

The crystal structure of freieslebenite, PbAgSbS_3 *

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Auszug

Die Struktur von Freieslebenit, PbAgSbS_3 , wurde mittels dreidimensionaler Zählrohrdaten mit Hilfe der Methode der „Hauptverschiebungen“ (key shifts) bestimmt ($R = 3,2\%$). Die erhaltene Struktur ist vom Modell von HELLNER (1957) verschieden; sie ist zu Marrit, PbAgAsS_3 , dem As-Analogen zu Freieslebenit, isomorph. Die Daten sind: Raumgruppe $P2_1/a$ mit $a = 7,518(1)$, $b = 12,809(4)$, $c = 5,940(1)$ Å, $\beta = 92,25(1)^\circ$ und $Z = 4$.

Die Struktur ist eine Überstruktur einer Substruktur vom PbS-Typ. Wohl wegen des größeren Radius von Sb gegenüber As sind die Verschiebungen der Atome aus der idealen Substruktur bei Freieslebenit kleiner als bei Marrit. Sb hat die normale trigonal-pyramidale Koordination der S-Atome mit den Abständen 2,431, 2,453 und 2,480(4) Å. Die SbS_3 -Pyramiden sind voneinander isoliert. Pb weist eine deformiert-oktaedrische Koordination von sechs S-Atomen auf, mit Abständen zwischen 2,806 und 3,167(4) Å. Die AgS_3 -Gruppe ist beinahe planar mit den (Ag–S)-Abständen 2,522, 2,575 und 2,687(4) Å. Ungefähr normal zur AgS_3 -Ebene befindet sich ein viertes S-Atom im Abstand von 2,928(4) Å. Der Temperaturkoeffizient des Ag ist wesentlich größer und anisotroper als diejenigen der übrigen Atome, ein gemeinsamer Zug bei Strukturen dieser Art.

Abstract

The crystal structure of freieslebenite, PbAgSbS_3 , has been determined with three-dimensional counter data ($R = 3.2\%$). The structure was solved by the method of key shifts. The obtained structure is different from the model proposed by HELLNER (1957); instead, it is isomorphous with marrite, PbAgAsS_3 , an As analogue of freieslebenite. The crystal is monoclinic, space group $P2_1/a$, with $a = 7.518(1)$, $b = 12.809(4)$, $c = 5.940(1)$ Å, $\beta = 92.25(1)^\circ$ and $Z = 4$.

The structure is a superstructure of a PbS-type substructure. The displacements of the atoms from the ideal substructure are less in freieslebenite than in marrite, probably because of the larger atomic radius of Sb than that of As. Sb has the usual trigonal-pyramidal coordination of S atoms. The Sb–S distances

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are 2.431, 2.453 and 2.480(4) Å. The SbS_3 pyramids are isolated from each other. Pb is coordinated with six S atoms in a distorted octahedral arrangement. The Pb—S distances range from 2.806 to 3.167(4) Å. Ag has three nearest S neighbours at the distances 2.522, 2.575 and 2.687(4) Å. The AgS_3 group is nearly planar. A fourth S atom is at a distance of 2.928(4) Å from Ag, the Ag—S being approximately perpendicular to the AgS_3 plane. The temperature factor of Ag is significantly larger and more anisotropic than those of the other atoms; this feature is common among related structures.

Introduction

Freieslebenite, PbAgSbS_3 , is one of the typical superstructures based on the PbS-type substructure. HELLNER (1957) deduced a complete structure of freieslebenite by a trial-and-error method using two-dimensional data ($R = 31,37$ and 41% for the three projections). More recently, WUENSCH and NOWACKI (1967) determined the structure of marrite, PbAgAsS_3 , an As analogue of freieslebenite. They showed that marrite is not isomorphous with the HELLNER's model of freieslebenite in spite of the same space group $P2_1/a$ and of the close similarity of the cell dimensions (Table 1). They also observed that there were several nearly homometric structures of marrite; five different models gave the R values less than 40% .

