)	85(2)	Ag(2) —S(3) —Ag(3)	108(3)
S(10) —Sb(3)—S(9)	95(2)	Bi(1) —S(4) —Sb(1)	110(3)
S(11) —Sb(3)—S(9)	96(2)	Bi(1) —S(4) —Sb(5)	108(2)

Table 3. (Continued)

(b) Interatomic angles

Sb(1)—S(4) —Sb(5)	106(2)°	Ag(1)—S(9) —Sb(5)	116(4)°
Ag(1)—S(5) —Ag(5)	100(2)	Ag(1)—S(9) —Sb(3)	102(3)
Ag(1)—S(5) —Sb(2)	101(3)	Sb(5)—S(9) —Sb(3)	89(3)
Ag(5)—S(5) —Sb(2)	101(3)	Sb(5)—S(10) —Ag(5)	92(3)
Ag(1)—S(6) —Ag(5)	116(3)	Sb(5)—S(10) —Sb(4)	98(2)
Ag(1)—S(6) —Sb(4)	113(3)	Ag(5)—S(10) —Sb(4)	88(2)
Ag(5)—S(6) —Sb(4)	90(3)	Sb(2)—S(11) —Ag(4)	102(2)
Sb(3)—S(7) —Ag(1)	98(2)	Sb(2)—S(11) —Sb(4)	97(2)
Sb(3)—S(7) —Ag(4)	108(3)	Ag(4)—S(11) —Sb(4)	88(2)
Ag(1)—S(7) —Ag(4)	110(2)	Bi(1)—S(12) —Sb(5)	107(3)
Ag(6)—S(8) —Ag(3)	101(4)	Bi(1)—S(12) —Sb(3)	109(3)
Ag(6)—S(8) —Ag(4)	96(3)	Sb(5)—S(12) —Sb(3)	95(2)
Ag(3)—S(8) —Ag(4)	115(4)		

