# The Crystal Structure of Fülöppite, Pb<sub>3</sub>Sb<sub>8</sub>S<sub>15</sub>

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Fülöppite, Pb<sub>3</sub>Sb<sub>8</sub>S<sub>15</sub>, from the type locality in Nagybánya, Romania, is monoclinic C2/c with a = 13.441 (15), b = 11.726 (15), c = 16.930 (15) Å,  $\beta = 94.71$  (8)°;  $D_{meas} = 5.22$ ,  $D_{calc} = 5.19$  g cm<sup>-3</sup>; Z=4. The structure was solved from 1568 'observed' ( $F_o^2 \ge 5\sigma F_o^2$ ) symmetry-independent reflexions collected on a Picker four-circle FACS-1 diffractometer using Mo Ka ( $\lambda = 0.71069$  Å) radiation. Absorption corrections were applied to the data and the structure was refined by full-matrix least-squares calculations with anisotropic temperature factors to an R value of 6.07% ( $R_w = 8.01\%$ ). The structure can be resolved into two kinds of interleaving and interlocked Pb-Sb-S complex, both of which extend parallel to [110]. The first kind, of composition Pb<sub>2</sub>Sb<sub>4</sub>S<sub>6</sub>, is similar to the groups that form the chains in stibnite (Sb<sub>2</sub>S<sub>3</sub>) but have Pb bonded to both ends. The second kind has the composition PbSb<sub>4</sub>S<sub>9</sub> and consists of a string of four SbS<sub>3</sub> polyhedra symmetrically arranged about a central twofold rotation axis and a Pb atom. Three of the four Sb atoms have three 'close' (2.43-2.56 Å) S neighbours; the other has five (2.48-3.14 Å). The two Pb atoms are irregularly coordinated by six and seven S atoms at distances of 2.76 to 3.32 Å.

#### Introduction

Fülöppite is a member of a group of four mineral sulphosalts with progressive chemical compositions that can be expressed as  $Pb_{3+2n}Sb_8S_{15+2n}$  in which n=0 to 3. Two cell constants, a and b remain invariant at  $13.5 \pm 0.1$  and  $11.8 \pm 0.1$  Å, respectively, while c increases with increasing Pb content (Table 1). The increase in c is not systematic and the values of  $\beta$  are neither constant (except for plagionite and semseyite) nor progressive but, as Jambor (1969) has noted, the parameter c sin  $\beta$  changes regularly and thus the systematic increase in calculated density with increase in Pb shown by the table, is to be expected.

The crystal structures of plagionite and semseyite have been solved, respectively, by Cho & Wuensch (1970) and Kohatsu & Wuensch (1974). The space group is C2/c for both structures. The systematically absent reflexions which have been recorded for the other two members of the group are in accord with C2/c.

## Experimental

Crystals of fülöppite are rare. Specimens from Romania, which have provided the best material, are usually less than a millimetre in diameter and irreg-

ularly intergrown and intimately associated with other minerals. The faces are typically curved, striated and dull. The crystals are, therefore, generally unsuitable for structural studies and the search for a crystal bounded by measurable faces or one suitable for grinding into a sphere had to be abandoned. The crystal selected for the present study is an oddly shaped fragment from Nagybánya, Romania (Royal Ontario Museum M 19239) measuring approximately  $0.23 \times$  $0.11 \times 0.14$  mm in the **a**, **b** and **c** directions. Only one face, later identified as  $(00\overline{1})$ , gave a distinct signal on an optical two-circle goniometer although two small striated zones were detected with a microscope under high magnification. But in contrast to most of the material, it gave sharp X-ray reflexions. The crystal was mounted to rotate about [010]. A series of Weissenberg and precession films established that the systematically absent reflexions are in agreement with the space group C2/c as previously reported.

The cell parameters were calculated from the measurement of selected high-order h00, 0k0 and 00l 2 $\theta$ angles, and the angle between the  $a^*$  and  $c^*$  rows on a Picker four-circle FACS-1 diffractometer. The parameters a=13.441 (15), b=11.726 (15), c=16.930 (15) Å;  $\beta=94.71$  (8)° are in substantial agreement with previous values. The calculated density for the cell contents 4[Pb<sub>3</sub>Sb<sub>8</sub>S<sub>15</sub>] is 5.19 g cm<sup>-3</sup> compared with 5.22

Table 1. The plagionite group

		с	β	$c \sin \beta$	$D_m$	$D_c$	Reference
Fülöppite	Pb <sub>3</sub> Sb <sub>8</sub> S <sub>15</sub>	16.930	94.71	16.87	5.22	5.19	1
Plagionite	Pb <sub>5</sub> Sb <sub>8</sub> S <sub>17</sub>	19.9834	107.17	19.09	5.54	5.55	2
Heteromorphite	Pb <sub>7</sub> Sb <sub>8</sub> S <sub>19</sub>	21.22	90.83	21.22	5.73	5.86	3
Semsevite	Pb <sub>0</sub> Sb <sub>8</sub> S <sub>21</sub>	24.435	106.047	23.48	6.03	6.12	4

References: (1) Nuffield (1946) and this study; (2) Nuffield & Peacock (1945), Cho & Wuensch (1970); (3) Dana & Dana (1944), Jambor (1969); (4) Nuffield & Peacock (1945), Kohatsu & Wuensch (1974).

measured (Nuffield, 1945). The linear absorption coefficient for Mo  $K\alpha$  ( $\lambda = 0.71069$  Å) is 267.9 cm<sup>-1</sup>.

The intensity data were collected on the Picker diffractometer with filtered Mo  $K\alpha$  radiation in the  $\theta/2\theta$ scan mode to 50° in  $2\theta$ . A scan rate of 1° min<sup>-1</sup> with a 20 s background count on either side of the peak was employed. A standard reflexion, monitored at 50-reflexion intervals, showed a maximum deviation of about 5.5% from the median and was used to place the data on a uniform scale. 2411 symmetry-independent reflexions were measured of which 1568 had  $|F^2| \ge 5\sigma F^2$  and were treated as observed. In addition  $\varphi$  sweeps were made at 10° intervals over the scan range (90–270°  $\varphi$ ) for the reflexions 040, 060, 0,10,0 and 0,16,0 for use in deriving absorption corrections. The data were reduced in the usual way. Absorption corrections were made in the late stages of the refinement.

### Determination and refinement of the structure

An analysis of the distribution of E values indicated the centrosymmetric space group C2/c rather than Cc:

av. $ E^2 $	=1.00	E  > 1 = 30.4 %
av. $ E^2 - $	1 =0.89	E  > 2 = 3.9
av. $ E $	=0.85	E  > 3 = 0.3.

A set of the 224 largest ( $E \ge 1.85$ ) normalized structure factors was used in a direct determination of the metal positions with the aid of the *TANFOR* (Drew & Larson, 1968) program. One of the iterations assigned phases to all 224 reflexions and yielded an *R*(Karle) value of 12%. An *E* map calculated for this solution revealed all the metal positions – two for Pb and four for Sb. A Fourier synthesis, based on  $F_o - F_c$  coefficients for the 1568 'observed' reflexions, gave the S positions. After introduction of corrections for anomalous dispersions and conversion to anisotropic temperature factors, the agreement index  $R = \sum ||F_o| - |F_c||/$  $\sum |F_o|$  reached a value of 0.116 for the 'observed' reflexions following several cycles of least-squares refinement using unit weights.

