The crystal structure of trechmannite, AgAsS$_2$*

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Auszug

Mit Hilfe von $3d$-Intensitätsdaten wurde die Struktur von Trechmannit, AgAsS$_2$, bestimmt: $a_{rh} = 8,62$ Å, $\alpha_{rh} = 108°17'$, $a_{hex} = 13,98$ Å, $c_{hex} = 9,12$ Å, Raumgruppe C_{3i}^2—$R\overline{3}$, mit $Z = 6$ (rh.) bzw. 18 (hex.) Formeleinheiten in der Elementarzelle. Die Struktur konnte durch Interpretation einer partiellen $3d$-Pattersonsynthese, berechnet nur mit Überstrukturreflexen, und mittels der Schweratommethode gefunden werden.

Die Struktur kann als defekter und deformierter PbS-Typ, bei welchem die Metall- und Schwefellagen auf den Trigyren unbesetzt sind, beschrieben werden. Sechs S- und sechs As-Atome umgeben die Leerstelle des Metalles bzw. Schwefels.

As bildet wie üblich mit den S-Atomen trigonale Pyramiden (As—S $= 2,21_8$ bis $2,30_7$ Å). Drei solcher Pyramiden bilden über gemeinsame S-Atome einen trigonalen Dreierring As$_3$S$_6$. Dieses Resultat konnte aus stereochemischen Gründen erwartet werden, weil bei einem Verhältnis As:S $= 1:2$ entweder unendliche Ketten oder Ringe verknüpfter AsS$_3$-Pyramiden einzig möglich sind; beim Vorhandensein einer Trigyre ist ein Dreierring wahrscheinlich.

Ag hat drei nächste S-Nachbarn im Abstand $2,59_9$ Å und $2,64_6$ Å, die eine sehr flache Pyramide bilden. Mit einem vierten S-Atom ($2,73_5$ Å) zusammen ergibt sich eine deformiert-tetraedrische Koordination.

Abstract

The crystal structure of trechmannite, AgAsS$_2$, has been determined with the use of three-dimensional intensity data. The crystal is rhombohedral, having the unit-cell dimensions $a_{rh} = 8.62$ Å, $\alpha_{rh} = 108°17'$, $a_{hex} = 13.98$ Å, $c_{hex} = 9.12$ Å, space group C_{3i}^2—$R\overline{3}$. There are 6 (rh.) or 18 (hex.) formula units in the cell. The structure was solved by interpretation of a three-dimensional

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partial Patterson function synthesized only with superlattice reflections and by the heavy-atom method.

The crystal has a defect, distorted, galena-type structure, the metal atom positions and the S-atom positions on the threefold rotation axes being vacant. Six S atoms and six As atoms surround the vacant sites for metal and for S respectively.

As has three nearest S neighbours at distances between $2,21_8$ Å and 2.30_7 Å, which form the usual trigonal AsS_3 pyramid. Three of these AsS_3 pyramids form a threefold As_3S_6 ring by sharing S atoms. This result could be expected for stereochemical reasons. If the ratio As:S is 1:2, the only possibilities are infinite chains of linked AsS_3 pyramids or rings, with a threefold axis a threefold As_3S_6 ring is probable.

Ag has three nearest S neighbours between 2.59_9 Å and 2.64_6 Å, with which it forms a very flat pyramid. A fourth S atom is at an intermediate distance of 2.73_5 Å. Together these four S atoms form a distorted tetrahedral coordination around the Ag atoms.

Introduction

Trechmannite is an extremely rare sulfosalt known only from the Lengenbach quarry in the Binnatal, Canton Wallis, Switzerland. This was first found by SOLLY (1905) as one of the red sulfosalts with hutchinsonite and smithite, and was studied morphologically by SMITH and PRIOR (1907). The lattice constants and diffraction group were first determined by NOWACKI and KUNZ (1961) ($a = 14.02$ Å, $c = 9.15$ Å, $C_{3i}^2 - R\overline{3}$; the macroscopic symmetry, $C_{3i} - \overline{3}$, indicates the space group $C_{3i}^2 - R\overline{3}$) and the chemical composition by NOWACKI and BAHEZRE (1963) by electron-microprobe analysis. Trechmannite turned out to have the same formula, $AgAsS_2$, as smithite. Thus $AgAsS_2$ is dimorphous.

The structure determination of trechmannite was carried out in order to obtain further precise information concerning the structural principles of Ag-As-S minerals. It was also desired to clarify the relationship of trechmannite with smithite (HELLNER and BURZLAFF, 1964) and nowackiite, $Cu_6Zn_3As_4S_{12}$ (MARUMO, 1967) which has very similar lattice constants ($a = 13.44$, $c = 9.17$ Å), but no centre of symmetry ($C_3^4 - R3$).

Experimental

A crystal of trechmannite, approximately 0.5 mm in diameter, was kindly provided by Prof. Dr. E. NICKEL, Fribourg University (sample B 768).

The unit-cell dimensions were obtained from Weissenberg photographs on which calibration powder patterns of Si were recorded.

For the lattice constants of Si the value of $a = 5.43054$ Å by PARRISH (1960) was used. A least-squares refinement was performed with the aid of an IBM-1620 program written by N. D. JONES. The unit-cell dimensions obtained are: $a_{hex} = 13.98 \pm 0.01$ Å, $c_{hex} = 9.12 \pm 0.02$Å, $c/a = 0.6523$ ($a_{rh} = 8.62$ Å, $\alpha = 108°17'$), and they are in accordance with those by NOWACKI and KUNZ (1961) ($a_{hex} = 14.02$ Å, $c_{hex} = 9.15$ Å, space group $C_{3i}^2 - R\bar{3}$) and with the morphological data ($c : a = 0.6530$) reported by SOLLY (1905).

The possible space groups obtained from the x-ray photographs are $C_{3i}^2 - R\bar{3}$ and $C_3^4 - R3$. A piezoelectricity test with the aid of H. BAETHGE and the Rogers plot for the [001] and [010] zones do not show an acentric feature, in accordance with the morphology. The centric holohedral space group $C_{3i}^2 - R\bar{3}$ was chosen as the correct space group, in accordance with the "macroscopic space-group determination" (see Introduction). A specimen with the approximate shape of an ellipsoid of revolution with $r_a = r_b = 0.0635$ mm ($\perp c_{hex}$), $r_c = 0.0423$ mm ($//c_{hex}$) was prepared for the intensity measurements.