Table 4. Structure factors

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c					
2	1	-6	196	209	-4	5	0	113	103	6	1	1	52	64	-2	1	2	141	181	-5	0	3	91	96	-1	0	4	39	53	4	1	5	92	81
4			108	78	-2			264	265	7			76	56	-1			52	77	-4			94	80	0			88	138	-8	2	5	60	58
1	2	-6	55	74	4			182	178	8			96	81	0			312	365	-2			61	70	1			98	92	-5			72	65
3			100	100	-8	6	0	57	67	-5	2	1	58	70	6			170	171	2			54	68	2			255	268	-4			81	70
4			166	141	-6			137	131	-4			72	75	8			84	47	3			74	67	4			96	94	-3			61	55
2	1	-5	52	45	0			316	275	-3			30	41	-6	2	2	98	132	4			76	60	8			82	94	4			89	74
3			76	81	2			109	105	2			58	39	-4			227	242	5			71	65	-4	1	4	137	138	-7	3	5	50	53
4			78	64	6			86	94	3			56	35	-3			70	61	6			94	97	-2			224	263	2			58	47
5			71	68	-4	7	0	190	192	4			155	142	0			61	55	7			74	68	-1			79	84	4	4	5	54	65
1	2	-5	71	71	2			178	152	5			72	58	2			405	422	-3	1	3	55	65	4			243	231	-8	5	5	43	44
4			85	79	-8	8	0	71	79	-8	3	1	49	70	4			108	95	-2			54	57	-8	2	4	64	73	3			51	56
6	1	-4	104	127	-5			64	47	-4			123	115	-2	3	2	334	391	2			87	89	-6			102	118	-7	6	5	34	36
1	2	-4	79	84	-2			168	161	-3			60	75	0			85	98	6			116	107	0			298	330	-1			72	55
2			221	248	4			108	104	3			92	78	4			185	181	7			90	40	6			78	113	2			47	53
4			111	111	-6	9	0	82	85	-7	4	1	52	70	-6	4	2	143	152	-6	2	3	86	90	-4	3	4	200	196	-5	7	5	58	57
1	-3		49	76	0			132	134	-6			72	89	-3			78	81	-3			49	59	0			110	111	2	-8	6	120	124
2			65	70	-4	10	0	110	107	-4			86	84	-2			112	130	-2			68	82	2			224	220	4	-7	6	141	134
3			71	64	-2	11	0	81	95	-1			94	92	0			308	289	2			82	83	-8	4	4	87	86	0	-6	6	158	158
6			89	93	3	-8	1	76	83	-5	5	1	90	82	6			91	121	5			58	58	-4			106	104	6			100	94
2	2	-3	64	53	5			54	33	-4			70	54	-6	5	2	99	93	-6	3	3	72	75	-2			217	224	0	-5	6	79	70
1	-2		56	96	8	-7	1	42	52	4			97	96	-4			214	197	-5			67	76	4			139	155	2			167	181
3			70	70	7	-6	1	76	76	-8	6	1	64	54	2			243	238	-2			55	55	-8	5	4	55	56	8			30	84
6			81	64	-2	11	0	81	95	-1			94	92	0			308	289	2			82	83	-8	4	4	87	86	0	-6	6	158	158
3			89	93	3	-8	1	76	83	-5	5	1	90	82	6			91	121	5			58	58	-4			106	104	6			100	94
2	2	-3	64	53	5			54	33	-4			70	54	-6	5	2	99	93	-6	3	3	72	75	-2			217	224	0	-5	6	79	70
1	-2		56	96	8	-7	1	42	52	4			97	96	-4			214	197	-5			67	76	4			139	155	2			167	181
3			70	70	7	-6	1	76	76	-8	6	1	64	54	2			243	238	-2			55	55	-8	5	4	55	56	8			30	84
6			81	64	-2	11	0	81	95	-1			94	92	0			308	289	2			82	83	-8	4	4	87	86	0	-6	6	158	158
3			89	93	3	-8	1	76	83	-5	5	1	90	82	6			91	121	5			58	58	-4			106	104	6			100	94
2	2	-3	64	53	5			54	33	-4			70	54	-6	5	2	99	93	-6	3	3	72	75	-2			217	224	0	-5	6	79	70
1	-2		56	96	8	-7	1	42	52	4			97	96	-4			214	197	-5			67	76	4			139	155	2			167	181
3			70	70	7	-6	1	76	76	-8	6	1	64	54	2			243	238	-2			55	55	-8	5	4	55	56	8			30	84
6			81	64	-2	11	0	81	95	-1			94	92	0			308	289	2			82	83	-8	4	4	87	86	0	-6	6	158	158
3			89	93	3	-8	1	76	83	-5	5	1	90	82	6			91	121	5			58	58	-4			106	104	6			100	94
2	2	-3	64	53	5			54	33	-4			70	54	-6	5	2	99	93	-6	3	3	72	75	-2			217	224	0	-5	6	79	70
1	-2		56	96	8	-7	1	42	52	4			97	96	-4			214	197	-5			67	76	4			139	155	2			167	181
3			70	70	7	-6	1	76	76	-8	6	1	64	54	2			243	238	-2			55	55	-8	5	4	55	56	8			30	84
6			81	64	-2	11	0	81	95	-1			94	92	0			308	289	2			82	83	-8	4	4	87	86	0	-6	6	158	158
3			89	93	3	-8	1	76	83	-5	5	1	90	82	6			91	121	5			58	58	-4			106	104	6			100	94
2	2	-3	64	53	5			54	33	-4			70	54	-6	5	2	99	93	-6	3	3	72	75	-2			217	224	0	-5	6	79	70
1	-2		56	96	8	-7	1	42	52	4			97	96	-4			214	197	-5			67	76	4			139	155	2			167	181
3			70	70	7	-6	1	76	76	-8	6	1	64	54	2			243	238	-2			55	55	-8	5	4	55	56	8			30	84
6			81	64	-2	11	0	81	95	-1			94	92	0			308	289	2			82	83	-8	4	4	87	86	0	-6	6	158	158
3			89	93	3	-8	1	76	83	-5	5	1																						

A final difference Fourier map showed no significant peaks. The unit-cell content corresponds to a unit of formula $\text{Ag}_5\text{Sb}_{3.75}\text{Bi}_2\text{S}_{12}$. Here the valence rule is not fulfilled: $5 \times 1 + 5.75 \times 3 = 22.5 \neq 12 \times 2$.