Table 1. Lattice constants of freieslebenite, PbAgSbS_3 , marrite, PbAgAsS_3 , and galena, PbS

	Freieslebenite			Marrite	Galena*
	Present work	PALACHE <i>et al.</i> (1938)	HELLNER (1957)	WUENSCH and NOWACKI (1967)	
a	7.518(1)	7.53	—	7.2705(6)	8.39 Å
b	12.809(4)	12.79	—	12.6319(4)	12.58 Å
c	5.940(1)	5.88	5.95(1)	5.9853(3)	5.93 Å
β	$92.25(1)^\circ$	$92^\circ 14'$	—	$91^\circ 13.7'(2)$	90°
V	571.57			549.56	625.6 \AA^3

* $a = [110]_{\text{PbS}}$, $b = \frac{2}{3} [\bar{1}10]_{\text{PbS}}$ and $c = [001]_{\text{PbS}}$, where $a(\text{PbS}) = 5.93 \text{ \AA}$.

In order to check the isomorphism of freieslebenite and marrite and also to examine more accurately the sulfur coordinations around the metal atoms, a redetermination of the structure of freieslebenite was undertaken using three-dimensional counter data. As will be described below, freieslebenite was shown to be isomorphous with marrite.

Crystal data

A specimen of freieslebenite from Vascongadas, Spain (British museum no. 1948.365) was used for the present investigation. A fragment was cut out of the specimen with a razor, and was made into a sphere with a radius of 0.086 mm by BOND's (1951) method. The powder attached to the surface was dissolved away with a hot aqueous HNO_3 solution. The unit-cell dimensions were obtained from back-reflection double-radius Weissenberg photographs of the spherical crystal about the a , b and c axes. Diffraction patterns of Si powder ($a = 5.43074 \text{ \AA}$) were used for calibration. The wave length used was 1.54051 \AA for $\text{CuK}\alpha_1$ radiation. A least-squares refinement was performed with the aid of a program written by N. D. JONES. The results agree well with those given by PALACHE, RICHMOND and WINCHELL (1938), and by HELLNER (1957) (Table 1)¹. The unit-cell content proposed by HELLNER (1957), $\text{Pb}_4\text{Ag}_4\text{Sb}_4\text{S}_{12}$, was assumed for the present structure determination, which was subsequently confirmed by the successful analysis of the structure. Microprobe analyses of freieslebenite given by SVESHNIKOVA and BORODAYEV (1972) confirmed the chemical composition. The calculated density, $d_x = 6.194 \text{ g} \cdot \text{cm}^{-3}$, is in good agreement with the observed value, $d_m = 6.20 \text{ g} \cdot \text{cm}^{-3}$, by PALACHE *et al.* (1938). The observed systematic absences of reflections were: $h0l$ with h odd and $0k0$ with k odd. Therefore, the space group $P2_1/a$ reported by HELLNER (1957) was confirmed.

Intensity measurements

The intensities were measured with a diffractometer of equi-inclination type (Buerger-Supper-Pace) using Ni-filtered $\text{CuK}\alpha$ radiation. The diffracted beams were detected with a proportional counter, and analyzed with a pulse-height analyzer. The spherical crystal was rotated in the ω -scan mode with the scanning speed from 0.5° (higher angles) to 1.0° per minute (lower angles), about the b (zero to 14th layer) and the c (zero to 4th layer) axes. The background was measured before and after each Bragg reflection for the time approximately equal to the scan time of the reflection. About 1100 independent reflections were measured, of which 972 reflections were considered to be observed ($I > 2.33 \sigma_I$). These were corrected for Lorentz, polari-

¹ Throughout the paper, the estimated standard deviations are given in parentheses in an abbreviated form; for example, 7.518(1) means 7.518 ± 0.001 .

zation and absorption (sphere with $\mu r = 11.7$ for $\text{CuK}\alpha$) effects. Extinction effects were ignored because no systematic discrepancies between F_o and F_c were observed in the course of the refinement.

Solution and refinement of the structure

The asymmetric unit of the structure of freieslebenite consists of PbAgSbS_3 . The structure was solved by the method of key shifts (Ito, 1973). Since the procedure used for the solution of the structure is described in detail in the above reference, only the results of the analysis are given in Table 2. The R value at this stage was 25% for all the observed reflections. The Fourier map calculated with the atomic

Table 2. *Approximate coordinates of freieslebenite as deduced by the method of key shifts*

	x/a	y/b	z/c	B
Sb	0.365	0.087	0.259	1.7 Å ²
Pb	0.352	0.413	0.259	1.7
Ag	0.380	0.766	0.208	1.7