The three-dimensional intensities, roughly in hemisphere region in reciprocal space, were obtained by the Buerger-Supper-Pace automated diffractometer, using $CuK\alpha$ radiation with Ni filter around the c_{hex} and $a_{2;hex}$ axes (for each reflection, the backgrounds before and after the peak were measured, beside of the integrated peak intensity). These data were averaged using an IBM 1620 program written by T. MATSUMOTO, and each datum was assigned a reliability code using

Table 1. *Electron microprobe analyses of trechmannite*

	I	II	III	IV	V
Ag	44.5 wt.$^0/_0$	44.5	43.9	43.7	42.8
As	29.3	28.9	30.8	30.3	29.7
S	26.3	27.2	26.1	26.0	27.5
Σ	100.1	100.6	100.8	100.0	100.0

I = L 1112; analyst: C. BAHEZRE, Paris, B. R. G. M., NOWACKI and BA-HEZRE (1963).

II = L 1112; analyst: G. BURRI, Bern, Anal. Nr. 48R, 17. 11. 1965.

III = Fragment from Fribourg University, used for intensity measurement; analyst: G. BURRI, Bern, Anal. Nr. 179, 8. 5. 1967 (proustite = standard).

IV = Ideal formula $Ag_6As_6S_{12}$.

V = Ideal formula $Ag_6As_6S_{13}$.

the difference in background intensities. Lorentz, polarization and absorption corrections for the ellipsoidal shape ($\mu r_x = \mu r_y = 4.511$, $\mu r_z = 3.005$) were applied.

After the measurement of the intensities the crystal was used for chemical microprobe analysis by G. BURRI in our laboratory for micro x-ray spectroscopy. With proustite, Ag_3AsS_3, as standard, the composition was determined to be $AgAsS_2$. No other metals were observed (Table 1).

The density calculated for $Ag_6As_6S_{12}$ (4.78_3 g/cm^3) is somewhat small in comparison with that of smithite ($d_x = 5.18_4$). This arises from the vacant metal and sulfur positions assuming a PbS structure. There was not sufficient material available for a density measurement by pycnometric technique.

During the refinement of the structure no evidence in contradiction to the above choices was found, namely C_{3i}^2—$R\bar{3}$ for the space group and $Ag_6As_6S_{12}$ for the chemical formula.

Structure determination

Diffraction patterns obtained from trechmannite implied the presence of a face-centered pseudocubic subcell. Even though the lattice constants of trechmannite have a strong relation to those of zinc blende, as shown in Table 3, the Grimm-Sommerfeld rule (PARTHÉ, 1964) predict that the two structures are different.

As the ratio of intensities between sublattice and superlattice reflections rapidly changes with increasing $(\sin \theta)/\lambda$, the satellite theory of KOREKAWA (1964) predicts that the deviation from the ideal structure (displacements) will be rather large.

Table 2. *Coordinates of atoms in an ideal galena-type structure referred to the hexagonal axes of trechmannite*

The origin of the coordinates is taken at the metal atom (3)

		Number of positions	Wykoff notation	Point symmetry	x	y	z
Metal	(1)	18	f	1	4/13	1/13	0
	(2)	18	f	1	8/13	2/13	0
	(3)	3	a	$\bar{3}$	0	0	0
Sulfur	(1)	18	f	1	4/13	1/13	1/2
	(2)	18	f	1	8/13	2/13	1/2
	(3)	3	b	$\bar{3}$	0	0	1/2

Table 3

Comparison of lattice constants of trechmannite, nowackiite, galena and zinc blende

| | Hexagonal | | | Cubic | | |
	Trech-mannite $Ag_6As_6S_{12}$	Nowackiite $Cu_6Zn_3As_4S_{12}$			Galena $a_0 = 5.936$	Zinc blende $a_0 = 5.409$
a_{hex}	13.98 Å	13.44 Å	$\frac{1}{2}$ [$\bar{1}4\bar{3}$]$_{cubic}$		15.13$_4$ Å	13.79$_0$ Å
c_{hex}	9.12	9.17	[111]$_{cubic}$		10.28$_2$	9.36$_9$
a_{rh}		8.34	$\frac{1}{2}$ [01$\bar{3}$]$_{cubic}$		9.38$_6$	8.55$_2$
$c_{hex}:a_{hex}$	0.6523	0.6823		0.679$_{37}$		

The ordinary three-dimensional Patterson function confirmed the galena-type structure. The relation between true cell and PbS-type cell is given by

$$a_{hex} \approx \tfrac{1}{2} [\bar{1}4\bar{3}]_{PbS},$$

$$c_{hex} \approx [1\,1\,1]_{PbS},$$

$$a_{rh} \approx \tfrac{1}{2} [0\,1\,\bar{3}]_{PbS}, \quad V_{rh} \approx \tfrac{13}{4}\, V_{PbS}.$$

The arrangement of equivalent points, as well as the relation of the subcells to the true cell, and the relation to the PbS-type cell is shown in Fig. 1. The coordinates of six independent atomic sites
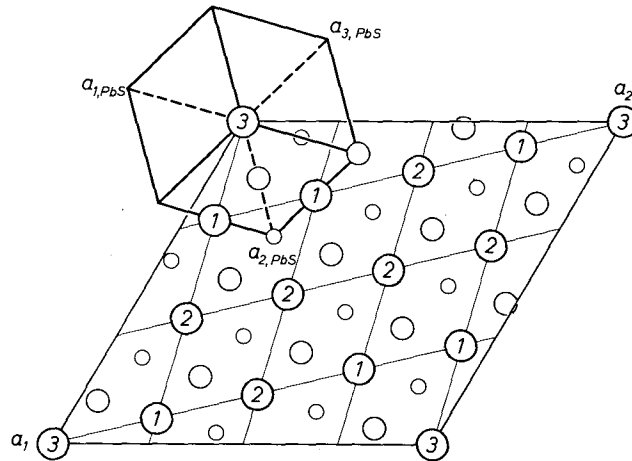

Fig. 1. Arrangement of equivalent points in trechmannite and the relation to the PbS structure

of the ideal PbS-type structure referred to the hexagonal cell are given in Table 2. From the chemical composition, one metal position and one sulfur position in the rhombohedral cell units, which correspond to metal (3) and sulfur (3) in Table 2, are expected to be vacant.

The partial Patterson function, that is, the Patterson function synthesized by the superstructure reflections only, was too complex to be readily interpretable. But applying the implication method to this partial Patterson function, the x and y coordinates of two metals were found, namely $x = .335$, $y = .082$ for metal (1), and $x = .625$, $y = .180$ for metal (2). There are two possible combinations for the metal atoms: (a) Metal (1)—As and Metal (2)—Ag, or (b) Metal (1)—Ag and Metal (2)—As.