Absorption corrections were effected with the DAT-RED (Fawcett, 1970) program which included the subroutine ABSORP (Coppens, Leiserowitz & Rabinovich, 1965). To obtain bounding plane data for the essentially anhedral crystal of fülöppite, the fragment was mounted on a two-circle device and its surface resolved, under a stereomicroscope, into nine bounding planes of which three consisted of faces [the  $(00\overline{1})$  face and the two striated zones mentioned above] and six represented the broken areas. The distance of each plane from a common centre was estimated with a micrometer evepiece. Spherical coordinates  $\varphi$  and  $\rho$ (de Jong, 1959) were read for each plane and used to prepare a gnomonic projection from which Miller indices were assigned to the planes. The  $(00\overline{1})$  face served as a reference plane to relate the coordinates to the corresponding Picker angles. Table 2 gives the observed and corrected intensities for the 040 reflexions at 20° intervals of  $\varphi$  and indicates the degree of success of the procedure. The variations in intensity that remain are due in part to the errors inherent in averaging broken surfaces as imaginary planes and in setting the planes into a chosen reference orientation for the purpose of reading the spherical coordinates.

Table 2. Net intensities of the 040 reflexions before
and after correcting the observed data for shape
and size of the crystal

$\varphi$	Iuncorr	Icorr
<b>90°</b>	2618	7987
110	47 <b>2</b> 5	9635
130	6971	10526
150	8966	11355
170	9309	11690
190	8764	10760
210	7203	959 <b>3</b>
230	5121	8596
250	3457	9299
270	2659	8113

The absorption corrections obtained with the subroutine for the four kinds of 0k0 reflexion in the  $\varphi$ 

Table 3. Fractional coordinates ( $\times 10^5$ ), anisotropic ( $\times 10^5$ , Å<sup>2</sup>) and isotropic (Å<sup>2</sup>) thermal parameters

The temperature factor has the form  $T = \exp \left[ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \right]$ . B values are from the final cycle of isotropic refinement. E.s.d.'s are in parentheses and were obtained from the last cycle of refinement.

	x	у	Z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	В
Pb(1)	0	37137 (17)	25	347 (12)	235 (14)	108 (7)	0	95 (7)	0	1.65 (4)
Pb(2)	30719 (9)	42895 (12)	33253 (9)	192 (̈́)	300 (10)	157 (5)	-27(7)	47 (4)	3 (6)	1.56 (3)
Sb(1)	37263 (14)	13632 (18)	49484 (13)	92 (10)	191 (15)	95 (8)	-35(10)	44 (7)	11 (8)	0·91 (4)
Sb(2)	40863 (15)	17955 (18)	15600 (12)	114 (10)	156 (15)	73 (7)	-16(10)	31 (6)	7 (8)	0.80 (4)
Sb(3)	8902 (15)	4903 (19)	41560 (14)	132 (11)	197 (17)	146 (9)	-82(10)	2 (7)	58 (9)	1.19 (5)
Sb(4)	14000 (14)	25122 (18)	6034 (12)	67 (10)	168 (15)	56 (7)	21 (9)	23 (6)	-25(8)	0.67 (4)
S(1)	35660 (60)	4863 (71)	25578 (51)	203 (41)	238 (61)	114 (29)	22 (41)	32 (27)	18 (33)	1.45 (16)
S(2)	50000	31669 (94)	25000	161 (57)	103 (72)	113 (40)	0 (	- 34 (36)	0 )	1.03 (20)
S(3)	26624 (52)	2731 (63)	3609 (47)	101 (35)	91 (48)	110 (28)	16 (35)	66 (25)	50 (30)	0.84 (14)
S(4)	18550 (57)	24606 (71)	39631 (53)	140 (40)	201 (58)	182 (33)	-40(39)	83 (28)	-78(37)	1.35 (15)
S(5)	46720 (54)	36518 (67)	46177 (69)	138 (39)	173 (54)	115 (29)	24 (39)	68 (27)	-35(33)	0.97 (14)
S(6)	2975 (53)	41679 (61)	8294 (44)	135 (36)	44 (46)	65 (25)	-2(34)	36 (23)	2 (29)	0.61 (13)
S(7)	7034 (54)	13327 (67)	16400 (49)	122 (37)	179 (53)	104 (27)	23 (38)	43 (25)	17 (33)	0.93 (14)
S(8)	27204 (53)	32013 (66)	15967 (48)	109 (39)	130 (52)	142 (31)	38 (37)	-57(26)	2(33)	1.07 (15)

sweeps were normalized to  $2\theta_{040}$  for each value of  $\varphi$  and then averaged for each 0k0 reflexion. The results were used to derive a curve of average absorption correction vs  $2\theta$ .

The DATRED program was employed to apply  $2\theta$  absorption corrections, selected at 2° intervals of  $2\theta$  from this curve, modified at 10° intervals of  $\varphi$  to account for the variation shown in Table 2, to all the data. The *R* value for the 1568 'observed' reflexions was reduced to 0.067. The minimum and maximum absorption corrections were respectively 276 and 1001.

### Table 4. Interatomic distances (Å)

(i) x, y, z; (ii)  $\bar{x}, \bar{y}, \bar{z};$  (iii)  $\bar{x}, y, \frac{1}{2} - z;$  (iv)  $x, \bar{y}, \frac{1}{2} + z;$  (v)  $\frac{1}{2} + x, \frac{1}{2} + y, z;$  (vi)  $\frac{1}{2} - x, \frac{1}{2} - y, \bar{z};$  (vii)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z;$  (viii)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z.$ E.s.d.'s are in parentheses.

Sb-S polyhedra More distant S Close S neighbours neighbours  $Sb(1)-S(4^{vi})$ 2.479 (9) S(5<sup>i</sup>) 3.041 (8) S(31) 2.525 (8) S(41) 3.174 (8) S(6"11) S(6<sup>v11</sup>) 2.560 (8) 3.220 (8)  $\begin{array}{c} S(3^i) \\ S(5^{i1i}) \end{array}$ Sb(2)-S(1i) 2.428 (9) 3.215 (8) S(8<sup>i</sup>) 2.472 (8) 3.471 (8) S(1111) S(2<sup>i</sup>) 3.711 (8) 2.511 (7) 3.742 (8) S(6<sup>v</sup>) Sb(3)-S(5<sup>vi</sup>) 2.480(8)S(8<sup>vii</sup>) 3.565 (8) S(7111) 2.628(8)S(41) 2.682 (8) S(5<sup>v</sup>) 2.855 (8) S(31) 3.137 (8) Sb(4)-S(7<sup>i</sup>) 2.478 (8) S(5viii) 3.067  $S(3^i)$ 3.171 S(8<sup>1</sup>) 2.478 (8) S(3v1) S(6<sup>1</sup>) 2.491(7)3.367 Pb-S polyhedra Pb(1)-S(1<sup>v11</sup>) Pb(2)-S(3<sup>vii</sup>) 2.842 (8) (×2) 2.75 S(7\*11) S(6<sup>i</sup>) 2.938 (7) (×2) 2.90 S(1<sup>vii</sup>) 2.91 S(7<sup>i</sup>)  $3.322(8)(\times 2)$ S(41) S(41) 2.95 3.674 (8) (×2) 3.03 S(51) S(8<sup>1</sup>) 3.19 S(2<sup>i</sup>) 3.31 S-metal polyhedra S(1)-Sb(2<sup>i</sup>)  $S(5)-Sb(3^{vi})$ 2.428(9)**2·4**8 Sb(3<sup>v</sup>) 2.85 2.842 (8) Pb(1\*) Pb(2vii) 2.917 (8)  $Pb(2^{l})$ 3.03 Sb(2111) 3.04 Sb(1<sup>i</sup>) 3.711 (8) Sb(4\*111) 3.06 Sb(2111) 3.47 2.511 (7)  $S(2)-Sb(2^{i})$ Sb(2111) 2.511(7)Pb(2i) S(6)-Sb(4<sup>i</sup>) 3.316 (5) 2.49 Sb(1\*11) Pb(2111) 2.56 3.316 (5)  $Pb(1^{i})$ 2.93 Sb(1\*11) 3.22 S(3)-Sb(11v) 2.525(8)Pb(2vii) 2.759 (8) Sb(2<sup>v</sup>) 3.74 Sb(31v) 3.137 (8) Sb(41)  $S(7)-Sb(4^{i})$ 2.473.171 (8) Sb(3111) Sb(2<sup>i</sup>) 2.623.215 (8) Pb(2<sup>vii</sup>) Sb(4vi) 3.367 (8) 2.90 Pb(11) 3.32 S(4)-Sb(1<sup>vi</sup>) 2.479 (9)