Table 2 is a list of the atomic parameters, Table 3 a listing of the interatomic distances and angles. Table 4 is a list of observed and calculated structure factors.

Description of the structure

The substructure of aramayoite is essentially a rocksalt-type structure, in agreement with the predictions of YARDLEY¹. The superstructure contribution serves to distort this ideal structure somewhat, and

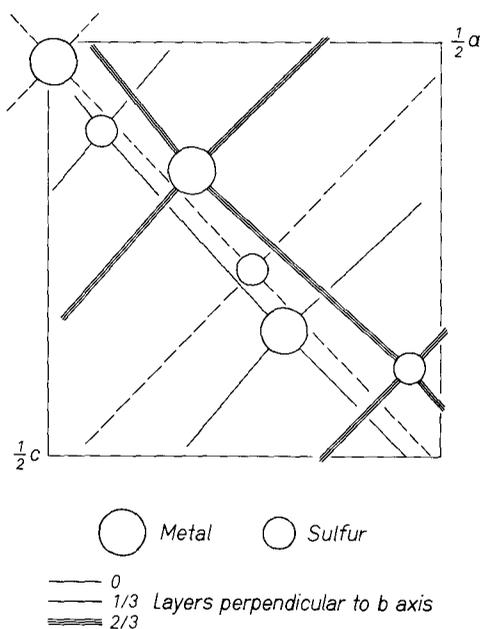


Fig. 1. Substructure of aramayoite

also to introduce substitution of bismuth for antimony and site occupancies at some metal-atom sites of less than unity.

Figure 1 shows the layers present in the substructure at approximately $y = 0, 1/3$ and $2/3$.

The complete structure essentially preserves this layer structure (Fig. 3) in the b direction, in accordance with the observed strong (010) cleavage. There are three layers in the unit cell. The layer at $y \sim 2/3$

is a layer of antimony atoms. In this layer Sb(3) and Sb(4) each consist of ($\frac{1}{2}$ Sb + $\frac{1}{2}$ Bi), i.e. partial substitution ($\sim 50\%$) of these antimony sites by bismuth. Sb(5) has a site occupancy of $\sim 75\%$.

The layer at $y \sim 1/3$ is a layer of silver atoms. These are characterized by isotropic temperature factors of the order of two or three