Beginning with the metal-atom position ($z = 0$) for the first model, the S-atom locations were determined with the aid of electron-density and difference maps. The S atoms were then added to the next cycle. Continuing with the Fourier method, the R value did not decrease below $37^0/_0$. Applying the Fourier method for the second model (b), the R value rapidly dropped down to $24^0/_0$. Therefore the second model (b) was judged to be the correct one.

Refinement

Two cycles of refinement for the second model were carried out moreover by means of the three-dimensional difference Fourier method. During the refinement, individual isotropic temperature factors were used. After scaling each layer, the R value decreased to $16^0/_0$, indicating the correctness of the model.

Then the structure was refined by a least-squares method with individual isotropic temperature factors using a programme written by D. van der Helm for the IBM-1620. The weighting scheme adopted was $w = 1/(k|F_o|^2)$ or $1/(3k|F_{o,\,min}|^2)$.

The atomic scattering amplitudes used for neutral Ag and As are those of Potter, and Freeman and Watson respectively, and for S those of Dawson (International tables for x-ray crystallography, Volume III). After five cycles of refinement of the structure, the R value was reduced to $8^0/_0$ for all reflections.

Anisotropic temperature factors were then introduced and further refinements were undertaken. After five cycles of least-squares refinement, all parameter shifts were smaller than their standard deviations and the refinement was terminated. The final R value is $5.4^0/_0$ for all 650 reflections and $4.8^0/_0$ for the observed reflections.

Table 4. *Atomic coordinates in trechmannite*

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Ag	0.3330	0.0822	0.9880	0.0001	0.0001	0.0001
As	0.6222	0.1700	0.0227	0.0001	0.0001	0.0002
S(1)	0.3608	0.1101	0.4996	0.0003	0.0003	0.0004
S(2)	0.6243	0.1752	0.5219	0.0003	0.0003	0.0004

Table 5. *Atomic temperature factors in trechmannite*

The values are the coefficients in the expression

$$\exp\,[-(\beta_{11}\,h^2 + \beta_{22}\,k^2 + \beta_{33}\,l^2 + \beta_{12}\,hk + \beta_{23}\,kl + \beta_{31}\,lh)]$$

(all values are multiplied by 10^5)

	β_{11}	$\sigma(\beta_{11})$	β_{22}	$\sigma(\beta_{22})$	β_{33}	$\sigma(\beta_{33})$	β_{12}	$\sigma(\beta_{12})$	β_{23}	$\sigma(\beta_{23})$	β_{31}	$\sigma(\beta_{31})$
Ag	387	28	347	28	805	49	329	30	93	18	—100	18
As	279	28	271	28	561	50	271	31	12	21	6	21
S(1)	200	35	213	35	474	61	161	47	—37	47	— 32	47
S(2)	228	35	227	35	495	61	225	47	—74	47	38	47

Table 6. *Axial lengths of the vibration ellipsoids and the direction cosines of the axes*
referred to orthogonal axes $1//a^*_{\text{hex}}$, $2//b_{\text{hex}}$ and $3//c_{\text{hex}}$ in trechmannite

	Equivalent isotropic temperature factor	Axes	B	$\sqrt{\overline{u^2}}$	$\cos\alpha_1$	$\cos\alpha_2$	$\cos\alpha_3$
Ag	2.37 Å⁻²	1	2.18Å⁻²	0.166	0.871	—0.122	0.476
		2	1.96	0.158	0.315	0.883	—0.349
		3	2.98	0.194	—0.377	0.453	0.807
As	1.70	1	1.65	0.145	0.866	—0.500	0.000
		2	1.59	0.142	0.498	0.863	—0.082
		3	1.86	0.153	0.041	0.071	0.997
S(1)	1.40	1	1.11	0.118	0.891	0.412	0.190
		2	1.49	0.137	—0.453	0.825	0.337
		3	1.60	0.142	—0.018	—0.387	0.922
S(2)	1.45	1	1.34	0.130	0.955	0.290	—0.062
		2	1.22	0.125	—0.224	0.842	0.491
		3	1.79	0.150	0.196	—0.455	0.869

The final atomic parameters with standard deviations and the temperature factors are given in Table 4 and 5. The axial lengths of the thermal vibration ellipsoids and the direction cosines of the axes referred to orthogonal axes $(1//a^*_{\text{hex}}$, $2//b_{\text{hex}}$ and $3//c_{\text{hex}})$ are

Table 7. *Comparison of the observed and the calculated structure amplitudes of trechmannite*
(Indices refer to a hexagonal cell)