 $S(8)-Sb(2^{i})$ 

 $Sb(4^{I})$ 

 $Pb(2^i)$ 

Sb(3\*11)

Sb(31)

 $Pb(2^i)$ 

Sb(11)

Pb(11)

2.682(8)

2.955 (8)

3.174 (8)

3.674 (8)

A weighting scheme of the form  $w=1/\sigma^2(F_o)$  was introduced at this stage. A plot of  $\overline{\Delta F_o}/\overline{F_o}$  vs  $1/F_o$  for blocks of 49 reflexions was fitted by a least-squares routine to a second-order polynomial from which the expression  $\sigma(F_o)=0.052F_o+1.39+1869/F_o$  was derived. Three cycles of least-squares refinement brought the value of R to 0.0607 and  $R_w = [\sum w(|F_o| - |F_c|)^2/$  $\sum w|F_o|^2]^{1/2}$  to 0.0801 for the 'observed' reflexions. The value of the standard deviation of an observation of unit weight  $\sigma_1 = [\sum w(F_o - F_c)^2/m]^{1/2}$  in which m = (number of observations – number of parameters varied in the refinement) was 0.984. The value of R for all 2411 reflexions was 10.78%. A final difference Fourier map revealed no anomalies.

The full-matrix least-squares program XFLS (Ellison, 1962) was used for the structure factor calculations and the refinement. The scattering factors for neutral atoms were taken from Cromer & Mann (1968). Anomalous dispersion corrections were made from the values computed by Cromer & Liberman (1970). Interatomic distances, angles and their standard deviations were calculated with the *BONDLA* (Rylarsdaam, 1970) program. Atomic and thermal parameters are given in Table 3 and the interatomic distances and angles in Tables 4 and 5 respectively. The comparison of observed and calculated structure factors is listed in Table 6.

### Table 5. Interatomic angles (e.s.d. $0.3^{\circ}$ )

067 (8)	A new storn Sh(	1)	A nev ato	m S(1)	
.171 (8)	Apex atom So(	1)	Арел аго		
·367 (8)	$S(3^{iv}) = S(4^{i})$	90∙6°	Pb(1 <sup>v</sup> )	$Pb(2^{vii})$	96·7°
	$S(3^{iv}) = S(4^{vi})$	89.8	Pb(1*)	Sb(2 <sup>1</sup> )	101.8
	$S(3^{iv}) = S(5^{i})$	167.4	Pb(1 <sup>v</sup> )	Sb(2 <sup>111</sup> )	76.1
2.759 (8)	$S(3^{iv}) = S(6^{vii})$	76.4	$Pb(2^{vii})$	Sb(2 <sup>1</sup> )	101.3
2.905 (8)	$S(3^{iv}) = S(6^{viii})$	96.5	Pb(2 <sup>vii</sup> )	Sb(2 <sup>111</sup> )	170.5
2.917(8)	$\tilde{S}(4^{i})$ $\tilde{S}(4^{vi})$	83.1	$Sb(2^{i})$	Sb(2111)	74.6
2.955(8)	$S(4^i) = S(5^i)$	82.6	20(-)		
3.033 (8)	$S(4^i) = S(6^{vii})$	116.2			
3.107 (8)	$S(4)$ $S(6^{11})$	170.0	A nev ato	m S(2)	
$3^{-1}$ $3$	S(4) = S(0)	78.0	прел аго	III 5(2)	
3.310 (2)	$S(4^{(1)}) = S(3^{(1)})$	155.0	$Pb(2^{i})$	$Ph(2^{iii})$	133·2°
	$S(4^{(1)}) = S(6^{(1)})$	155.9	$Pb(2^i)$	$Sb(2^{i})$	$99.4(\times 2)$
2.480(8)	$S(4^{v1}) = S(6^{v11})$	89.9	Pb(2i)	Sb(2)	$110.2(\times 2)$
2.855 (8)	$S(5^{1}) = S(6^{v(1)})$	116-1	FD(2)	SD(2)	$110.2(\times 2)$
2.033 (0)	$S(5^{1}) = S(6^{v111})$	89.1	50(2)	50(2)	100.4
3.033(0)	$S(6^{vii})$ $S(6^{viii})$	7 <b>2</b> ·5			
3.041(8)			Apex ato	m S(3)	
3.007 (8)			Dh(Qvii)	Sh(1in)	08.80
3.4/1 (8)	Apex atom Sb(	2)	$PD(2^{-1})$		90'0
		,	$PD(2^{m})$	$SD(2^{\circ})$	87.5
2.491 (7)	$S(1^i) = S(2^i)$	96·8°	PD(2 <sup>-11</sup> )	SD(3)	95.9
2.560 (8)	$S(1^{i}) = S(3^{i})$	84.1	Pb(2''')	Sb(4 <sup>1</sup> )	90.6
2.938 (7)	$S(1^{i}) = S(5^{ii})$	167•4	Pb(2 <sup>v11</sup> )	Sb(4 <sup>v1</sup> )	152.4
3.220 (8)	$S(1^{i}) = S(6^{v})$	82.4	Sb(1 <sup>1</sup> )	$Sb(2^{i})$	106.0
3.742 (8)	$\tilde{S}(1^i) = \tilde{S}(8^i)$	98.5	Sb(1 <sup>iv</sup> )	Sb(3 <sup>1v</sup> )	91·2
• •	$S(2^i) = S(3^i)$	172.2	Sb(1 <sup>iv</sup> )	Sb(4 <sup>1</sup> )	1 <b>70·4</b>
2.478 (8)	$S(2^{i}) = S(5^{i})$	74.3	Sb(1 <sup>iv</sup> )	Sb(4 <sup>vi</sup> )	1 <b>02·1</b>
2.628 (8)	$S(2i) = S(6^{v})$	122.2	$Sb(2^i)$	Sb(3 <sup>iv</sup> )	161.8
2.905 (8)	S(2) = S(0) S(2i) = S(8i)	82.2	Sb(2 <sup>i</sup> )	Sb(4 <sup>1</sup> )	75.9
3.322 (8)	S(2) = S(0)	106.0	$Sb(2^i)$	$Sb(4^{vi})$	69.6
5 522 (0)	$S(3^{(1)}) = S(3^{(1)})$	100.0	$Sb(3^{i^{\prime}})$	$Sb(4^{i})$	86.3
a 450 (0)	S(3) = S(0)	02.0	Sb(3 <sup>iv</sup> )	$Sb(4^{vi})$	101.5
2.472 (8)	S(3') = S(8')	88.9	Sb(3)	Sb(4 <sup>vi</sup> )	69.5
2.478 (8)	$S(5^{11}) = S(6^{v})$	94.8	50(4)	50(4)	575
3·192 (8)	$S(5^{111}) = S(8^{11})$	89.4			
3.565 (8)	$S(6^{v}) = S(8^{i})$	154•4			

