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-Analogon zu Freieslebenit, isomorph. Die Daten sind: Raumgruppe $P2_1/a$ mit $a = 7,518(1)$, $b = 12,809(4)$, $c = 5,940(1)$ Å, $\beta = 92,25(1)°$ 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, $\beta = 92.25(1)°$ 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 et al. (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)°	92°14′	—	91°13.7′(2)	90°
V	571.57			549.56	625.6 Å^3

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

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 ($a = 5.43074$ Å) were used for calibration. The wave length used was 1.54051 Å for $CuK\alpha_1$ 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), $Pb_4Ag_4Sb_4S_{12}$, 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, $d_x = 6.194$ g $\cdot$ cm^{-3}, is in good agreement with the observed value, $d_m = 6.20$ g $\cdot$ 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 $CuK\alpha$ 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-

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[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 Cu$K\alpha$) effects. Extinction effects were ignored because no systematic discrepancies between F_0 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:

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

	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. *Observed and calculated structure factors*

Column headings throughout: h | |Fo| | Fc

Column 1

```
h 0 0
2  145 -135
4  522 -525
6  215  208
8  196  187

h 1 0
1   64   54
2   81   75
3  117 -111
4   98  -95
5   57   55
6   31  -32
7   54   50
8   88   84
9   73  -73

h 2 0
0   79   55
1   84   77
2   67  -59
3   30  -21
4   35  -34
5   65  -68
6   92   92
7   74   75
9    9    5

h 3 0
1   53   41
2  675  669
3   45  -41
4  184 -180
5   19  -15
6  306 -304
7   25   24
8  174  170

h 4 0
0  121 -107
1  130  116
2   65   59
3   71   72
5   96  -97
6  223 -215
7   68   67
8   23  -22

h 5 0
1   23  -26
2   34   35
3   72   72
4   78  -77
5   53  -52
7   27  -25
8   74   70

h 6 0
0  530 -539
1   66   62
2   93   86
3   38   38
4  375  364
5   51  -49
6  153 -151
7   14  -12
8  145 -136

h 7 0
1   62  -59
2  101 -100
3  108  106
4   83   80
5   31  -32
6   50   50
7   64  -62
8   81  -76

h 8 0
0   42  -42
1   57  -56
2   40   40
4   22   26
5   49   47
6   71  -70
7   53  -51

h 9 0
1   50  -49
2  326 -317
3   59   55
4   95   94
5   26   25
6  169  164
7   41  -39

h 10 0
0   98   99
1   67  -67
```

Column 2

```
2   40  -39
4   71  -72
5   66   66
6   72   72
7   42  -42

h 11 0
1   27   28
2   41  -43
3   55  -53
4   51   52
5   24   24
6   17   17

h 12 0
0  216  212
1   40  -42
2   34  -35
3   29  -30
4  157 -154
5   39   38

h 13 0
1   16   17
2   76   78
3   36  -39
4   51  -51
5   22   23

h 14 0
0   49   47
1   39   39
2   24  -23
4   32  -33

h 15 0
1   26   26

h 0 1
-8  104 -107
-6  186  194
-4  109  116
-2  458 -451
 2  472  462
 4  128 -125
 6  223 -215
 8  110  109

h 1 1
-8   23  -23
-7   64  -65
-6   91  -94
-5   47   55
-4   59   62
-3   34   30
-2   63   61
-1   83  -73
 0  101  -83
 1   45   43
 2   61   55
 3   45   48
 5   48  -50
 6   94  -90
 7   50   49
 9    7    4

h 2 1
-9   52   54
-8   76  -78
-7   53  -55
-6   28   32
-5   31  -33
-4   97   97
-3  117  118
-2   61  -61
-1   73  -67
 0   28  -28
 1   86  -77
 2   60   57
 3  112  114
 4   58  -59
 5   30  -30
 6   25  -27
 7   56  -55
 8   67   65
 9   54   53

h 3 1
-8  101 -100
-7   24   23
-6  120 -126
-4  317  314
-3   34  -33
-2   75   71
-1   28   20
 0  512 -495
 1   33   29
 2   79   79
 4  325  331
 6  122 -125
```