h	k	l	$\frac{1}{6}\|F_o\|$	$\frac{1}{6}F_c$	h	k	l	$\frac{1}{6}\|F_o\|$	$\frac{1}{6}F_c$	h	k	l	$\frac{1}{6}\|F_o\|$	$\frac{1}{6}F_c$	h	k	l	$\frac{1}{6}\|F_o\|$	$\frac{1}{6}F_c$
3	0	0	9.9	9.1	-4	7	1	15.8	16.0	-1	12	2	7.8	6.9	-9	15	3	0.9	- 0.1
6			20.2	- 19.9	-3	8	1	8.0	- 10.6	-4			20.3	- 21.2	-12			20.4	20.2
9			7.0	6.1	-6			25.8	- 28.8	-7			41.3	- 43.5	-5	16	3	8.5	- 8.4
12			25.9	26.6	-2	9	1	27.7	- 30.6	-10			21.2	21.4	-8			26.1	- 26.9
1	1	0	29.5	- 26.4	-5			6.4	- 6.1	-3	13	2	47.3	- 46.7	-11			4.9	- 4.4
4			74.9	- 78.6	-8			38.8	40.0	-6			16.5	16.1	1	0	4	3.9	6.2
7			39.4	- 40.4	-1	10	1	4.6	- 4.6	-9			28.5	28.8	4			60.7	- 63.6
10			20.3	- 19.9	-4			21.4	- 22.9	-12			13.1	12.8	7			3.6	- 2.1
13			25.2	- 25.7	-7			13.0	- 13.5	-2	14	2	15.0	- 14.3	10			46.5	- 45.5
2	2	0	18.3	- 17.9	-3	11	1	29.3	30.5	-5			27.4	- 26.4	13			11.0	12.1
5			58.3	60.2	-6			53.3	54.8	-8			13.5	- 14.1	2	1	4	11.3	11.4
8			7.7	- 7.1	-9			33.6	- 35.1	-11			29.1	- 29.9	5			39.0	- 40.4
11			6.6	4.8	-2	12	1	15.6	- 15.3	-1	15	2	46.3	44.5	8			15.0	- 14.6
3	3	0	43.9	- 45.9	-5			4.1	- 4.8	-4			9.4	9.9	11			2.3	- 1.2
6			62.4	- 66.4	-8			17.0	18.0	-7			19.5	20.7	0	2	4	3.7	- 2.6
9			43.8	46.8	-11			8.1	7.1	-10			26.0	- 24.6	3			65.0	- 69.8
12			15.6	15.9	-1	13	1	0.0	- 0.4	-13			6.4	6.7	6			86.6	88.0
1	4	0	13.1	- 13.7	-4			29.7	- 31.2	-6	16	2	2.8	- 1.2	9			19.3	19.5
4			23.1	- 24.4	-7			10.3	- 9.2	-9			19.4	18.0	12			3.7	2.7
7			11.0	- 12.0	-10			10.5	11.1	-12			25.0	- 25.0	1	3	4	63.4	- 65.7
10			60.9	60.3	-3	14	1	18.6	18.6	0	0	3	109.8	112.9	4			15.5	- 14.6
2	5	0	144.1	150.9	-6			30.7	31.1	3			24.2	25.9	7			52.8	51.3
5			36.8	38.5	-9			1.4	0.7	6			10.0	- 9.0	10			12.4	- 12.7
8			7.0	7.0	-12			16.0	- 16.8	9			6.3	5.9	2	4	4	51.6	52.9
11			9.7	- 9.8	-2	15	1	24.9	- 24.5	12			31.7	32.3	5			4.0	4.9
3	6	0	32.7	35.2	-5			9.9	- 10.3	1	1	3	2.1	- 1.1	8			3.9	- 2.4
6			38.3	- 39.3	-8			8.1	- 8.2	4			10.6	- 10.1	11			19.2	18.7
9			14.0	- 13.6	-11			20.7	- 22.1	7			27.0	- 26.3	0	5	4	13.7	17.4
1	7	0	37.4	38.7	-14			1.3	- 1.3	10			15.6	- 15.5	3			12.6	- 13.1
4			32.5	- 35.2	-4	16	1	13.8	14.8	13			13.7	- 16.3	6			38.2	- 36.4
7			15.3	15.6	-7			21.7	- 21.5	2	2	3	5.5	- 6.6	9			1.2	- 1.5
10			6.9	6.7	-10			10.0	10.7	5			19.2	17.1	1	6	4	19.9	- 21.1
2	8	0	1.8	0.6	-13			25.5	27.5	8			1.5	- 0.9	4			26.3	24.9
5			26.3	- 26.8	-9	17	1	10.8	- 11.1	11			8.2	- 8.8	7			1.1	- 0.8
8			27.7	- 27.0	2	0	2	57.7	- 58.6	0	3	3	8.1	7.8	2	7	4	1.6	0.9
3	9	0	14.4	15.0	5			24.0	- 23.0	3			3.8	2.8	5			56.5	- 54.0
6			5.8	- 6.5	8			5.8	4.7	6			22.9	- 24.5	8			20.3	20.2
1	10	0	53.3	- 55.2	11			53.4	54.0	9			37.1	39.4	0	8	4	5.8	5.4
4			27.2	28.8	14			21.0	- 22.1	12			11.1	11.9	3			33.0	- 31.3
7			12.0	13.1	0	1	2	49.0	- 50.5	1	4	3	24.5	- 27.9	6			36.7	- 34.0
2	11	0	22.1	- 22.9	3			221.4	219.1	4			33.0	- 34.3	1	9	4	52.9	52.9
5			32.2	30.8	6			29.9	29.3	7			25.1	- 24.9	4			20.0	19.7
3	12	0	40.7	39.1	9			8.5	- 8.1	10			7.6	5.2	2	10	4	29.1	26.8
1	13	0	16.5	- 16.1	12			3.3	- 2.4	2	5	3	80.2	82.2	5			5.5	5.1
1	0	1	2.5	- 2.3	1	2	2	19.4	- 18.4	5			38.7	39.8	0	11	4	42.1	39.8
4			7.6	- 9.4	4			31.0	32.2	8			12.3	11.9	3			14.8	- 14.2
7			17.9	- 18.4	7			46.1	- 46.7	11			2.3	- 0.3	1	12	4	5.0	4.0
10			20.5	- 22.4	10			35.7	- 35.6	0	6	3	10.4	- 10.5	-2	3	4	30.1	- 33.5
13			21.1	23.8	13			3.5	- 2.9	3			6.4	- 4.9	-1	4	4	163.3	163.2
2	1	1	12.4	8.3	2	3	2	8.6	- 8.4	6			16.7	- 16.7	-3	5	4	2.2	5.0
5			11.6	- 13.9	5			4.5	- 6.2	9			16.3	- 15.7	-2	6	4	2.8	- 1.2
8			17.9	- 18.6	8			38.0	38.9	1	7	3	3.2	- 2.5	-5			36.9	37.1
11			15.8	- 15.6	11			9.8	- 8.8	4			9.5	- 8.8	-1	7	4	3.8	2.4
14			18.8	19.6	0	4	2	22.3	- 24.4	7			16.8	17.7	-4			12.1	12.1
0	2	1	11.3	- 14.9	3			28.7	- 30.8	2	8	3	7.2	7.1	-3	8	4	21.3	- 23.1
3			20.6	- 22.9	6			17.8	- 17.8	5			0.6	0.1	-6			35.4	- 36.9
6			82.5	84.5	9			42.6	- 43.3	8			25.3	- 25.3	-2	9	4	71.7	- 73.0
9			27.5	29.1	12			8.9	10.5	0	9	3	4.0	- 2.5	-5			17.4	18.2
12			2.6	- 1.5	1	5	2	20.5	21.3	3			7.1	- 6.8	-8			41.7	40.4
1	3	1	31.8	- 32.2	4			1.1	- 1.0	6			11.2	- 11.6	-1	10	4	24.4	- 24.8
4			25.1	- 26.2	7			16.0	- 16.4	1	10	3	22.7	- 23.1	-4			48.2	- 48.7
7			3.2	- 2.5	10			20.5	- 20.0	4			24.6	25.5	-7			5.9	- 5.9
10			17.5	- 18.3	2	6	2	81.6	- 83.5	2	11	3	15.9	- 15.7	-3	11	4	31.7	31.4
13			17.0	- 17.9	5			61.9	65.2	5			3.1	- 2.3	-6			46.6	47.9
2	4	1	36.9	38.4	8			18.3	19.0	0	12	3	31.7	32.1	-9			51.4	- 48.8
5			6.6	6.1	0	7	2	49.3	- 50.9	3			21.5	20.6	-2	12	4	1.0	0.8
8			3.0	- 3.7	3			50.3	- 50.1	1	13	3	14.4	- 14.2	-5			4.0	3.5
11			25.4	- 27.0	6			52.8	52.2	-1	2	3	32.4	- 37.5	-8			22.5	21.3
0	5	1	17.9	- 16.8	9			9.0	- 8.8	-2	4	3	10.2	- 11.9	-11			31.2	- 31.1
3			20.1	- 22.0	1	8	2	47.4	48.5	-1	5	3	22.0	- 24.9	-1	13	4	11.5	- 10.4
6			8.7	- 6.9	4			31.9	30.9	-4			10.9	- 13.1	-4			22.4	- 21.7
9			19.3	- 20.0	7			13.7	- 13.7	-3	6	3	27.7	- 30.8	-7			35.1	34.9
1	6	1	19.7	- 21.0	2	9	2	17.2	- 16.7	-2	7	3	22.8	24.1	-10			8.2	8.6
4			13.1	13.9	5			9.3	- 8.4	-5			79.5	80.1	-3	14	4	13.4	11.6
7			8.6	8.1	0	10	2	36.7	- 37.2	-1	8	3	2.5	1.6	-6			19.2	18.0
10			0.7	0.7	3			5.6	4.9	-4			2.8	- 0.8	-9			7.1	6.8
2	7	1	1.4	1.1	6			9.9	9.3	-7			7.1	7.4	-12			4.0	3.6
5			29.5	- 31.3	1	11	2	8.5	- 7.3	-3	9	3	24.0	- 26.4	-5	15	4	2.2	1.3
8			21.5	22.8	4			39.7	- 37.7	-6			27.3	- 26.4	-8			24.2	- 23.4
0	8	1	21.3	- 22.5	2	12	2	11.7	- 10.9	-2	10	3	12.9	13.8	-11			16.0	- 16.3
3			22.2	- 23.4	0	13	2	22.4	22.3	-5			33.0	34.1	2	0	5	31.3	- 33.9
6			16.8	- 16.3	1	14	2	13.8	12.6	-8			20.5	20.8	5			38.4	- 38.4
9			3.0	2.9	-1	3	2	46.6	48.2	-1	11	3	30.9	- 32.0	8			17.3	- 16.9
1	9	1	53.4	57.0	-3	4	2	21.8	- 21.4	-4			13.2	- 14.2	11			9.5	9.0
4			39.3	39.5	-2	5	2	47.7	- 51.3	-7			11.0	- 11.7	0	1	5	7.3	- 11.2
7			19.3	18.4	-1	6	2	7.1	- 6.5	-10			17.4	- 18.5	3			69.3	71.5
2	10	1	7.4	- 7.1	-4			43.4	44.1	-3	12	3	34.4	37.2	6			30.6	31.0
5			25.8	- 25.7	-3	7	2	14.4	- 13.6	-6			34.2	- 35.5	9			7.0	6.0
0	11	1	12.3	12.9	-6			53.0	- 56.1	-9			4.9	- 4.9	12			8.0	8.3
3			10.6	- 11.3	-2	8	2	109.7	112.4	-2	13	3	4.4	2.7	1	2	5	3.1	- 2.4
1	12	1	6.8	5.9	-5			68.0	- 71.7	-5			5.7	5.2	4			4.6	4.6
4			4.1	3.0	-1	9	2	12.2	13.0	-8			10.0	- 11.3	7			6.8	- 7.1
2	13	1	1.6	0.2	-4			3.3	3.4	-11			5.8	0.9	10			30.5	- 28.4
0	14	1	13.3	- 13.0	-7			39.2	- 41.3	-1	14	3	17.9	- 18.0	2	3	5	16.0	- 16.5
-2	3	1	27.6	- 27.3	-3	10	2	46.1	49.6	-4			1.7	1.1	5			3.7	- 1.2
-1	4	1	119.3	122.8	-6			32.9	34.1	-7			18.0	19.2	8			20.0	19.3
-3	5	1	5.8	- 7.2	-9			57.8	61.4	-10			17.9	19.5	11			7.7	7.4
-2	6	1	22.1	- 21.7	-2	11	2	15.1	15.1	-13			33.1	- 32.7	0	4	5	12.9	13.8
-5			4.5	4.1	-5			6.2	- 7.9	-3	15	3	13.1	11.9	3			5.9	- 6.1
-1	7	1	29.9	30.9	-8			4.8	- 7.5	-6			0.9	- 0.3	6			2.6	1.7