# Table 5 (cont.)

Apex a	tom Sb(	3)	Apex atom S(4)			
$\begin{array}{c} S(3^{1v})\\ S(3^{1v})\\ S(3^{1v})\\ S(3^{1v})\\ S(3^{1v})\\ S(3^{1v})\\ S(4^{1})\\ S(4^{1})\\ S(4^{1})\\ S(4^{1})\\ S(5^{v})\\ S(5$	S(4 <sup>t</sup> ) S(5 <sup>v1</sup> ) S(5 <sup>v1</sup> ) S(7 <sup>111</sup> ) S(8 <sup>v11</sup> ) S(5 <sup>v1</sup> ) S(7 <sup>111</sup> ) S(8 <sup>v11</sup> ) S(5 <sup>v1</sup> ) S(5 <sup>v1</sup> ) S(5 <sup>v1</sup> )	88:6° 91:6 80:7 169:8 68:0 167:9 86:3 89:7 109:4 81:7 87:9	Pb(1 <sup>1</sup> ) Pb(1 <sup>1</sup> ) Pb(1 <sup>1</sup> ) Pb(2 <sup>1</sup> ) Pb(2 <sup>1</sup> ) Pb(2 <sup>1</sup> ) Sb(1 <sup>1</sup> ) Sb(1 <sup>1</sup> ) Sb(1 <sup>1</sup> )	Pb(2 <sup>1</sup> ) Sb(1 <sup>1</sup> ) Sb(3 <sup>1</sup> ) Sb(1 <sup>1</sup> ) Sb(1 <sup>1</sup> ) Sb(1 <sup>1</sup> ) Sb(3 <sup>1</sup> ) Sb(3 <sup>1</sup> ) Sb(3 <sup>1</sup> ) Sb(3 <sup>1</sup> )	80.1° 168.8 92.3 96.8 92.7 94.9 163.2 96.9 87.5 101.8	
$S(5^{\circ})$ $S(5^{\circ})$ $S(5^{\circ})$ $S(7^{111})$	$S(8^{11})$ $S(7^{111})$ $S(8^{v11})$ $S(8^{v11})$	81:9 89:2 144:0 121:9	Apex atc Pb(2 <sup>i</sup> ) Pb(2 <sup>i</sup> ) Pb(2 <sup>i</sup> ) Pb(2 <sup>i</sup> )	om S(5) Sb(1 <sup>i</sup> ) Sb(2 <sup>iii</sup> ) Sb(3 <sup>v</sup> ) Sb(3 <sup>vi</sup> )	93·9° 94·9 90·3 104·9	
Apex a	tom Sb(	4)	$\frac{Pb(2^{i})}{Sb(1^{i})}$	$Sb(4^{viii})$ $Sb(2^{iii})$	164·3 77·3	
$\begin{array}{c} S(3^{i}) \\ S(3^{i}) \\ S(3^{i}) \\ S(3^{i}) \\ S(3^{i}) \\ S(3^{v1}) \\ S(3^{v1}) \\ S(3^{v1}) \\ S(3^{v1}) \\ S(3^{v1}) \end{array}$	S(3 <sup>v1</sup> ) S(5 <sup>v111</sup> ) S(6 <sup>1</sup> ) S(7 <sup>1</sup> ) S(8 <sup>1</sup> ) S(5 <sup>v111</sup> ) S(6 <sup>1</sup> ) S(7 <sup>1</sup> ) S(8 <sup>1</sup> )	110·5° 87·2 175·3 82·4 89·8 112·1 74·0 162·2 78·6	Sb(1') Sb(1') Sb(2''') Sb(2''') Sb(2''') Sb(3'') Sb(3'') Sb(3'')	Sb(3 <sup>°1</sup> ) Sb(3 <sup>v1</sup> ) Sb(3 <sup>v1</sup> ) Sb(3 <sup>v1</sup> ) Sb(3 <sup>v1</sup> ) Sb(4 <sup>v111</sup> ) Sb(4 <sup>v111</sup> ) Sb(4 <sup>v111</sup> )	167-1 92-5 79-4 90-1 158-3 69-8 98-3 93-4 89-7	
$S(5^{viii})$ $S(5^{viii})$	S(6 <sup>1</sup> ) S(7 <sup>1</sup> )	89·8 79·8	Apex ato	om S(6)		
S(5') S(6') S(6') S(7')	S(8') S(8') S(8') S(8')	93.6 92.5 89.6	Pb(1 <sup>1</sup> ) Pb(1 <sup>1</sup> ) Pb(1 <sup>1</sup> ) Pb(1 <sup>1</sup> ) Sb(1 <sup>v11</sup> ) Sb(1 <sup>v11</sup> )	$\begin{array}{c} Sb(1^{vii})\\ Sb(1^{viii})\\ Sb(2^{v})\\ Sb(4^{i})\\ Sb(1^{viii})\\ Sb(2^{v})\\ Sb(2^{v})\\ Sb(2^{i})\end{array}$	129·1° 110·2 74·6 97·8 107·5 71·3	
Apex a	tom Pb(	1)	$\frac{Sb(1^{viii})}{Sb(1^{viii})}$	Sb(2 <sup>v</sup> ) Sb(4 <sup>i</sup> )	91·9 101·2	
$S(1^{v})$ $S(1^{v})$ $S(1^{v})$ $S(1^{v})$ $S(1^{v})$ $S(1^{v})$	$S(1^{v_{11}}) \\ S(6^{i}) \\ S(6^{i_{11}}) \\ S(7^{i}) \\ S(7^{i_{11}}) \\ S(6^{i_{11}}) \\ S(6^{i$	$\begin{array}{c} 86.0^{\circ} \\ 92.7 (\times 2) \\ 71.8 (\times 2) \\ 148.0 (\times 2) \\ 112.4 (\times 2) \\ 159.1 \end{array}$	Sb(2 <sup>v</sup> ) Apex ato	$Sb(4^{i})$ om $S(7)$	166.6	
$S(6^{i})$ $S(6^{i})$ $S(7^{i})$	S(7 <sup>1</sup> ) S(7 <sup>111</sup> ) S(7 <sup>111</sup> )	70·4 (×2) 129·8 (×2) 65·6	Pb(1 <sup>1</sup> ) Pb(1 <sup>1</sup> ) Pb(2 <sup>v11</sup> ) Pb(2 <sup>v11</sup> ) Sb(3 <sup>111</sup> )	$     Sb(3^{111}) \\     Sb(4^{1}) \\     Sb(3^{111}) \\     Sb(3^{111}) \\     Sb(4^{1}) \\     Sb(4^{1}) $	106.9 88.8 97.9 103.2 100.7	
Apex a	tom Pb(	2)	~ /			
$S(1^{v11}) = S(1^{v11})$	S(3 <sup>vii</sup> ) S(4 <sup>i</sup> )	84·7° 96·9	Apex ato	om S(8)		
S(1 <sup>v11</sup> ) S(1 <sup>v11</sup> ) S(3 <sup>v11</sup> ) S(3 <sup>v11</sup> ) S(3 <sup>v11</sup> ) S(3 <sup>v11</sup> ) S(3 <sup>v11</sup> ) S(3 <sup>v11</sup> ) S(4 <sup>1</sup> ) S(4 <sup>1</sup> ) S(4 <sup>1</sup> ) S(4 <sup>1</sup> ) S(4 <sup>1</sup> ) S(5 <sup>1</sup> ) S(5 <sup>1</sup> ) S(7 <sup>v11</sup> )	$\begin{array}{c} S(5^{i})\\ S(7^{v1i})\\ S(8^{i})\\ S(4^{i})\\ S(5^{i})\\ S(5^{i})\\ S(7^{v1i})\\ S(8^{i})\\ S(5^{i})\\ S(7^{v1i})\\ S(8^{i})\\ S(7^{v1i})\\ S(8^{i})\\ S(8^{i})\\ S(8^{i})\\ S(8^{i})\\ S(8^{i})\end{array}$	161-6 90·9 71·0 76·3 78·5 83·0 150·5 86·5 157·1 90·0 79·7 127·3 112·9	Pb(2 <sup>1</sup> ) Pb(2 <sup>1</sup> ) Pb(2 <sup>1</sup> ) Sb(2 <sup>1</sup> ) Sb(2 <sup>1</sup> ) Sb(3 <sup>v11</sup> )	Sb(2 <sup>1</sup> ) Sb(3 <sup>v11</sup> ) Sb(4 <sup>1</sup> ) Sb(3 <sup>v11</sup> ) Sb(4 <sup>1</sup> ) Sb(4 <sup>1</sup> )	103·6° 89·1 142·8 94·7 104·9 111·7	

# Discussion of the structure

The Sb atoms are surrounded by six [seven in the case of Sb(2)] S atoms within a radius of 4.0 Å in a distorted but readily recognizable octahedral arrangement. The distances vary from 2.428 to 3.742 Å (Table 4) as compared to 4.05 Å for the sum of the van der Waals radii for Sb and S (Evans, 1964). The coordination in stibnite  $(Sb_2S_3)$  is similar, both kinds of Sb atom being surrounded by seven S atoms at distances ranging from 2.455 to 3.642 Å (Table 7). Bayliss & Nowacki (1972), who have recently refined the structure, describe the Sb(1) atom of stibnite as trivalent and Sb(2) as quinvalent on the basis of the number of 'close' S neighbours. A comparison of Tables 4 and 7 shows that the coordination of S about Sb(1), Sb(2) and Sb(4) in fülöppite resembles the Sb(1) polyhedron in stibnite while the arrangement around Sb(3) is similar to Sb(2)in stibnite.