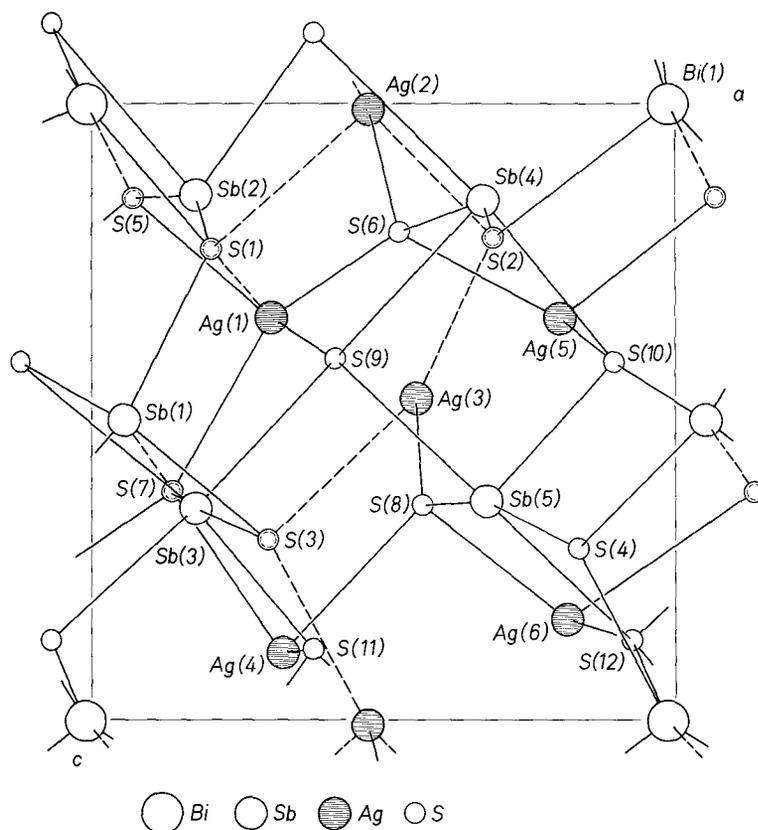


Fig. 2. Aramayoite, [010] projection (the dotted lines are bonds to cell-shifted atoms)

times the values for the antimony atoms, a feature also found in many other sulfosalts.

The third layer (at $y \sim 0$) is a mixed layer containing silver, antimony and bismuth atoms. These occur in alternate rows of Ag and of Sb and Bi atoms, running approximately perpendicular to the a direction. The two silver atoms have site occupancies of $\sim 50\%$.

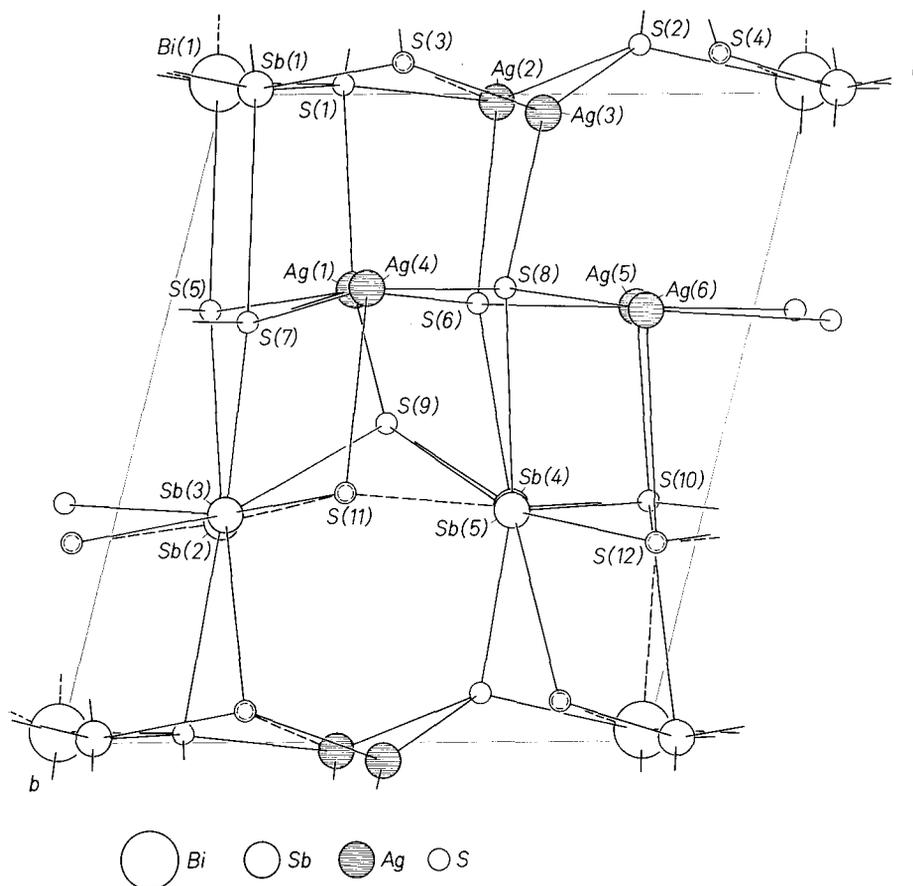


Fig. 3. Aramayoite, [001] projection

The other row contains alternate antimony and bismuth atoms. This detail may be seen in Fig. 2.