Table 2. *(Continued)*

Column group 1:

h	k	l	$\frac{1}{6}|F_o|$	$\frac{1}{6}F_c$
9	4	5	18.4	-17.9
1	5	5	3.2	-4.3
4			13.9	-13.9
7			20.3	-19.9
2	6	5	17.8	-18.9
5			39.8	40.6
8			24.4	25.8
0	7	5	36.2	-36.2
3			20.1	-19.0
6			4.6	-3.9
1	8	5	30.1	29.5
4			11.1	10.8
7			3.3	-0.4
2	9	5	1.9	-4.1
5			9.1	-7.8
0	10	5	14.4	-15.1
3			5.0	4.4
1	11	5	16.5	14.9
2	12	5	23.0	-21.3
0	13	5	19.4	18.7
-1	3	5	10.3	12.8
-3	4	5	9.9	12.4
-2	5	5	5.6	-9.2
-1	6	5	8.8	9.4
-4			15.2	14.6
-3	7	5	14.1	-15.8
-6			9.9	-11.6
-2	8	5	49.8	52.2
-5			30.2	-30.9
-1	9	5	6.2	5.0
-4			3.3	3.3
-7			13.6	-14.7
-3	10	5	17.5	-16.5
-6			12.9	13.7
-9			34.1	36.1
-2	11	5	16.7	16.1
-5			14.0	13.8
-8			2.2	0.4
-1	12	5	8.1	-7.5
-4			6.6	-6.4
-7			20.6	-21.2
-10			17.5	-17.2
-3	13	5	20.9	19.3
-6			11.1	11.2
-9			29.6	27.7
-12			7.6	7.7
-2	14	5	10.5	-10.0
-5			22.9	-21.7
-8			2.8	1.0
-11			7.5	-7.4
-7	15	5	11.2	11.2
0	0	6	133.2	132.7
3			29.6	33.4
6			9.2	-9.4
9			17.0	17.2
12			25.8	24.7
1	1	6	8.0	10.3
4			2.9	-4.2
7			53.5	-53.1
10			8.6	8.7
2	2	6	16.4	18.0
5			30.6	30.3
8			24.7	-24.2