The coordination about Pb, as in most sulphosalts, is irregular. Pb(1), which occupies the special position  $4(e^2)$ , has six S neighbours at distances ranging from



Fig. 1. ORTEP plots of metal-S polyhedra showing anisotropic thermal vibrations of the atoms drawn with 90% probability.

H= 0. E- 0 2 8250 1334 6 7770 -399 6 2127 -2599	-19 1689 -1257 -18 11830 -1257 -18 11830 359 -17 4687 3079 -15 10830 -250	-12 4234 461 -10 1704 -1762 -8 7274 7234 -6 1685 -2124 -5 114 7240	M+ 2. E- 12 0 2836 -2820 1 7464 1047	1 773- 421 9 1917 -2214 13 1507 1978 11 979 -115	-18 12124 1244 -18 12124 1244 -17 11374 147	7 1309 1474 4 1734 1421 4 749 - 428 10 1412 - 1440	-6 53/0 366 -3 1667 1996 -2 3010 -177 -1 2010 -2366	-3 1072 -3007 -2 4401 4510 -1 5313 5202	+ 1282 1362 10 7670 433 11 1764 -1870 12 1454 -4082 13 1454 -2145	-4 3767 1506 -3 1174 -1181 -2 2519 -7419 -1 1979 -1938	-3 3447 3785 -2 4478 382 -1 3402 -5245	-7 3134 -3213 -6 4949 -4993 -5 1952 -1490 -4 3424 3364 -3 1299 -1151	-3 1245 8/4 -3 1924 1884 -1 1855 1417
8 [10] -1241 10 1183 -6342 1213468 12014 14 14114 -811 14 12274 -322 18 7508 2334 20 2762 2464	-14 1170+ 1767 -13 6266 5635 -17 6496 5635 -11 653- 471 -10 620- 707 -0 6500 -5655 -6 6272 3807	-2 828 -791 He 2. E 2 0 1467 -1847 1 6124 -261 2 7938 2333	2 772328 3 1265 1275 4 2653 -2647 5 401+ 1314 6 434-464 7 2715 1005 8 1005+ 1165	13 ve) 163 14 466 110 3. 4. 4	-15 1#20 -1453 -14 1017# -506 -13 2#00 2717 -12 1#V# -2044 -11 2268 2085 -10 3043 -4414 -4 3840 3825	12 #*** 1053 13 4877 5145 14 9014 157 15 3427 3745 18 9544 -380 17 1549 1847	0 1370 - 1145 1 2488 2379 2 4040 4449 3 2021 - 1488 4 301 - 1488	0 1+30 722 1 7240 - 2701 2 1+17 - 1 107 3 1+44 1457 4 5555 3141 9 6341 4153	1+ 1+13 -1525 15 854* -445 1+ 1705 -2153 8, 8+ 2 -18 1114*-1888	0 3354 3078 1 2318 -2139 2 2417 -2767 3 5400 5440 4 873-1000	0 1036 -2761 1 1785 3453 2 6714 -273 3 6774 -425 6 1495 -1384 5 3425 -3312	-2 718* -411 +1 1322 -1240 #* 11. #* 7 0 3001 -2703 1 777* -410	C 763+ -660 1 +808 -4674 2 1747 1695 3 1354 -1304 4 764+ -335 3 1851 1715
Me 0, 14 2 0 7244 366 1 3204 3566 2 1456 -1420 3 4456 -1420	-7 44/6 -413 -6 2323 2314 -5 2876 3276 -4 686* -107 -3 3371 -3420 -7 614405 -1 7715 7445	3 4746 -4733 4 7175 7278 4 476 7255 4 476 7255 4 476 7255 7 4546 -7057 4 546 -7057 4 546 -7057 4 546 -7058	* 1024* 514 10 1227 5447	-13 1680 /814 -12 1045- 1051 -11 1288 1231 -10 64W -443 -9 9410 1245 -8 4568 -4409	-8 803+ -163 -7 75** -840 -6 2225 -2053 -5 64** 672 -6 615* -17* -7 281* -2648 -7 11** 7318		4 2140 2100 • 3507 3140 7 1473 1416 8 1670 -1147 • 7541 -7483 10 1801 -1776	6 2883 2643 7 2224 2037 8 2308 2144 9 4648 -4641 10 2452 3021 11 1856 -1472	-17 10031167 -16 4526 177 -15 1632 1484 -16 8556 -138 -13 1712 -1751 -17 1278 354	5 1015 -674 6 1084 924 7 640- 373 8 734- 574 9 1523 1501 10 765- 676 11 807-1167	a 1404 1482 7 5551 5275 8 1634 1253 9 2498 2244 10 5095 4047 11 3138 -2014	2 4423 4137 3 3160 -3140 4 7674 -3080 4 1611 1714 7 8144 -346 8 3514 3047	6 2335 -2423 7 6124 -324 8 6410 751 9 8314 50 84 13, 8- 3
4 2070 -379 5 1460 1280 6 2010 -435 7 4020 -117 8 4450 -102 9 1702 1310 1010		10 1543 1437 11 4220 919 12 1729 -1756 13 4790 313 14 9070-1040 15 9077 -3363	-4 1617 -1548 -7 1031- 1248 -6 1764 1616 -5 1675 1666 -5 1677 1666	-6 3711 3702 -5 3405 3506 -6 756376 -3 4662 -6361 -2 1622 1626 -1 1530 1400	1 316 44 	-11 210+ -415 -12 486+ 408 -11 4365 4074 -10 3172 -3345 -4 1755 -1182 -4 1755 -1182	12 2450 -3142 13 2448 2724 14 4630 371 15 1747 -1407 16 1610 -1717 17 1700 -30	11 3247 -3701 14 1530 -1570 15 4734 -402 14 4504 1525	-10 2690 2858 -4 7380 -161 -8 1398 -1078 -7 3283 3336 -5 1733 -1738 -5 1037 -7138	12 2188 2551 13 2050 -2215 14 1307 -1462 15 3310 3348	13 1546 1451 	• 2376 2520 = 11. K= 7 -11. 5700 -338 -10. 5700 -338	-12 %63* %7 -11 1456 -1475 -10 878* -183 -4 851* 849 -6 1267 -1217 -7 158* 1849
11 2472 -2048 12 2700 2503 13 2244 2112 14 2441 -2310 15 4144 -2310 15 4142 -2153	6 1722 1482 5 2836 -2747 6 4245 -5163 7 7510 100 6 3164 346	17 13734 A74 14 10-24 757 14 1275 -248A		** 3. ** 11 0 1561 -1177 1 2512 2*** 2 4010 -5017 3 1685 -1573	3 1965 - 1910 2 227 2445 3 463 - 1364 3 1947 - 1364 7 7404 - 4916	-4 1425 -2607 -5 4710 525 -4 5730 241 -1 5470 508 -7 1421 -1287 -1 2249 -2231	-18 3254 3367 -17 1650 412 -18 10744 11.22 -18 4021 -3721	-10 1038 -391 -17 1038 -308 -10 2200 2008 -15 3560 +3627 -15 3560 1200 -13 1416 120	-3 3032 3740 -2 1531 -1491 -1 2240 -1845	-17 2001 2766 -10 2721 2387 -15 2464 2711 -16 2305 2706 -13 9684 -276 -12 1912 2140	-12 /442 -2497 -11 /743 1417 -10 /911 1497 -4 /792 -1875 -6 /7844 -255 -7 /511 -2650	-3 834 -342 -7 839 541 -6 2007 1898 -3 3036 2000 -4 344 3428 -3 2718 2720	-5 3106 -3063 -4 7660 -381 -1 2170 -2153 -2 2961 -2892 -1 1846 1765