The bonding in general is comparable to other sulfosalts of this type (i.e. containing these atomic species).

The coordination of antimony is either threefold or sixfold. Sb(1) (Fig. 4*a*) has a pyramidal arrangement of three bonds ranging from 2.48–2.62 Å (mean value 2.55) Å. In Sb(2) three bonds range from 2.39–2.83 (mean 2.67) Å, and there are three further neighbours from 3.08–3.27 (mean 3.16) Å. The sum of covalent radii⁷, $r_{\text{Sb}} + r_{\text{S}}$ is 2.45 Å.

⁷ L. PAULING, *The nature of the chemical bond*. Ithaca: Cornell Univ. Press, p. 224 (1960).

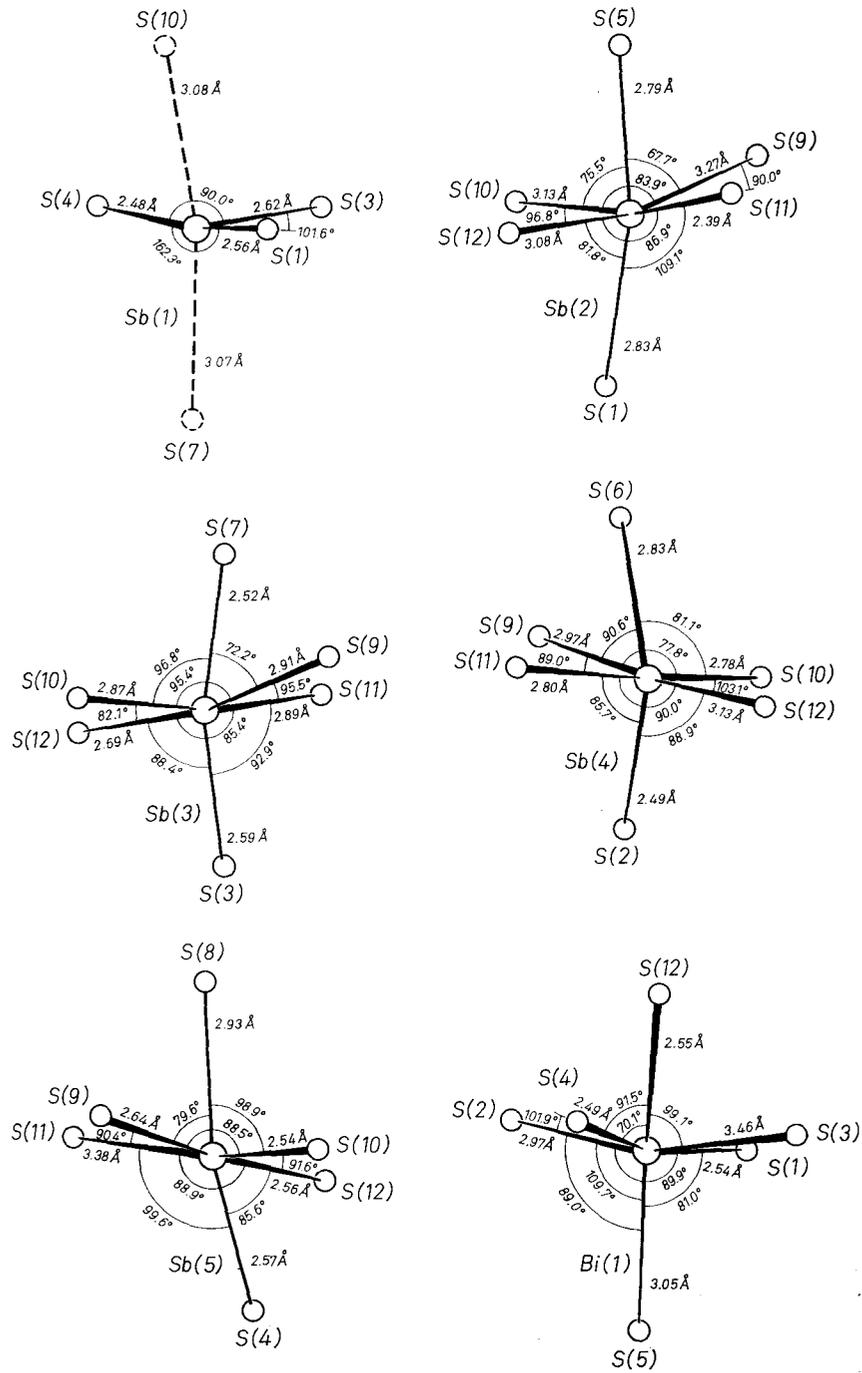


Fig. 4a. Coordination of the Sb and Bi atoms in aramayoite

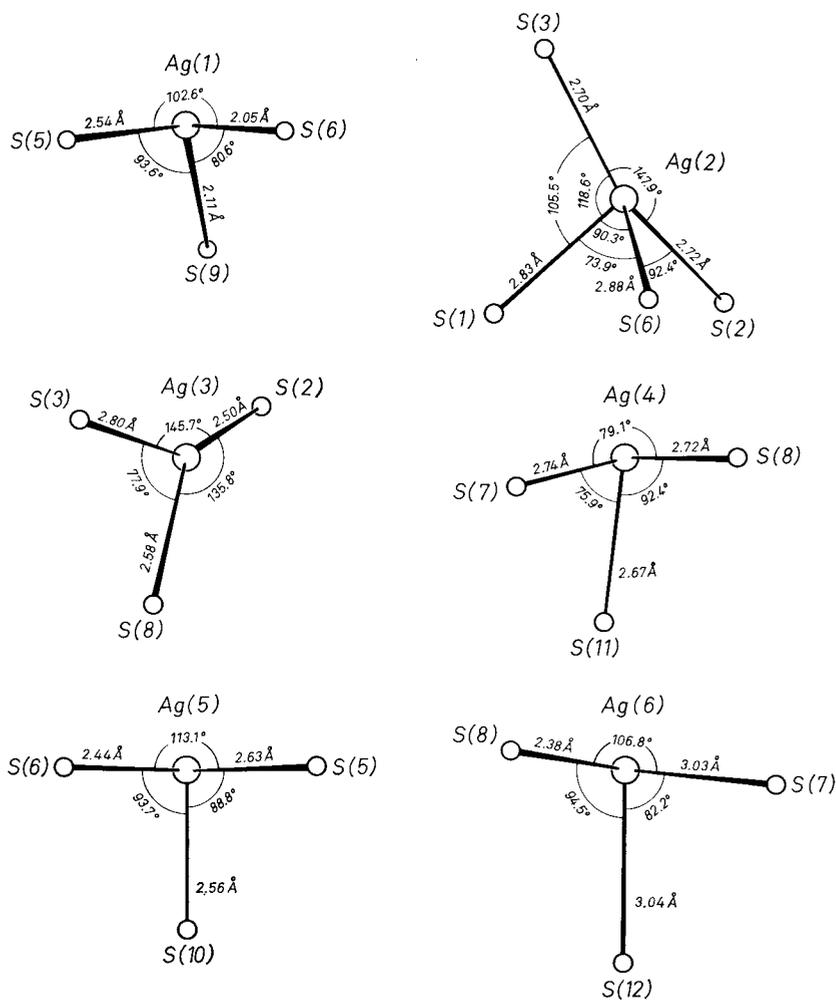


Fig. 4b. Coordination of the Ag atoms in aramayoite

In Sb(3) [$= \frac{1}{2}\text{Sb} + \frac{1}{2}\text{Bi}$] the three plus three octahedrally (or twice pyramidal) arranged sulfur atoms are at distances ranging from 2.52–2.69 (mean 2.60) and 2.87–2.91 (mean 2.89) Å. Sb(4) [$= \frac{1}{2}\text{Sb} + \frac{1}{2}\text{Bi}$] has an octahedral configuration with Sb–S distances ranging from 2.49–3.13 (mean 2.83) Å, resp. a coordination number 4 + 2 with distances 2.49–2.83 (mean 2.73) and 2.97 and 3.13 (mean 3.05) Å. The atoms Sb(3) and especially Sb(4) show a more continuous change from shortest to longest Sb–S distance in contrast with the other atoms