Column group 2:

h	k	l	$\frac{1}{6}|F_o|$	$\frac{1}{6}F_c$
11	2	6	8.5	-8.7
0	3	6	15.8	-18.3
3			9.6	8.9
6			50.5	-50.8
9			21.3	21.7
1	4	6	19.1	-20.5
4			44.7	-43.9
7			17.8	-16.6
2	5	6	71.5	74.4
5			27.6	26.7
8			8.7	7.4
0	6	6	16.5	-17.9
3			31.9	32.2
6			8.6	6.6
1	7	6	10.0	10.2
4			6.1	-5.7
7			17.4	15.8
2	8	6	16.3	-16.6
5			6.3	4.9
0	9	6	2.3	-1.9
3			10.4	9.7
1	10	6	52.1	-49.0
2	11	6	34.4	-32.0
0	12	6	12.7	12.0
-1	2	6	41.7	-43.2
-2	4	6	20.6	-23.9
-1	5	6	65.4	-66.7
-4			7.5	8.5
-3	6	6	54.7	-58.5
-2	7	6	43.1	45.4
-5			66.5	71.2
-1	8	6	13.2	11.0
-4			10.2	10.5
-7			22.3	22.0
-3	9	6	17.8	-17.1
-6			1.0	0.5
-2	10	6	18.4	17.6
-5			19.4	18.6
-8			15.0	14.7
-1	11	6	31.9	-29.4
-4			7.9	8.1
-7			31.7	-31.5
-10			11.8	-11.7
-3	12	6	23.6	22.9
-6			48.2	-45.6
-9			16.7	16.6
-2	13	6	7.9	6.5
-5			8.2	-8.6
-8			36.8	-35.3
-11			4.9	2.3
-7	14	6	9.2	9.2
1	0	7	5.2	8.2
4			12.7	-13.8
7			11.5	10.0
10			6.5	-5.5
2	1	7	2.6	-4.2
5			18.6	-19.2
8			27.0	-25.9
0	2	7	9.9	12.5
3			7.1	-7.7
6			33.1	35.1
9			19.4	18.6
1	3	7	32.3	-34.0

Column group 3:

h	k	l	$\frac{1}{6}|F_o|$	$\frac{1}{6}F_c$
4	3	7	12.2	-12.8
7			2.1	-0.4
2	4	7	20.1	20.0
5			3.3	2.0
8			5.8	5.3
0	5	7	10.8	11.8
3			8.4	6.9
6			15.2	-13.2
1	6	7	5.6	-5.6
4			2.6	2.7
2	7	7	15.2	13.5
5			11.5	-10.7
0	8	7	13.3	-13.1
3			28.0	-25.8
1	9	7	27.8	27.6
2	10	7	2.0	-0.5
0	11	7	1.5	-1.5
-2	3	7	16.7	-19.6
-1	4	7	39.3	41.7
-3	5	7	5.6	5.2
-2	6	7	25.8	-26.3
-5			4.6	4.8
-1	7	7	5.8	6.8
-4			22.1	22.2
-3	8	7	5.5	-5.7
-6			5.3	-6.3
-2	9	7	18.0	-17.0
-5			1.8	1.0
-8			16.4	15.5
-1	10	7	9.1	-7.8
-4			23.3	-22.6
-7			2.5	1.7
-3	11	7	16.4	16.4
-6			21.3	21.9
-9			32.9	-30.2
-2	12	7	9.1	7.4
-5			10.7	8.6
-8			6.8	6.2
2	0	8	39.7	-42.2
5			33.6	-33.5
8			7.1	7.3
0	1	8	28.2	-29.7
3			65.4	63.9
6			25.1	23.5
9			2.3	1.6
1	2	8	3.2	-0.1
4			18.2	18.3
7			6.5	4.2
2	3	8	16.8	-16.4
5			14.6	13.9
8			26.6	23.7
0	4	8	18.4	18.8
3			32.3	-30.7
6			13.9	12.3
1	5	8	6.9	6.8
4			7.8	6.7
2	6	8	48.4	-45.1
5			23.9	21.4
0	7	8	46.6	-43.3
3			27.1	-24.0
1	8	8	27.0	24.5
0	10	8	4.4	-4.1

Column group 4:

h	k	l	$\frac{1}{6}|F_o|$	$\frac{1}{6}F_c$
-1	3	8	35.3	37.0
-3	4	8	11.1	12.5
-2	5	8	5.1	4.5
-1	6	8	16.9	16.7
-4			11.7	12.1
-3	7	8	2.6	-2.2
-6			28.6	-29.2
-2	8	8	35.1	34.7
-5			49.1	-47.9
-1	9	8	14.4	13.1
-4			8.1	-8.4
-7			38.1	-36.6
-3	10	8	7.7	8.6
-6			24.1	23.6
-9			15.0	15.0
-5	11	8	14.6	12.6
-8			10.4	9.4
0	0	9	21.3	19.3
3			12.9	14.2
6			2.7	-2.3
1	1	9	9.3	12.1
4			7.0	6.6
7			17.2	-15.2
2	2	9	3.1	1.2
5			1.6	0.0
0	3	9	2.3	-3.2
3			15.2	14.4
6			2.9	-0.8
1	4	9	15.3	-15.2
4			27.1	-24.9
2	5	9	20.3	21.1
0	6	9	3.7	-3.0
3			3.5	1.7
1	7	9	10.5	-9.5
-1	2	9	22.0	-22.7
-2	4	9	3.7	-3.6
-1	5	9	6.9	-6.4
-4			1.2	0.1
-3	6	9	20.5	-20.2
-2	7	9	7.3	7.3
-5			17.3	18.9
-1	8	9	15.9	13.9
-4			13.8	12.6
-7			2.5	2.5
-3	9	9	5.6	-7.0
-6			26.3	-23.7
1	0	10	22.3	20.5
4			29.3	-29.1
2	1	10	4.2	2.5
5			25.1	-23.8
0	2	10	8.9	10.0
3			23.9	-24.3
1	3	10	38.5	-38.7
2	4	10	27.3	25.7
0	5	10	12.1	11.6
-2	5	10	16.9	-18.4
-1	4	10	31.1	32.6
-3	5	10	2.4	-1.0
-2	6	10	17.1	-15.6
-5			26.5	25.0
2	0	11	13.9	-14.0
0	1	11	2.8	-1.6

given in Table 6. The observed and calculated structure amplitudes are given in Table 7 (scalings of $|F_o|$ and $|F_c|$ are half value for the rhombohedral cell, and thus one sixth for the hexagonal cell).