Column 3

```
8  128 -120

h 4 1
-8   83   84
-6   47  -49
-5   67  -67
-4   95  -92
-2   99   95
-1   45   33
 2   84  -84
 4   91   90
 5   45  -45
 6   31   32
 8   87  -86

h 5 1
-7   35   35
-6   88  -90
-5  101 -102
-4   31   34
-3   44   42
-2   90   84
-1  121  118
 0   48  -50
 1  141 -142
 3   15  -12
 4   35   40
 5  110  111
 6   45  -44
 7   58  -56
 8   16  -17

h 6 1
-8  107  110
-6  183 -184
-5   44   43
-4  117 -115
-2  405  390
-1   50  -48
 1   22   19
 2  392 -399
 3   32   31
 4  105  106
 5   14  -13
 6  207  204
 7   17  -15
 8  104 -102

h 7 1
-8   27   26
-7   62   62
-6   99  101
-4   83  -82
-3   64  -56
-2   67  -66
-1   23  -14
 0  110  114
 1   29   22
 2   42  -43
 3   44   42
 4   72  -74
 6   90   89
 7   54  -53
 8   20   19

h 8 1
-7   65   63
-4   87  -84
-3  108 -103
-2   26   30
-1  106  104
 0   50   50
 1   49   49
 2   32  -36
 3  135 -135
 5   40   41
 6   23   24
 7   75   70

h 9 1
-7   36  -36
-6  113  116
-4  254 -252
-3   48   45
-2   68  -67
 9   54   53
 0  345  360
 1   39  -40
 2   49  -50
 4  265 -266
 5   25   25
 6  102  102

h 10 1
-7   23  -24
-5   50   51
-5   53   53
-4   99   98
-2  108 -108
-1   36  -32
 0   26  -25
```

Column 4

```
1   34  -30
2  105  109
4   58  -58
5   49   49
6   53  -54

h 11 1
-6   58   58
-5   69   66
-4   13   -9
-3   52  -50
-2   59  -56
-1   61  -60
 0   18   20
 1  108  110
 2   19   18
 4   16  -19
 5   91  -89
 6   15   11

h 12 1
-5   31  -32
-4   85   86
-3   14  -12
-2  258 -258
-1   33   33
 1   13   13
 2  256  263
 3   28  -28
 4   72  -73
 5   13  -13

h 13 1
-5    9   -6
-4   74   75
-3   29   29
-2   67   67
 0  108 -109
 1   11   -4
 2   10    9
 3   29  -30
 4   82   83

h 14 1
-4   39   40
-3   49   46
-1   61  -60
 0   25  -24
 1   15  -13
 2   11    9
 3   78   77

h 15 1
-2   38   37
-1   24  -22
 0  206 -203
 1   22   20
 2   32   32

h 0 2
-8  135 -136
-6  164 -177
-4  379  398
-2   92   91
 0  605 -625
 2  116  116
 4  400  405
 6  173 -172
 8  152 -149

h 1 2
-8  127  131
-7   46  -48
-6   14  -16
-4  189 -196
-3   77   84
-2   72   73
-1  133 -120
 0  184  165
 2   91  -95
 3  142  147
 4   24  -22
 5   82  -81
 6   55   56
 7   69  -68
 8   31  -28

h 2 2
-7   27   30
-6  143 -150
-5   64  -70
-4   47   50
-3   54   54
-2  177  165
-1   62   60
 0   98  -93
 1  153 -153
 2   56  -54
 3   44   42
 4   62   69
```

Column 5

```
5  108  110
6   33  -32
7   91  -91
8   24  -26

h 3 2
-8  143  150
-7   21  -23
-6  228 -236
-4  143 -146
-3   49   44
-2  502  504
 0   17  -17
 1   57  -52
 2  467 -506
 4  150  155
 5   31   31
 6  248  247
 7   13  -11
 8  140 -141

h 4 2
-7   35   36
-6  156  162
-5   66  -69
-4   42  -46
-3   37   34
-1   62   62
 0   92   93
 1  123 -122
 2   84   82
 3   31   33
 4   74  -80
 5   93   95
 7   84  -84
 8   37   37

h 5 2
-8   90   94
-7   36   36
-6   35  -35
-4  118 -120
-3   74  -75
-2   79   78
-1   86   85
 0   62   60
 1   21   21
 2   69  -76
 3  109 -117
 4   32   33
 5   59   59
 6   31   33
 7   58   55
 8   52  -52

h 6 2
-8  106  108
-7   18   19
-6  130  135
-5   52  -52
-4  308 -302
-2   65  -65
-1   77   74
 0  435  443
 2   85  -87
 3   60  -59
 4  304 -312
 5   22   20
 6  141  137
 7   34   33

h 7 2
-7   36   38
-6   26   28
-5   24   25
-4  144  143
-3   64  -66
-2   77  -79
-1   48   47
 0   99  -98
 1   20   22
 2   84   89
 3   79  -83
 5   47   49
 6   52  -52
 7   43   43

h 8 2
-7   36  -37
-6   76   78
-5   49   50
-4   59  -60
-3   15  -12
-2   55  -53
-1   55  -55
 0   69   74
 1   73   77
 2   23  -23
 4   39  -42
```