Table 3. *Atomic coordinates of freieslebenite with standard deviations*

	x/a	y/b	z/c
Sb	0.36516(12)	0.08716(7)	0.27172(15)
Pb	0.35000(8)	0.41512(5)	0.25309(10)
Ag	0.37786(18)	0.75971(11)	0.2117(2)
S(1)	0.1384(5)	0.2192(3)	0.3457(7)
S(2)	0.1350(5)	0.6215(3)	0.1308(6)
S(3)	0.1475(5)	0.9416(3)	0.2659(6)

Table 4. *Thermal parameters of freieslebenite with standard deviations ($\times 10^4$)*

The thermal parameters refer to the expression:

$$T = \exp \{ -2\pi^2 (b_{11}h^2a^{*2} + \dots + 2b_{12}hka^*b^* + \dots) \}$$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Sb	130(4)	155(4)	162(4)	-9(3)	3(3)	8(4)
Pb	194(3)	237(2)	230(3)	5(2)	12(2)	13(3)
Ag	354(7)	347(7)	386(7)	-141(6)	31(6)	41(6)
S(1)	142(17)	134(17)	249(18)	-11(13)	28(14)	-20(14)
S(2)	170(17)	198(18)	151(17)	35(14)	24(13)	-1(14)
S(3)	142(17)	131(16)	180(16)	-16(13)	38(13)	12(14)

Table 5. (Continued)

h	F _o	F _c	h	F _o	F _c	h	F _o	F _c	h	F _o	F _c	h	F _o	F _c	h	F _o	F _c	h	F _o	F _c	h	F _o	F _c	h	F _o	F _c								
-2	85	79				-2	126	126				2	197	-201	-2	50	-50				3	18	16	-1	15	-14								
-1	46	44	h	11	4		0	75	-79			h	4	5		3	12	-12	0	158	153	h	2	6		4	66	-65	0	67	68			
0	98	-99	-4	55	-57	1	52	56	-6	40	-40	4	46	43	1	13	14	-5	52	-52				h	5	6			1	79	79			
1	91	-94	-3	26	-24	2	69	-73	-5	18	-17	5	17	17	2	15	-14	-4	75	77				h	0	7			h	0	7			
2	20	-17	-2	63	63	3	33	-33	-4	136	-129				h	7	5		3	10	-11	-3	41	40	-4	94	-90			h	0	7		
3	16	14	-1	45	46	4	62	65	-3	38	36				h	10	5	-2	87	82	-3	45	-44				-2	94	89			h	0	7
4	65	68	0	28	27	5	48	-48	-2	94	91	-5	42	-41				-1	44	43	-2	83	84	0			44	47			h	0	7	
5	78	77	2	53	-55	6	13	13	-1	29	-29	-4	78	-80	-3	51	-51	0	98	-101	-1	75	73	2			119	-113			h	0	7	
h	9	4				h	2	5				0	102	99	-2	108	-105	-2	94	-98	1	82	-86	0			64	61	h	1	7			
												2	94	-98	-1	50	49	-1	16	17	2	32	-30	1			11	8			h	1	7	
-5	11	11	h	12	4		-6	12	7			3	55	57	0	110	111	0	54	-54	3	13	13	2			82	-82	-2		98	-98		
-4	91	-92	-2	57	-58	-4	107	107				4	30	-28	1	44	-43	1	38	37	4	74	72	3			87	-85	-1		12	13		
-3	34	32	-1	30	29	-2	43	-40	5	29	-28	2	43	44	2	93	95				h	3	6				6	6			0	52	52	
-2	217	208	0	179	180	-1	46	-49	6	59	58	3	13	-12				h	0	6				h	0	6			1	60	-59			
-1	24	-24	1	29	-30	0	95	-97	h	5	5	4	86	-84				-5	23	23	-4	105	-97	2			69	67			2	69	67	
0	15	15	2	11	-10	1	35	31	-6	72	-68	5	50	49	-4	122	115	-4	79	-79	-3	42	41				4	1			h	2	7	
1	26	-24	h	0	5	3	62	62	-3	40	36	h	8	5	0	175	-174	-1	30	-28	0	157	154	-2			36	38			h	2	7	
2	220	-224	h	0	5	3	62	62	-3	40	36	h	8	5	0	175	-174	-1	30	-28	0	157	154	-2			36	38			h	2	7	
3	25	27	-6	107	102	4	41	40	-2	89	86	-4	66	-61	2	39	35	0	11	10	1	40	-39	-1			54	55			h	2	7	
4	63	61	-4	126	129	5	65	-66	-1	18	-14	-3	11	-8	4	142	135	2	164	-162	2	17	-13	0			78	77			h	2	7	
5	13	12	-2	240	-235	6	31	-32	0	25	-30	-2	19	19				3	20	21	3	14	14	h	3	7			h	3	7			
												1	69	-70	-1	66	63	h	1	6				h	7	6			-2		67	-70		
h	10	4				h	3	5				2	58	-56	0	57	54	-4	91	-87	h	4	6				3	24	-25	0		114	108	
-4	41	-43	4	50	-46	-6	126	-124	3	57	56	1	26	-26	-3	54	53				h	4	6				3	24	-25	0		114	108	
-3	14	-11	6	170	-164	-4	162	158	4	27	26	2	22	-24	-2	92	94	-4	64	-65	-2	63	-64	1			23	23			h	2	7	
-2	88	-86	h	1	5	-2	87	90	5	54	50	3	72	-70	-1	59	-59	-3	24	23	-1	35	35	h	4	7			h	4	7			
0	65	68	h	1	5	0	248	-251	h	6	5	4	24	-21	0	56	54	-2	74	-73	0	57	-56				57	-56			h	4	7	
1	19	-20	-6	112	-109	4	211	206	h	6	5				1	17	-17	-1	31	30	2	68	69	-1			34	34			h	4	7	
2	39	38	-5	13	9	6	66	-62	-4	97	-97	h	9	5				2	91	-91	0	86	88	h	8	6			0	82	-80			
3	28	30	-4	43	45				-2	185	178	-4	101	-96	3	81	78	1	63	-63	h	8	6				82	-80			h	8	6	
4	52	-53	-3	14	-13				0	30	30	-3	8	-7				2	30	27	-2	73	-71				73	-71			h	8	6	