17 [1]A= -174 18 2476 -29407 19 [11]7401 20 2712 -2447 H= 0, t= 4	10 440 - 440 11 1502 1446 12 4614 557 13 3358 17-3 14 724 276 14 7270 - 7650 14 7270 - 7650	-73 (2310 402 -10 3232 2316 -10 110-2276 -11 110-2276 -12 110-12276 -15 110-1051 -15 110-758 -16 507	2 4144 6114 1172 8 103*+ 4 7171 944 3 4124 -211 6 443 44 7 402214 6 463 44 7 402214	4 273-444 3 3141-2542 4 1935-1623 7 1965-1623 4 883-228 4 883-228 4 1977-2623 3 4 465-312	0 023- 041 10 023- 041 11 0510-129 12 013- 224 13 1010- 1098 14 401570	4. 4. 4. 7 C 2350 -2500 1 402 -1050 2 5746 3409 3 6100 187	-14 1544 Je17 -13 9010 -70 -17 8434 647 -10 2345 2104 -10 2345 2104 -7 7710 -710 -7 1545 -3143	-12 8000-1310 -11 8310-700 -10 1740-1870 -0 2270 2010 -0 2270 2010 -7 1570 10-5	0 914 -1045 1 5744 -5352 2 1178 -1079 3 6094 -5053 4 618 3510 4 1277 -1014	-11 ++++ -++++ -10 +11++1048 +-0 275+ 2839 -2 284+ 30+0 -7 2839 -2480 -6 498+ -346 -5 1001 +34	-6 746 837 -5 5364 5277 -6 1867 -1746 -3 1929 1712 -2 1042 2862 -1 1245 -1086	-2 764* 790 -1 1315 -1071 H* 11. K* 4 0 926*-1475 1 884*-1134	H+ 13, 4+ 5 D 801+ 845 1 2734 2405 2 3445 - 3340 3 3445 - 278 4 824+ 773
0 1424 - 1708 1 3301 1544 2 3301 3322 5 0124 - 237 4 4454 - 4354 5 4124 - 7277 6 4000 - 2787	17 11000-1444 17 11751471 18 1. 44 5 -18 7305 -7354	-13 1/0 672 -12 974 617 -11 2040 -2117 -12 1044 1970 -0 4725 -0513 -0 504 1970 -14 104	1 2307 2454 10 704- 325 11 2442 2004 12 1544 -1725 13 4915 -5164 14 3736 5727	11 407-552 3 11 -14 112	-14 4036 -3420 -15 2050 -1574 -14 11164 1043	+ 010+ 761 + 3730 2004 + 2470 - 2726 1 2472 - 2735 = 763+ - 378 + 1673 1761 10 0273 400	-7 1071 475 -6 244 -230 -5 344 757 -5 344 757 -6 1015 -1044 -3 4045 -2071 -2 1044 -2071	-5 505+ 40 2441 2114 -3 7544 -7432 -7 5946 34-7 -1 1431 -1243	7 077 -444 4 403 -4450 4 1453 -1378 10 1558 -1512 11 1753 1565 12 1530 -1015 13 1575 -1015	1347 1328 -3 500* ++13 -2 7808 2538 -1 2179 148+	P* 10, P* • 0 492* •05 1 1284 -1237 2 168* 1465 3 2703 239* • 1897 1401	7 1948 1449 3 2727 2518 4 1544 -1425 5 1258 995 6 2374 2295	5 1144 1518 6 8344 881 7 2206 -2165 8 1338 -1115 H+ 13, K+ 3
7 4417 4743 4 4104 -5744 4 1545 1155 10 1545 1155 10 1545 -2745 11 2451 -2745 12 5437 -4745 13 1976 1542	-15 3046 4734 -15 3020 -1442 -16 10***134 -13 4616 354 -13 4616 354 -13 772 3547	-6 104 -7411 -51105 -17137 -6 4777 -4621 -7 353 -4624 -7 3653 2451 -1 2610 7617	17 1-11501 17 1-11501 14 10-2+ 145 14 11211235		-12 1362 497 -11 2040 1926 -16 921 -477 -9 2017 -1817 -9 4546 4921 -7 1922 1241	11 1164 3292 12 3278 -2435 13 2207 2199 14 1474 1491 15 9207 -444	4	0 ++12 +747 1 1423 1418 2 +977 10+0 3 2791 -2245 4 1873 -1337	15 1452 1344 15 1452 1344 14 15 1452 1344	0 1970 1760 1 9355 -8807 7 1600 -1615 3 6440 -1615 4 1601 1853 5 1976 1760	5 751+ 1017 6 1537 -1445 7 1442 5121 4 2238 -1009 6 2412 2703 10 2435 -2367	-8 4124 -454 -7 4004 -384 -5 2413 2594 -5 1344 -1147 -4 8444 217	-10 2448 -2323 -9 2212 -2420 -8 880+ 994 -1 1827 1727 -6 8154 -223 -5 3119 -3138
14 13110 726 15 10074 1146 14 10810 -341 17 7250 -3123 10 1116 - 430	-0 5845 -5.35 -7 2116 1469 -7 2770 2775 -6 383 -6.55 -6 4049 6257	- 2. ** 4 C 3143 -3119 1 1246 1470 2 13-* 1181 1 243 476	-20 275' 2143 -15 2521 2717 -14 1177-1141 -17 1047- 570 -16 1046- 153 -15 2402 2500		-1 748- 48 -1 147 -1414 -3 1477 -1414 -7 4414 1004 -1 4114 124	-14 1534 813 -14 10448 250 -14 5461 5471 -11 2291 -2441 -12 4739-1524	414 -507 2417 -2148 4304 -417 7774 451 4304 -417 451 451 451	+ 1647 [444 7 2667 -7876 4 6342 + 168 9 7664 - 413 10 7230 -7176 11 4074 746	-15 4174 -313 -16 4624 -363 -15 3025 1240 -12 1661 -3661 -11 4312 -367 -10 4124 -4213	7 74210% 15% 15%7 4 4015 4027 10 830* 847 11 1414 -1712 12 871* 226	12 1572 -1372 	-2 8344 -770 -1 4909 4857 Re 12, Re 0 0 7874 422	-3 2628 2618 -7 1199 -909 -1 5267 5091
H. C. E 0 3(17) - 3393 1 2007 - 2761 2 1301 - 1(17) 3 4640 - 276	-1 1173 -1 144 -1 474 - 2757 	\$ 187- 573 \$ 1813 1485 7 7327 -7177 \$ 1531 -1408 7 744 1007 13 546 1773	-11 353/ 324 -12 3763 -3041 -12 3763 -3041 -11 854- 373 -13 5517 555 -5 7767 7466 -3 505 570	2 1012 1510 1 1947 -1342 5 1766 -2370 6 1917 -1440	0 1474 3444 1 4674 -770 2 1542 1333 3 7144 -5157 4 7444 -5197	-10 1514 3551 -4 4421 4415 -4 7054 2041 -7 4567 4655 -4 174 -137 -5 1624 -3484	10 1743 1737 11 6104 -418 12 6344 167 13 6048-168 14 7761 2316 15 9316 647 16 10224 1290	1) 1-30 1113 1- 477- 114 15 415- 1-37 1- 4-1475 1- 4-1475 m- 7, 4- 5	-0 746 1000 -1 448 -1641 -7 5297 5292 -6 5271 1410 -3 1288 -1849 -4 1444 -1841 -3 2269 -2017	1. 4251107 9, 4- 5 -1. 1024- 485 -1.5 /468 /761	-11 0374 -004 -10 1538 -1515 -0 2534 2525 -0 2511 2242 -7 8110 -5173	+ 1259 1196 + 1259 1196 + 1259 1196 + 1259 12876 + 1287 - 12876 + 1287 - 12876 + 1287 - 12876 + 1259 1196 + 1259 1	1 834- 444 2 1324 -1224 3 850- 320 4 1413 -1784 3 850- 97