Column 6

```
5   64  -65
6   61   61
7   51   50

h 9 2
-7   40   41
-6  144  145
-4   89   88
-3   66  -63
-2  293 -288
-1   16   15
 1   62   62
 2  288  296
 3   27  -27
 4   92  -94
 5   40  -41
 6  168 -162

h 10 2
-6   87  -92
-5   38   41
-4   60   62
-3   12   11
-2   80   79
-1   37  -41
 0   82  -87
 1   36   39
 2   13  -10
 4   61   63
 5   40  -40
 6   36  -35

h 11 2
-6   34   37
-5   23  -23
-4   46   45
-3   48   47
-2   58  -60
-1   30  -26
 1   27  -25
 2   45   48
 3   49   51
 4   48  -49
 5   22  -21

h 12 2
-5   40   42
-4  148  148
-3   40  -43
-2  122 -119
-2   42   41
-1   47  -46
 0  214 -213
 1   31   31
 2   33   33
 3   34   34
 4  166  166
 5   30  -30

h 13 2
-5   50  -55
-3   26   28
-2   76   75
-2   12   12
 1   13  -12
 2   68  -69
 3   17   20
 4   33   35

h 14 2
-2   15   15
-1   29   27
 0   40  -41
 1   29  -29
 2   22   22

h 15 2
 0   13   13

h 0 3
-8  119  123
-6  164 -171
-4  118 -129
-2  367  384
 2  391 -409
 4  107  104
 6  230  223
 8  102 -102

h 1 3
-8   25   27
-7   55   56
-6   97  100
-5   23  -27
-4   63  -70
-3   30  -27
-2   95  -98
-2   93   93
-1   41  -41
 0  133 -134
 1   22   24
 4   88   92
```

Column 7

```
3   17   16
4   56  -60
5   36   38
6   47   45
7   52  -51
8   15   16

h 2 3
-8   72   73
-7   12    9
-6   19  -21
-5   28   29
-4  105 -110
-3   38  -38
-2   43   48
-1   35   34
 0   87   80
 2   41  -49
 3   60  -65
 5   57   56
 6   22   23
 7   29   26
 8   29  -27

h 3 3
-8   81   81
-7   27  -28
-6  127  134
-4  257 -261
-3   37   37
-2   81  -81
-1   15  -15
 0  410  407
 1   32  -31
 2   52  -55
 3   13   15
 4  287 -303
 5   16   16
 6  108  107
 7   10   -9
 8  131  132

h 4 3
-8   85  -89
-6   60   65
-5   53   54
-4  109  111
-3   40  -43
-2   79   79
 0   52  -51
 1   22   23
 2  105  110
 3   32  -38
 4   40  -39
 5   25   27
 6   50  -50
 7   20   20

h 5 3
-7   17  -18
-6   86   -7
-2  167  167
-5   31   33
-3   32  -35
-2  110 -109
 0   24   25
 1   91   93
 2   60   57
 3   44  -46
 4   21  -23
 5   66  -67
 7   79   77

h 6 3
-6  130  135
-5   50  -50
-4  109  111
-3   18   15
-2  294 -295
-1   50   50
 0   18  -16
 1   27  -22
 2  312  317
 3   32  -32
 4   83  -79
 6  187 -181
 7   15   16

h 7 3
-7   50  -51
-6  107 -113
-5   27   29
-4   97  101
-3   28   27
-2   93   93
-1   41  -41
 0  133 -134
 1   22   24
 4   88   92
```