Description of the structure

The structure of trechmannite viewed along the hexagonal c axis is shown in Fig. 2. Fundamentally the structure is a galena type with one vacant metal site and one vacant sulfur site on the threefold axis in a rhombohedral cell, containing six chemical units of AgAsS₂. As shown in Table 8, the deviations of the atoms from the ideal galena-type structure (containing the deviations of scattering power and the displacements) are not at all small. The displacements of the atoms are between 0.25 Å and 0.65 Å.
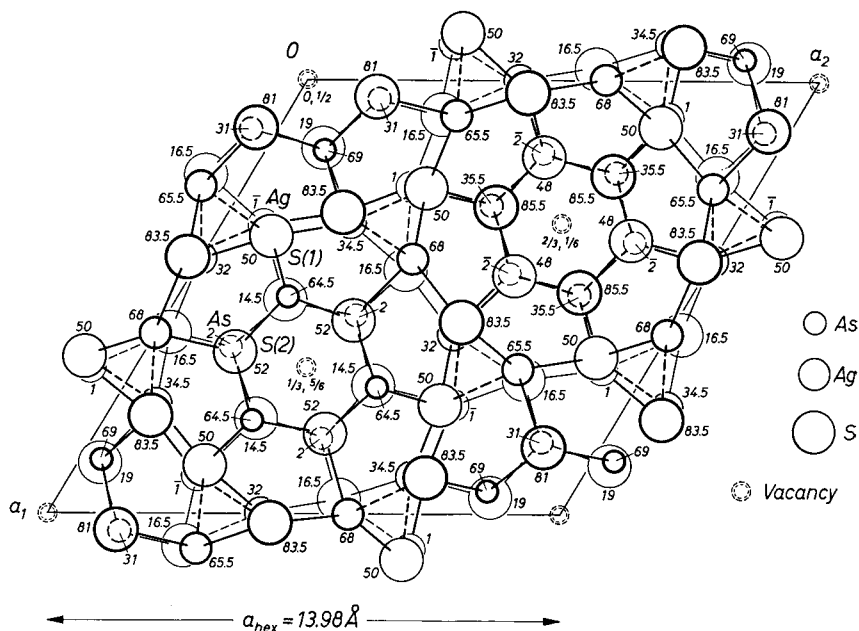
Fig. 2. Projection of the trechmannite structure onto (0001)

$$\left(83_5 \text{ means } z = \frac{83.5}{100} \text{ etc.}\right)$$

The structure of this distorted defect galena type is quite different from that of nowackiite (MARUMO, 1967; a defect-distorted zinc blende type) and that of smithite (HELLNER and BURZLAFF, 1964; a distorted galena type).

The hexagonal c and the a axes of trechmannite are respectively compressed or expanded in comparison with the cubic cell; this means

Table 8. *Deviation from a PbS-like structure*
($M_{13}S_{13}$; M = 36.9; S = 14.8)

		Deviation	
		Weight	Displacement
Metal	Vacant Metal	— 36.9	—
	Ag	+ 10.1	0.34_1 Å
	As	— 3.9	0.28_6
Sulfur	Vacant S	— 14.8	—
	S(1)	+ 1.2	0.65_0
	S(2)	+ 1.2	0.24_7

Table 9. *Atomic distances in trechmannite*

(a) Metal—sulfur and sulfur—sulfur distances

	Ag	As	S(1)	S(2)
S(1)	2.59_9 Å 2.60_3 2.73_5	2.21_8 Å 3.31_1 3.43_0	3.68_5 Å 3.87_5 3.87_5 4.47_6 4.47_6	3.32_0 Å 3.33_0 3.72_6 4.03_7 4.10_1 4.13_0
S(2)	2.64_6 3.09_2 3.26_9	2.29_5 2.30_8	3.32_0 3.33_0 3.72_6 4.03_7 4.10_1 4.13_0	3.43_2 3.43_2 3.96_8 3.96_8 4.38_3
	$\sigma \approx 0.004$	0.005	0.007	

(b) *Metal—metal distances*

	Ag	As		Ag	As
Ag	3.63_4 Å 3.63_4 4.02_0 4.20_6 4.20_6	3.60_4 Å 3.71_3 3.81_0 3.81_0 3.87_8 3.93_1	As	3.60_4 Å 3.71_3 3.81_0 3.81_0 3.87_8 3.93_1	3.54_1 Å 3.54_1 4.01_2 4.01_2 4.26_6
	$\sigma \approx 0.004$			$\sigma \approx 0.004$	

Table 10. *Bond angles in trechmannite*

S(1)—Ag—S(1')	139.9°	As—S(1)—Ag	104.2°
S(1)—Ag—S(2)	100.6	As—S(1)—Ag'	109.0
S(1)—Ag—S(1'')	114.2	As—S(1)—Ag''	102.6
S(1')—Ag—S(2)	102.8	Ag—S(1)—Ag'	107.9
S(1')—Ag—S(1'')	93.1	Ag—S(1)—Ag''	143.5
S(2)—Ag—S(1'')	100.3	Ag'—S(1)—Ag''	85.9
S(1)—As—S(2)	94.7	As—S(2)—As'	100.6
S(1)—As—S(2')	94.7	As—S(2)—Ag	93.5
S(2)—As—S(2')	96.2	As'—S(2)—Ag	96.9

$\sigma \approx 0.2$

that the axial ratio (c/a) of the former is 0.6523, which is smaller than that of a cubic cell ($[1\,1\,1]_{\text{cubic}}: \frac{1}{2}\,[\bar{1}4\bar{3}]_{\text{cubic}} = 0.6793$).

Interatomic distances and bond angles are given in Table 9 and 10. They are also shown in Fig. 3.