parameters of Table 2 revealed reasonable peaks for the three sulfur atoms.

The whole structure was then refined by a block-diagonal least-squares method. Unit weights were given to all reflections. After three cycles of isotropic refinement R was 9.0%. Additional several cycles of anisotropic refinement reduced R to the final value of 3.2%. The atomic scattering factors for the neutral atoms were used². The final atomic coordinates and the thermal parameters are given in Tables 3 and 4, respectively. The observed and calculated structure factors are compared in Table 5.

Discussion of the structure

Isomorphism

The present analysis has shown that freieslebenite, PbAgSbS_3 , is isomorphous with marriite, PbAgAsS_3 (WUENSCH and NOWACKI, 1967), and that HELLNER's model of freieslebenite (1957) is one of the nearly homometric models (ITO, 1973). Therefore, the discussions on the structure of marriite given by WUENSCH and NOWACKI are generally valid also for freieslebenite.

Several isomorphous pairs of As and Sb sulfosalts have been reported (Table 6). Two isomorphous pairs of Sb and Bi sulfosalts or sulfides are also known: wolfsbergite, CuSbS_2 and emplectite, CuBiS_2 (HOFMANN, 1933a); stibnite, Sb_2S_3 and bismuthinite, Bi_2S_3 (HOF-

² *International tables for x-ray crystallography* (1962), Vol. III, pp. 202 (S and Ag) and 210 (Sb and Pb). Birmingham: Kynoch Press.

Table 6. *Isomorphous pairs of As and Sb sulfosalts*

Structure type*	As sulfosalt	Sb sulfosalt	Formula**
I. c_1	binnite ¹	tetrahedrite ²	$Cu_{12}X_4S_{13}$
II. a_1	marrite ³	freieslebenite ⁴	$PbAgXS_3$
II. a_1	proustite ⁵	pyrargyrite ⁵	Ag_3XS_3
II. a_1	seligmannite ⁶	bourmonite ⁶	$PbCuXS_3$
VI.	arsenopyrite ⁷	gudmundite ⁸	$FeXS$
VI.	gersdorffite ⁹	ullmannite ¹⁰	$NiXS$

¹ WUENSCH *et al.* (1966).⁶ HELLNER and LEINWEBER (1956).² WUENSCH (1964).⁷ BUERGER (1936).³ WUENSCH and NOWACKI (1967).⁸ BUERGER (1939).⁴ Present work.⁹ BAYLISS and STEPHENSON (1967).⁵ ENGEL and NOWACKI (1966).¹⁰ TAKÉUCHI (1957).

* Classification of sulfosalts by NOWACKI (1969).

** X = As or Sb.

MANN, 1933 b). However, no As—Sb—Bi isomorphous series have thus far been reported. BUERGER (1939) attributed the non-existence of the isomorphous series to the differences of the atomic radii of X (X = As, Sb and Bi) in the case of the arsenopyrite-type compounds, FeXS.