Column 8

```
4   29   27
5   55   56
6   58  -59
7   66   66

h 2 4
-7   11  -10
-6  137  141
-5   80   85
-4   78  -83
-3   69  -67
-2  151 -145
-1   76  -75
 0  122  123
 1  138  143
 2   59   60
 4   88  -92
 5  113 -114
 6   14   15
 7   66   67

h 3 4
-7   12   11
-6  129  125
-4   92   97
-3   15  -14
-2  283 -272
 0   17   13
 1   11   11
 2  268  282
 3   13   -9
 6  155 -149
 7    7    7

h 4 4
-7   22  -22
-6  131 -132
-5   43   46
-4   48   50
-3   31  -31
-2  153  145
-1   34  -35
 0   84  -88
 1   88   89
 2   75  -73
 3   31  -32
 4   68   70
 5   73  -72
 7   72   70

h 5 4
-7   52  -53
-6   58   60
-5   21   20
-4  131  129
-3   85   82
-2  116 -113
-1  106 -103
 0   83  -81
 1   31  -32
 2  103  111
 3  120  127
 4   45  -43
 6   59  -59

h 6 4
-6  108 -111
-5   24   24
-4  192  186
-3   16  -12
-2   57   57
 1   20  -22
 2   21   20

h 0 4
-6  110  114
-4  202 -208
-2   45  -48
 0  310  313
 2   76  -79
 4  222 -224
 6  117  115

h 7 4
-6   21  -21
-5   16  -16
-4  124 -122
-3   21   22
-2   62   63
-1   30  -30
 0   96   93
 2   68  -72
 3   49   51
 4   27  -24
 5   54  -54
 6   42   42

h 8 4
 0  130 -124
 1   20   23
 2   94  103
 3  121 -126
```

Table 5. *(Continued)*

Column 1:

h	$|F_o|$	F_c
-2	85	79
-1	46	44
0	98	-99
1	91	-94
2	20	-17
3	16	14
4	65	68
5	78	77
h 9 4		
-5	11	11
-4	91	-92
-3	34	32
-2	217	208
-1	24	-24
0	15	15
1	26	-24
2	220	-224
3	25	27
4	63	61
5	13	12
h 10 4		
-4	41	-43
-3	14	-11
-2	88	-86
0	65	68
1	19	-20
2	39	38
3	28	30
4	52	-53

Column 2:

h	$|F_o|$	F_c
h 11 4		
-4	55	-57
-3	26	-24
-2	63	63
-1	45	46
0	28	27
2	53	-55
3	58	-59
h 12 4		
-2	57	-58
-1	30	29
0	179	180
1	29	-30
2	11	-10
h 0 5		
-6	107	102
-4	126	129
-2	240	-233
0	48	-46
2	244	263
4	50	-46
6	170	-164
h 1 5		
-6	112	-109
-5	13	9
-4	43	45
-3	14	-13

Column 3:

h	$|F_o|$	F_c
-2	126	126
0	76	-79
1	52	56
2	69	-73
3	33	-33
4	62	65
5	48	-48
6	13	13
h 2 5		
-6	12	7
-4	107	107
-2	43	-40
-1	46	-49
0	95	-97
1	33	31
2	46	51
3	62	62
4	41	40
5	65	-66
6	31	-32
h 3 5		
-6	126	-124
-4	162	158
-2	87	90
0	248	-251
4	211	206
6	66	-62

Column 4:

h	$|F_o|$	F_c
h 4 5		
-6	40	-40
-5	18	-17
-4	136	-129
-3	38	36
-2	94	91
-1	29	-29
0	102	99
2	94	-98
3	55	57
4	30	-28
5	29	-28
6	59	58
h 5 5		
-6	72	-68
-3	40	36
-2	89	86
-1	18	-14
0	25	-30
1	69	-70
2	58	-56
3	57	56
4	27	26
5	54	50
h 6 5		
-4	97	-97
-2	185	178
0	30	30

Column 5:

h	$|F_o|$	F_c
2	197	-201
3	12	-12
4	46	43
5	17	17
h 7 5		
-5	42	-41
-4	78	-80
-2	108	-105
-1	50	49
0	110	111
1	44	-43
2	43	44
3	13	-12
4	86	-84
5	50	49
h 8 5		
-4	66	-61
-3	11	-8
-2	19	19
-1	66	63
0	57	54
1	26	-26
2	22	-24
3	72	-70
4	24	-21
h 9 5		
-4	101	-96
-3	8	-7

Column 6:

h	$|F_o|$	F_c
-2	50	-50
0	158	153
1	13	14
2	15	-14
3	10	-11
h 10 5		
-3	51	-51
-2	94	-98
-1	16	17
0	54	-54
1	38	37
2	93	95
h 0 6		
-4	122	115
-2	47	46
0	175	-174
2	39	35
4	142	135
h 1 6		
-4	91	-87
-3	54	53
-2	92	94
-1	59	-59
0	56	54
1	17	-17
2	91	-91
3	81	78