which generally have three short and three much longer distances. Sb(3) and Sb(4) are sites occupied by $\sim (\frac{1}{2}\text{Sb} + \frac{1}{2}\text{Bi})$, i.e. statistical substitution of Sb by Bi and this may account for the observed trends in bonding. We may expect some averaging of Sb—S and Bi—S bonding.

Sb(5) (Fig. 4*a*) has four bonds from 2.54 to 2.64 (mean 2.58) Å and two further S neighbours at 2.93 and 3.38 (mean 3.15) Å.

For comparison, pyrargyrite⁸, Ag_3SbS_3 , has three Sb—S bonds of 2.46 Å, and miargyrite⁹, AgSbS_2 , has two Sb atoms with Sb—S bonds from 2.48–2.58 Å. In stibnite¹⁰, Sb_2S_3 , one Sb atom has one S neighbour at 2.521(3) Å and two at 2.539(2) Å, and the other Sb atom has five S neighbours: one at 2.455(3) Å, two at 2.678(2) Å, and two at 2.854(2) Å. The average Sb—S distance derived from many sulfosalts¹⁰ is 2.54 Å for threefold coordination.

The coordination of the bismuth atom (Fig. 4*a*) is similar to that of the Sb(3) and Sb(4) atoms, with an octahedral configuration of S neighbours. In this case there are three short distances from 2.49 to 2.55 (mean 2.53) Å and three longer distances of 2.97, 3.05 and 3.46 (mean 3.16) Å. The mean Bi—S distance according to NOWACKI¹¹ is 2.71 Å for threefold coordination. In good agreement the mean Bi—S distance in aramayoite is 2.84 Å [Bi(1)—S(3) = 3.46 included] and 2.72 Å [excluded]; the mean distance for $(\frac{1}{2}\text{Bi} + \frac{1}{2}\text{Sb})$ —S is 2.79 Å. In cosalite¹², $\text{Pb}_2\text{Bi}_2\text{S}_5$, it is as long as 2.835, 2.832 and 2.925 Å.

The coordination of Ag(2) (Fig. 4*b*) is tetrahedral, with rather long Ag—S distances from 2.70–2.88 (mean 2.78) Å. Ag(3) (Fig. 4*b*) has a pyramidal configuration of three Ag—S bonds, two short at 2.50 and 2.58 Å and one long at 2.80 Å. This bonding is found in other silver sulfosalts. Ag(4) (Fig. 4*b*) has three Ag—S distances ranging from

⁸ P. ENGEL und W. NOWACKI, Die Verfeinerung der Kristallstruktur von Proustit, Ag_3AsS_3 , und Pyrargyrit, Ag_3SbS_3 . Jahrb. Min., Monatsh. **1966**, 181–184.

⁹ C. R. KNOWLES, A redetermination of the structure of miargyrite, AgSbS_2 . Acta Crystallogr. **17** (1964) 847–851.

¹⁰ P. BAYLISS and W. NOWACKI, Refinement of the crystal structure of stibnite, Sb_2S_3 . Z. Kristallogr. **135** (1972) 308–315.

¹¹ W. NOWACKI, Zur Klassifikation und Kristallchemie der Sulfosalze. Schweiz. Min. Petr. Mitt. **49** (1969) 109–156.