It seems that another important factor of the non-existence is the different bonding nature of X. In As sulfosalts, coordinations of S about As are usually AsS_3 pyramids. In Bi sulfosalts, however, fivefold coordinations (or $3 + 2$ coordinations) of S about Bi are almost as common as BiS_3 pyramids: for example, cosalite, $Pb_2Bi_2S_5$ (SRIKRISHNAN and NOWACKI, 1974) and aikinite, $CuPbBiS_3$ (OHMASA and NOWACKI, 1970). In other words, the bonding nature of As is characterized by p^3 (or sp^3 with one lone-pair of electrons) orbitals of As, whereas that of Bi is more complicated because it is more easily influenced by the contribution of d orbitals of Bi. Coordinations of S about Sb are generally more similar to those of As than of Bi. In stibnite (ŠČAVNIČAR, 1960; BAYLISS and NOWACKI, 1972), however, one Sb is coordinated with three S (an ordinary SbS_3 pyramid) but the other is coordinated with five S (a distorted square pyramid).

Crystal structure

The atomic arrangements in freieslebenite are shown in Fig. 1. SbS_3 trigonal pyramids are isolated from each other. Therefore, freieslebenite belongs to the structure type II. a_1 of NOWACKI's classification of sulfosalts (1969).

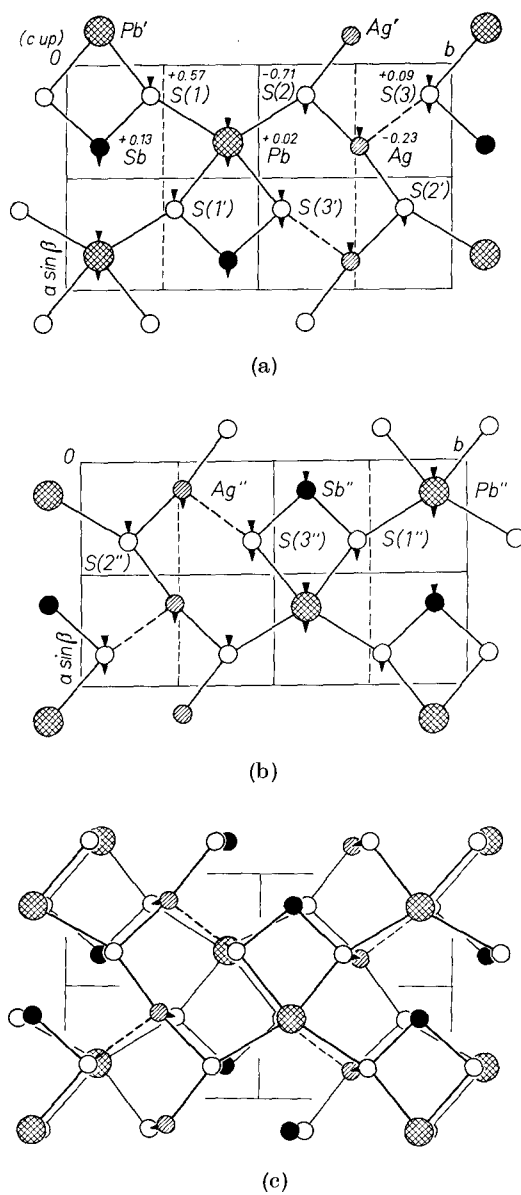


Fig. 1. Atomic arrangements in freieslebenite, viewed along the c axis: (a) the atomic layer at $z \approx 1/4$ and (b) at $z \approx 3/4$, and (c) = (a) + (b), i.e. the whole structure. The thick broken lines indicate the longest Ag—S bonds, the black arrowheads indicate the bonds between the adjacent layers, and the signed numbers in (a) are the deviations (in Å) of the atoms from $z = 1/4$

Table 7. Displacements, Δ , of the atoms of freieslebenite from the ideal PbS-type structure