1 5444 -5447 6 3443 1334 7 4427 4511 8 3504 5440 4 444 -714 13 461712	7 2010 2017 2 000 - 110 5 000 - 110 7 2152 - 1105 7 2152 - 250 7 3100 - 3557	17 2000 2000 11 710-1070 10 017 1000 10 017 1000 10 017 027 10 017 027 10 017 027	-6 1621 -1768 -5 236 -2364 -6 356 -376 -3 3204 -305 -2 1204 -1636 -1 1040 -190	-7 1.61. 434	6 2238 - 2342 7 17-7 - 1528 6 8748 114 10 1573 2175 11 2057 1848	-1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -	-17 1507+ 1301 -18 1745 1564 -18 3040 -1544 -18 3040 -2974	-17 1430 1757 -16 1560 1156 -15 4770 -416 -16 2567 -2355 -13 267 -2368 -13 2677 -2568 -13 2677 -3568	-1 3044 2914 	-13 3610 -3676 -12 1177 3740 -11 2031 -3079 -10 1376 -1571 -0 2553 2031 -0 1299 1227	-4 2783 -2440 -3 4185 4034 -2 708- 301 -1 1348 1078	-14 1814 -333 -12 2979 1249 -10 2748 -2823 -8 2981 -1420	-7 1530 -1734 -6 4756 4796 -5 4730-1238 -4 658- 344 -3 1712 1821
12 1041 464 12 1041 - 464 13 1010 - 470 14 1055 - 600 14 1055 - 535 14 1055 - 535 14 1124 - 1232	• 2077 2131 10 1785 -2074 11 2606 -3017 12 2511 -2752 11 6436 105	10 13740 233 10 1.54 -1965 10 2.44 -10 11670 -276 -10 1260 1205	3. 4. 1 3 7642031 1 3530 -3+44 2 3144 1074 3 3117 3135	-1 -11 -112 -1 -111 -112 -1 -111 -112 -1 -112 	-12 7020 -1007 -12 1032 -1007 -12 1032 - 1012 -11 1040 - 10	0 7716 -7440 1 0454 -243 2 2804 2750 1 1654 1704 4 1654 -1582 4 3745 -3755	-13 1010 -733 -11 1773 -345 -11 1773 -345 -10 4703 4155 -7 450+ 451 -8 400+ 451 -8 400+ 451	-11 1075 1476 -10 #478-1219 -9 7478-1219 -9 7478-2361 -7 7465 #332 -0 7188-1260 -5 2777 2360	2 2427 -2443 3 3627 1041 4 3256 1924 4 1257 1124 6 446 4633 7 7509 742 8 2740 -2121	-> 100* -110 -> 270* -120 -> 270* -120 -> 127* 132 -3 22*1 22*1 -2 +3** 107 -1 4** -****	0 4819 -4577 1 2333 -1764 2 1615 -1627 3 1780 -1455 4 2592 2307 5 1880 1829	-2 3930 -3948 -2 3930 -3948 H- 12, 4- 2 0 1007 471 3 1916 1459	-7 8000 120 -1 2802 -2722 -1 14, 4+ 0 0 1705 1014 2 4462 4478
14 11831344 W- D. R. A 0 1413 -1036 1 3043 -1147 2 4430 4454	15 12414 627 16 2549 -2473 17 11104 AN2 H+ 1. 44 7 -17 2024 1674	-17 (162* 613 -16 (702*-1343 -15 1708*-1776 -14 1706*-1035 -13 1675 3036 -12 4416 -4511 -11 2745 2079	<pre></pre>	<pre>% 1716 -2222 # 2247 -2152 # 3561 -3568 10 4050 -7400 12 5111 -3022 14 2071 -2184 16 1090 -1512</pre>	-10 1012 -1176 -4 1517 -1454 -7 1517 -1780 -2 2334 2322 -6 1331 -057 -3 2435-1404 -4 2044 2221	J 1408 -2024 # 154 -458 4 458 -4603 10 7014 4255 11 872-1002 12 1408 -1883 13 1784 -2131	-6 2651 -26.50 -5 2740 873 -6 2485 6743 -1 8216 -7546 -2 5836 -246 -1 2719 -2471	3136 3154 3136 3154 3136 2507 5176 181 7. 56 7	4 7554 -134 10 9044 293 11 1348 1348 12 2746 2344 13 7373 -7269 14 3344 -3348	0 7052 -2740 1 7607 2500 2 2374 -2171 3 2030 -2577	+ 10, + 10,	2 7174 -158 3 6165 -3874 4 7104 344 5 3624 3408 8 3584 -3526 7 7174 -186 8 2672 -2845	403+ 705 41295 -1507 431+7 3144 - 14, 4- 0 -10 674+ 701
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<ul> <li>india -460</li> <li>2004 2121</li> <li>2200 2123</li> <li>7 2777 2253</li> <li>10154 553</li> <li>10256 1646</li> <li>10 10376 1646</li> </ul>	2 1125 1018 3 1883 1462 4 2884 -3245 5 8494 -3245 6 2264 2418 7 2047 2142 4 2178 2448	* 13%* 13%1 * 43%*-1108 10 5110 -3570 11 516 4368 12 6***-1787 13 10%** 1514 16 675 -842	-13 2134 343 -4 2324 2174 -4 2347 -2742 -7 1143 -1043 -8 3710 -3410 -1 740 -831 -4 740 -831	+ 1434 -1478 5 766 -1014 6 981 243 7 745 -2016 8 341 -3472 6 4565 4756 14 841 -6325	-6 9'0' 355 -5 559 3211 -6 14te 1622 -3 3779 -3185 -7 8240 6 -1 7020 650	1 3#70 -3710 3 2756 -2173 3 1427 -1024 4 1880 -1878 4 673+ 1085 4 873+ 204 7 873+ 1085	-14 1024 -177 -13 1444 -1776 -17 7103 7044 -11 7103 7044 -11 7004 -141 -10 9104 -47 -4 1449 1697	-17 0100 -200 -11 0100 1110 -10 1600 1010 -0 0100 -107 -0 0100 -107 -0 0100 -107 -7 5322 5033	0 5910 5771 1 1346 -705 2 2766 2738 3 7346 -358 4 7176 277 5 7638 -635	-5 737 -112 -6 3032 -4601 -3 744 141 -7 1736 1874 -1 888+ -467	-+ 10. ++ 13 -+ 2111 2017 -+ 2777 -+35 -5 #934 -7*4 -+ #56+ -7*5 -1 2211 -2054	4 12. 5 4 0 758- 416 1 72699 2 5340 5018 3 7333 -2397 5 3017 2115	-4 927+ 1245 -4 7590 2946 -7 2349 2588 -4 8140 119 -4 8020 -734 -1 411 -899
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15 2110 -2061 16 10524 343 17 11474 1224 18 10474 -741 19 10474 3453	10 1755 - 1100 	- 1044 - 1150 -7 444 - 1150 -6 9159-1101 -5 1044 - 1044 -5 1074 170	0 434- 764 1 4594 4459 2 634- 145 3 4493 4441 4 1673 -1615 4 724- 2161 4 7241 2178	11 434 -370 17 417-1381 14 1482 1441 14 4934 -982 15 1563 1477 16 276 3356	0 630* 417 110724 4616 2 3441 -3110 3 3451 1154 4 3630 -384	-12 4310 307 -11 4135 8204 -10 5496 -5770 -4 1545 -1145 -6 1705 1642 -7 2357 2049	-11 c146 -6-33 -10 2700 -2146 -4 2567 -273 -4 6010 -2746 -7 1567 -1106 -6 461 761	1 1412 -1175 2 1064 2114 3 244 357 4 1727 -1444 4 2440 2682 6 6514 -840 2 4522 -840	-17 //	-11 Par547 -10 4044 -67 -4 7616 -2686 -6 7661 -6177 -7 2770 -2777 -6 1767 -1702	-14 11014-1704 -13 10044 -304 -12 2343 -741* -11 1400 1330 -10 744 474	-11 2352 -2668 -10 4347 4080 -9 8754-1168 -8 2378 2668 -7 2523 -2610 -6 1551 -1542	16, 5- 0 0 919+ 1187 16, 5- 0