¹² T. SRIKRISHNAN and W. NOWACKI, A redetermination of the crystal structure of cosalite, $\text{Pb}_2\text{Bi}_2\text{S}_5$. Wiss. Verh. Schweiz. Natf. Ges. Luzern **1972**; Z. Kristallogr. (in press).

2.67–2.74 (mean 2.71) Å, and Ag(5) Fig. 4*b* has three Ag–S distances from 2.44–2.63 (mean 2.54) Å. Ag(6) (Fig. 4*b*) has three Ag–S distances, one short (2.38 Å) and two which are rather longer than usual (3.03 and 3.04 Å). Ag(1) (Fig. 4*b*) has three short distances (2.05, 2.11, 2.54 Å) (mean 2.23) and two at 2.70 Å. This is an unusual configuration for silver and must be treated with caution in view of the large standard deviations and the limitations of the data. However, distances of the order of 2.1 Å for Ag–S are not unknown¹³. Ag (4, 5, 6 and 1) all have pyramidal configurations, but that of Ag(1) is a rather flattened pyramid. The Ag(2) tetrahedral coordination is very distorted with three S atoms almost coplanar with the Ag atom (Fig. 4*b*).

For comparison, distances of 2.43 to 2.45 Å for Ag–S occur in pyrargyrite⁸, Ag₃SbS₃. In miargyrite⁹ a shorter Ag–S distance of 2.36 Å is found.

NOWACKI¹¹ gives the following mean Ag–S distances, respectively for two-, three-, and fourfold coordination of the silver atom: 2.45, 2.55 and 2.64 Å.

Sulfur shows in general a pyramidal configuration with three bonds. A fourth, longer distance is present in some cases, making a very distorted tetrahedron. The metal–S–metal angles range from 82.8° to 116.5°.

Comparison of the structures of aramayoite, Ag(Sb,Bi)S₂, miargyrite AgSbS₂, and matildite, AgBiS₂

Miargyrite⁹, AgSbS₂, also has a superstructure, but crystallizes in the space group *Cc*. In physical properties such as cleavage it is very different from aramayoite, having no pronounced cleavage. Also it appears to be a non-statistical, ordered structure. The bond lengths compare well with those of aramayoite, Ag–S distances ranging from 2.36 to 2.89 Å, and Sb–S distances from 2.48 to 2.58 Å. The large variation in isotropic temperature factors of sulfur found in aramayoite is also apparent in miargyrite (0.40 to 1.72).

Matildite, AgBiS₂, is in many ways more similar to aramayoite than is miargyrite. Both matildite and aramayoite are layer structures with pronounced cleavages. In the case of matildite, the layers are alternate Ag, Bi, S, with metal layers in between sulfur layers. In aramayoite both sulfur and metal atoms lie approximately in the same layers parallel to (010).

¹³ A. EDENHARTER (private communication).

Matildite also shows Ag—S bonding not common to sulfosalts in general. One silver atom has an octahedral configuration of sulfur at distances of 2.74 Å. The other silver atom has a slightly distorted octahedral configuration with three sulfur atoms at 2.75 Å and three at 2.78 Å. Bi—S distances are long, ranging from 2.90 to 2.95 Å.

Both matildite and aramayoite have distorted rocksalt-type substructures and statistical superstructures.

The three sulfosalts have different space groups: $P1$ for aramayoite, Cc for miargyrite, and $P\bar{3}m1$ for matildite.

It is interesting to note that matildite and several binary and ternary sulfosalts and selenides with rocksalt-type substructures have semiconducting properties¹⁴. No evidence is available on the behaviour of aramayoite in this respect.

Acknowledgments

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¹⁴ S. GELLER and J. H. WERNICK, Ternary semiconducting compounds with sodium chloride-like structure: AgSbSe₂, AgSbTe₂, AgBiS₂, AgBiSe₂. Acta Crystallogr. **12** (1959) 46–54.