The Ag atom has six neighbouring S atoms, of which the three nearest form a nearly planar (sum of the bond angles $= 343.3°$), trigonal-pyramidal coordination. There is a fourth S atom at 2.73_5 Å.
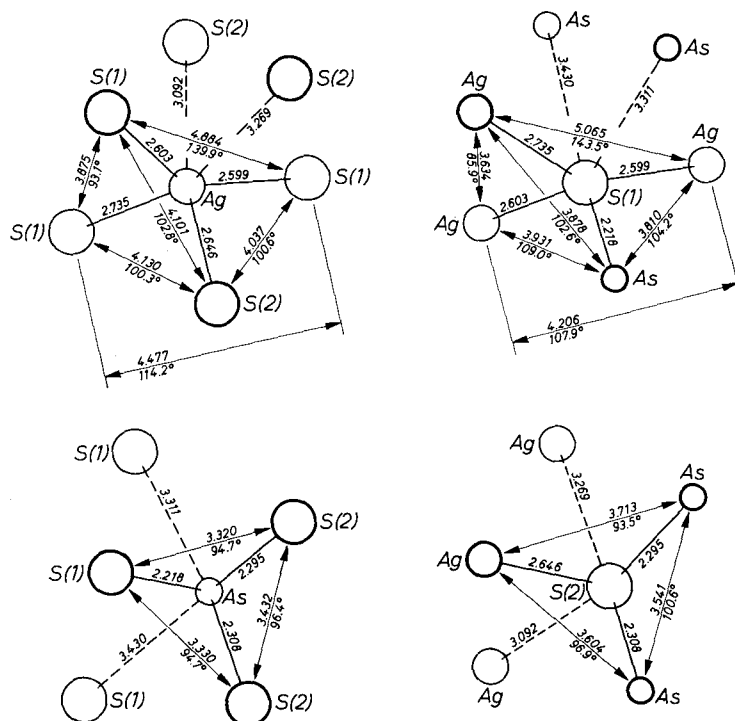
Fig. 3. Coordinations, bond lengths and bond angles (between short distances only) for Ag, As and S of trechmannite

Together these $(3 + 1)$ S atoms yield a distorted tetrahedral coordination around the Ag atom, quite similar to the coordination in the other Ag sulfosalts: smithite, $AgAsS_2$ (HELLNER and BURZLAFF, 1964), miargyrite, $AgSbS_2$ (KNOWLES, 1964), marrite, $PbAgAsS_3$ (WUENSCH and NOWACKI, 1967) and hatchite, $PbTlAgAs_2S_5$ (MARUMO and NOWACKI, 1967).

The As atom has five neighbouring S atoms. The three nearest form the usual trigonal pyramid, the mean As—S distance $(2.27_4$ Å) agrees
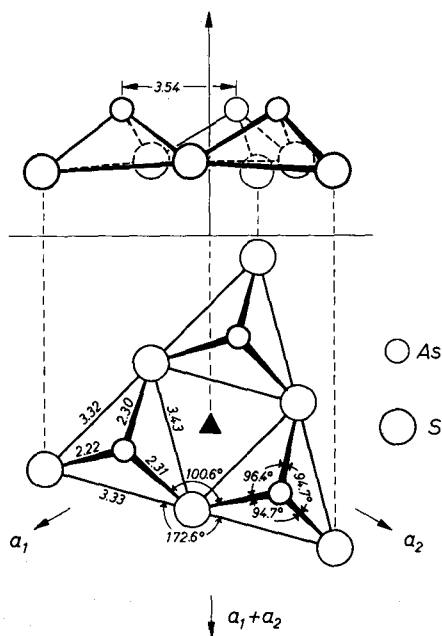
Fig. 4. The threefold As_3S_6 ring in trechmannite

a ○ As   ○ S b
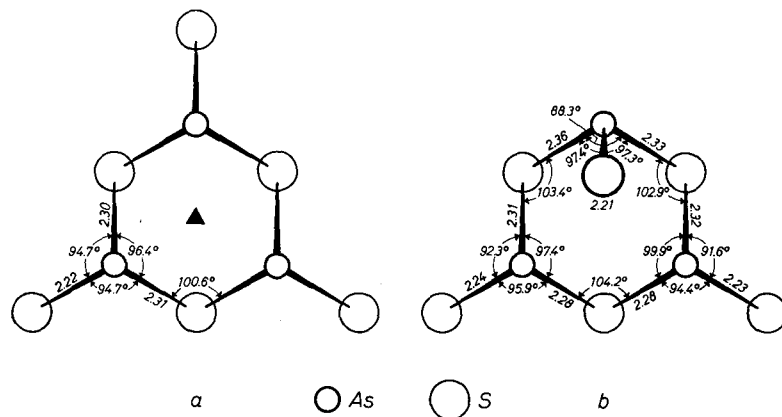
Fig. 5. As_3S_6 group in (a) trechmannite and (b) smithite

well with the normal As—S covalent-bond distance. By sharing
S atoms, three AsS_3 pyramids form a threefold As_3S_6 ring (Fig. 4).
This ring is quite a new type and different from the As_3S_6 molecule
in smithite (Fig. 5). The former has approximately C_{3v}—$3m$ symmetry
(exactly C_3—3), the latter C_s—m. Both As_3S_6 rings (without the

outer S) have the crown form. In both As_3S_6 groups, the inner As—S distances are a little longer, and the outer a little shorter, than the usual As—S covalent bonds. In hutchinsonite (TAKÉUCHI, GHOSE and NOWACKI, 1965) some of the As atoms show one short and two long As—S bonds. These features may result from the As—As repulsion.

On the suggestion of V. M. GOLDSCHMIDT, HOFMANN (1933, 1934, 1935) first gave a classification of all sulfosalts according to the structure and the ratio S:(As,Sb,Bi), assuming (As,Sb,Bi)S_3 pyramids. This classification was taken up again by BÜRKI (1967) and NOWACKI (1968). Smithite and trechmannite, having the same kind of topological combination of three AsS_3 pyramids to a threefold As_3S_6 ring, belong to the same category (IV, a_1).

There are vacant positions in the trechmannite structure; a vacant metal position [000] and a vacant sulfur position [$00\frac{1}{2}$] are surrounded by six S atoms and six As atoms respectively. The six As atoms are shifted towards the vacant metal position, and two threefold As_3S_6 rings are combined with six Ag atoms using the two shortest bonds. We therefore can consider $Ag_6(As_3S_6)_2^{-3}$ blocks which have a vacant metal position in their center, combined to each other by the third (and fourth) Ag—S bond(s).

Acknowledgments

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