Table 6.  $F_o [F_o^2 < 5\sigma(F_o^2) \text{ are marked }^*]$  and  $F_c$  values (×10)

E. W. NUFFIELD

Table 7. Sb-S distances in stibnite\*

<b>S</b> b(1)	Close S neighbours 2·521 Å 2·539 (×2)	More distant S neighbours 3.111 Å (× 2) 3.167 3.642
Sb(2)	2·455 2·678 (×2) 2·854 (×2)	3·373 (×2)

\* Bayliss & Nowacki (1972).

2.842 to 3.322 Å (av. 3.03 Å) in a distorted octahedral arrangement, and two additional S neighbours at 3.674 Å. The coordination is remarkably similar to Pb(3) in plagionite (which occupies the same special position), the corresponding distances being 2.85-3.38Å (av. 3.06 Å) and 3.68 Å (Cho & Wuensch, 1970). Pb(2) has six S neighbours between 2.759 and 3.192 Å (av. 2.96 Å) in an octahedral configuration and a seventh neighbour at 3.316 Å. Its coordination resembles Pb(2) in plagionite which has comparable distances of 2.83-3.17 Å (av. 2.97 Å) and 3.33 Å.

Fig. 1 shows the ORTEP plots of the various metal-S polyhedra.

A prominent feature of the structure of fülöppite (Fig. 2) is the segregation of metal and S atoms into alternating layers parallel to ( $\overline{2}01$ ). The single exception is S(2) which, along with Pb(1), occupies the special (0, y,  $\frac{1}{4}$ ) positions on the twofold rotation axes and lies in the metal layers. Plagionite (Cho & Wuensch, 1970) has a similar arrangement except that the layering is parallel to (100) and this difference accounts for some of the non-homologous cell parameters in the group. A cell chosen to give the fülöppite layers a (100) identity as in plagionite, would be related to the conventional cell by the transformation matrix  $\overline{100/010/\frac{1}{2}01}$ and have the dimensions a=13.441, b=11.726, c'=17.695 Å;  $\beta'=107.53^{\circ}$ .

The value of c' (17.695 Å) and the values of c for plagionite and semseyite (Table 1) show the expected systematic increase with increase in Pb. Also the  $\beta'$  angle is in substantial agreement with the  $\beta$  angles of these two minerals.

The layering of the structures of fülöppite and plagionite show another difference. The metal (as well as S) layers in fülöppite are identical except for their relative positioning as dictated by the symmetry elements. The plagionite structure, however, is composed of two kinds of metal layer. The layers in this structure cannot be made identical by withdrawing one Pb position. It follows that the fülöppite structure cannot be derived by the removal of an appropriate amount of Pb and S and collapsing the structure along [001].

The structure of fülöppite can be resolved into two kinds of interleaving and interconnected Pb–Sb–S complex, both of which extend parallel to [110] as illustrated in Fig. 3. The first kind, of composition  $Pb_2Sb_4S_6$ , includes the Sb(1), Sb(3) and Pb(2) atoms. Except that Pb is bonded to the ends of these groups, they are remarkably similar to the units that form the chains in stibuite  $(Sb_2S_3)$ . Corresponding distances in the two minerals are compared in Table 8. Adjacent



Fig. 2. Projection of the fülöppite structure on (010) showing the interatomic distances corresponding to Table 4.



Fig. 3. The structure of fülöppite projected on (010). The  $Pb_2Sb_4S_6$  complexes (hatched) are elongated parallel to (102); the  $PbSb_4S_9$  complexes are parallel to ( $\overline{102}$ ).

groups along [110] are separated by metal-S distances: Sb(1)-S(4)= $3\cdot174$ , Sb(3)-S(3)= $3\cdot137$ , Pb(2)-S(5)= $3\cdot033$  Å.

Table 8. Sb–S distances in the Pb<sub>2</sub>Sb<sub>4</sub>S<sub>6</sub> complexes and in stibnite chains

	Fülöppite	Stibnite		
Sb(1)	2∙479 Å	Sb(1)	2·521 Å	
	2.525		<b>2</b> ·539	
	3.041		3.111	
Sb(3)	2.480	Sb(2)	<b>2</b> ·455	
	2.682		<b>2</b> ·678	
	2.855		2.854	

The second kind of group consists of a string of four SbS<sub>3</sub> polyhedra [two Sb(2) and two Sb(4) atoms] symmetrically arranged about a central twofold rotation axis and a Pb(1) atom. The group has the composition  $PbSb_4S_9$ . Actually the strings include, at either end, the Sb(1) atoms of the groups of the first kind linked by an Sb-S bond of length 2.560 Å. If the concept of the group is expanded to include the Sb(1) atoms and their coordinating S atoms, the group is comprised of all the trivalent Sb atoms and their three closest S neighbours and has the composition  $PbSb_6S_{13}$ . Sb(1)links the two kinds of group by being a part of both. Pb(2) forms another type of link between the two groups and between groups of the second kind. Pb(1) is the only other metal atom that plays an important role in binding groups of the second kind.

A discussion of the relation between the structure of fülöppite and the structures of plagionite and semseyite must necessarily wait on the publication of more complete accounts than are now available in the literature.

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#### References

- BAYLISS, P. & NOWACKI, W. (1972). Z. Kristallogr. 135, 308-315.
- Cho, S.-A. & WUENSCH, B. J. (1970). Nature, Lond. 225, 444-445.
- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). Acta Cryst. 18, 1035–1038.
- CROMER, D. T. & LIBERMAN, D. (1970). J. Chem. Phys. 53, 1891–1898.
- CROMER, D. T. & MANN, J. B. (1968). Acta Cryst. A24, 321-324.
- DANA, J. D. & DANA, E. S. (1944). System of Mineralogy, Vol. 1, 7th ed., p. 466. Edited by C. PALACHE, H. BER-MAN & C. FRONDEL. New York: John Wiley.
- DREW, M. & LARSON, A. C. (1968). TANFOR: a Program for Investigating Phase Relationships in Centrosymmetric and Non-centrosymmetric Crystals (2nd version extensively modified by S. MOTHERWELL). Lawrence Radiation Laboratory, Berkeley, California.
- ELLISON, R. D. (1962). XFLS: an Extensively Modified Version of ORFLS. Oak Ridge National Laboratory Report ORNL-TM-305.
- EVANS, R. C. (1964). Crystal Chemistry, 2nd ed. Cambridge Univ. Press.
- FAWCETT, J. K. (1970). DATRED: a Universal Data Reduction and Absorption Program. Univ. of Toronto, Canada (unpublished).
- JAMBOR, J. L. (1969). Miner. Mag. 37, 442-446.
- JONG, W. F. DE (1959). *General Crystallography*, p. 68. San Francisco: Freeman.
- KOHATSU, J. J. & WUENSCH, B. J. (1974). ACA Berkeley Program and Abstracts, Paper B6.
- Nuffield, E. W. (1946). Univ. Toronto Geol. Ser. 50, 49-62.
- NUFFIELD, E. W. & PEACOCK, M. A. (1945). Univ. Toronto Geol. Ser. 49, 17–39.
- RYLARSDAAM, J. C. (1970). BONDLA: a Bond Length and Angle Program. Univ. of Toronto, Canada (unpublished).