		Ideal coordinates	Freieslebenite Δ_{F}	Marrite Δ_{M}	$\Delta_{\text{F}}/\Delta_{\text{M}}$
Sb or	x	3/8	- 0.074 Å	- 0.140 Å	+ 0.53
As	y	1/12	+ 0.050	+ 0.092	+ 0.54
	z	1/4	+ 0.129	+ 0.171	+ 0.75
	Δr	—	0.159	0.242	0.66
Pb	x	3/8	- 0.188	- 0.267	+ 0.70
	y	5/12	- 0.020	- 0.071	+ 0.28
	z	1/4	+ 0.018	+ 0.013	+ 1.38
	Δr	—	0.191	0.276	0.69
Ag	x	3/8	+ 0.022	+ 0.096	+ 0.23
	y	9/12	+ 0.124	+ 0.168	+ 0.74
	z	1/4	- 0.228	- 0.388	+ 0.59
	Δr	—	0.261	0.436	0.60
S(1)	x	1/8	+ 0.101	+ 0.153	+ 0.66
	y	3/12	- 0.395	- 0.448	+ 0.88
	z	1/4	+ 0.568	+ 0.788	+ 0.72
	Δr	—	0.696	0.917	0.76
S(2)	x	1/8	+ 0.075	+ 0.202	+ 0.37
	y	7/12	+ 0.489	+ 0.501	+ 0.98
	z	1/4	- 0.708	- 0.942	+ 0.75
	Δr	—	0.866	1.089	0.80
S(3)	x	1/8	+ 0.169	+ 0.297	+ 0.57
	y	11/12	+ 0.319	+ 0.397	+ 0.80
	z	1/4	+ 0.094	+ 0.221	+ 0.43
	Δr	—	0.372	0.541	0.69

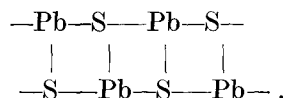
Freieslebenite is a superstructure of a PbS-type substructure. The displacements of the atoms from the ideal PbS-type structure are given in Table 7. The magnitudes of the displacements, especially those of the S atoms, are so large (up to 0.9 Å) that the S coordinations around the metal atoms are essentially different from those in PbS; although Pb is coordinated with six S in a similar way as in PbS, Sb and Ag are coordinated with three and four (or 3 + 1) S, respectively. It can be seen from Table 7 that the directions of the displacements in freieslebenite and marrite are almost the same, but the magnitudes in freieslebenite are systematically less than those in marrite, probably

because of the larger covalent radius of Sb (1.41 Å) than that of As (1.21 Å)³.

It should be noted that even the ideal PbS-type structure of freieslebenite (or marrite) is different from the true PbS structure, because the unit cell of freieslebenite (marrite) is significantly deformed compared with the corresponding cell of the true PbS; the *a* axis of freieslebenite (marrite) is shorter as much as 10% (13%) than that of PbS, whereas the *b* and *c* axes and the β angle remain approximately the same (Table 1). The above deformation of the unit cell results in the following differences in coordinations: the metal—S distance parallel to (001) in the ideal freieslebenite (marrite) structure is 2.84 (2.78) Å, whereas the Pb—S distance in PbS is 2.96 Å; the S—metal—S angles in the former deviate from that in the latter (90°) up to 7.3 (8.4°).

The structure of freieslebenite consists of two kinds of atomic layers parallel to (001) alternately piled up along the *c* direction. One layer at $z \approx 1/4$ and the other at $z \approx 3/4$ (Figs. 1*a* and *b*, respectively) are related by the inversion center and also by the 2_1 screw along the *b* axis. The deviations of the atoms from the plane at $z = 1/4$ are given in Fig. 1*a*; the S atoms deviate more (up to 0.71 Å) than the metal atoms (up to 0.23 Å). Each layer is an infinite two-dimensional network of metal—S bonds (Fig. 1). It is combined to the neighbouring two layers also by metal—S bonds, as indicated by the black arrowheads in Fig. 1; it should be noted that the Sb—S and Ag—S bonds alternately combine the successive layers. Thus, the structure of freieslebenite can be looked upon as an infinite three-dimensional network of metal—S bonds (Fig. 2).

The metal-S arrays along the *c* direction can be seen from Figs. 1*c* and 2. Pb, Ag and Sb make up their own metal—S arrays; no two metals are mixed within each array because one pair of metal—S constitutes the unit of repetition. The Pb-S array is an infinite chain, whereas Ag-S and Sb-S arrays are terminated at every metal-S pair. Two adjacent Pb-S chains are directly connected to form an infinite double chain along the *c* axis:



The Pb-S double chains seem to serve as backbones of the structure; the surrounding Ag-S and Sb-S arrays connect adjacent Pb-S

³ Unless otherwise stated, the atomic radii used in the discussion are all taken from PAULING (1960).