Column 7:

h	$|F_o|$	F_c
h 2 6		
-5	52	-52
-4	75	77
-3	41	40
-2	87	82
-1	44	43
0	98	-101
1	82	-86
2	32	-30
3	13	13
4	74	72
h 3 6		
-5	23	23
-4	79	-79
-2	154	149
-1	30	-28
0	11	10
2	164	-162
3	20	21
4	58	54
h 4 6		
-4	64	-65
-3	24	23
-2	74	-73
-1	31	30
0	86	88
1	63	-63
2	30	27
-2	73	-71

Column 8:

h	$|F_o|$	F_c
3	18	16
4	66	-65
h 5 6		
-4	94	-90
-3	45	-44
-2	83	84
-1	75	73
0	64	61
1	11	8
2	82	-82
3	87	-85
h 6 6		
-4	105	-97
-3	42	41
-2	59	-59
0	157	154
1	40	-39
2	17	-13
3	14	14
h 7 6		
-3	24	-25
-2	63	-64
-1	35	35
0	57	-56
2	68	69

Column 9:

h	$|F_o|$	F_c
-1	15	-14
0	67	68
1	79	79
h 0 7		
-2	94	89
0	44	47
2	119	-113
h 1 7		
-2	98	-98
-1	12	13
0	52	52
1	60	-59
2	69	67
h 2 7		
-2	36	38
-1	54	55
0	78	77
h 3 7		
-2	67	-70
0	114	108
1	23	23
h 4 7		
-1	34	34
0	82	-80

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 $9^0/_0$. Additional several cycles of anisotropic refinement reduced R to the final value of $3.2^0/_0$. The atomic scattering factors for the neutral atoms were used[2]. 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 marrite, $PbAgAsS_3$ (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 marrite 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-

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]	bournonite[6]	$PbCuXS_3$
VI.	arsenopyrite[7]	gudmundite[8]	$FeXS$
VI.	gersdorffite[9]	ullmannite[10]	$NiXS$

[1] WUENSCH *et al.* (1966).

[2] WUENSCH (1964).

[3] WUENSCH and NOWACKI (1967).

[4] Present work.

[5] ENGEL and NOWACKI (1966).

[6] HELLNER and LEINEWEBER (1956).

[7] BUERGER (1936).

[8] BUERGER (1939).

[9] BAYLISS and STEPHENSON (1967).

[10] TAKÉUCHI (1957).

[*] Classification of sulfosalts by NOWACKI (1969).

[**] X = As or Sb.

MANN, 1933b). 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, $Pb_2Bi_2S_5$ (SRIKRISH-NAN 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 (ŠĆAVNIČAR, 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).

(a)

(b)

(c)
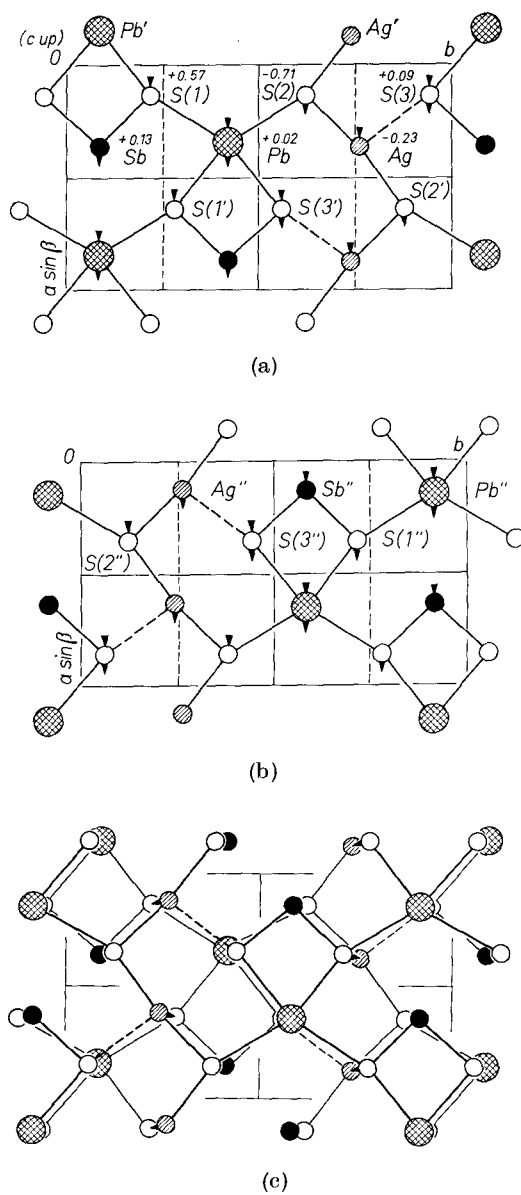
Fig. 1. Atomic arrangements in freieslebenite, viewed along the c axis: (a) the atomic layer at $z \approx 1/4$ and (b) at $z \approx 3/4$, and (c) $= (a) + (b)$, i.e. the whole structure. The thick broken lines indicate the longest Ag—S bonds, the black arrowheads indicate the bonds between the adjacent 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	Δ_F/Δ_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 $10^0/_0$ ($13^0/_0$) 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:

$$
\begin{array}{c}
\text{—Pb—S——Pb—S—} \\
|\quad\ |\quad\ |\quad\ | \\
\text{—S——Pb—S——Pb—} \ .
\end{array}
$$
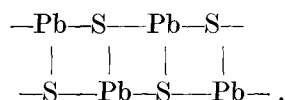
The Pb-S double chains seem to serve as backbones of the structure; the surrounding Ag-S and Sb-S arrays connect adjacent Pb-S

[3] Unless otherwise stated, the atomic radii used in the discussion are all taken from PAULING (1960).
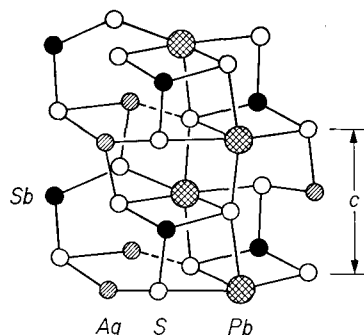
Fig. 2. Network of metal-sulfur bonds in freieslebenite
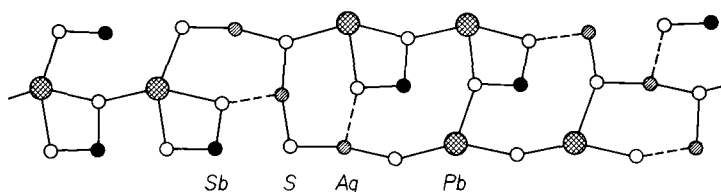
Fig. 3. Structure of the metal-sulfur array along [320] within each layer in
freieslebenite

double chains and fill in the space between them as shown in Figs. 1 c
and 2.

Figure 3 shows the structure of the metal-S array along [320]
within each layer parallel to (001). The array is of a mixed-metal type
contrary to those along the c direction; the six pairs of metal—S,
2(Pb—S, Ag—S and Sb—S), constitute the unit of repetition. There are
no infinite metal-S chains like the Pb-S chains along the c direction,
because the two Sb and one of the two Ag terminate the chain.

Bond distances and angles

The bond distances and angles in freieslebenite and marrite
(WUENSCH and NOWACKI, 1967) are compared in Tables 8 and 9,
respectively; they are in fairly good agreement with each other except
those associated with Sb or As. The coordination around the individual
atoms are shown in Fig. 4.

Sb has the usual trigonal-pyramidal coordination of S atoms.
The three Sb—S distances are 2.431, 2.453 and 2.480(4) Å. The mean
value, 2.46 Å, is in good agreement with the covalent Sb—S distance
(2.45 Å) and also with those found in some sulfosalts of the II.a$_1$ type:
2.46, 2.46 and 2.463 Å in bournonite, PbCuSbS$_3$ (EDENHARTER,

Table 8. *Bond distances in freieslebenite and marrite*

X = Sb or As for freieslebenite or marrite, respectively. Notation of the symmetry operations: single primed . . . a glide; double or triple primed . . . 2_1 screw

	Freies-lebenite	Marrite		Freies-lebenite	Marrite
X—S(2″)	2.431 Å	2.259 Å	S(1)—X	2.453 Å	2.279 Å
—S(1)	2.453	2.279	—Ag‴	2.687	2.682
—S(3)	2.480	2.269	—Pb′	2.806	2.837
Mean	(2.455)	(2.269)	—Pb	3.033	2.962
Pb—S(1′)	2.806	2.837	S(2)—X″	2.431	2.259
—S(3‴)	2.877	2.799	—Ag′	2.522	2.473
—S(3′)	2.892	2.976	—Ag	2.575	2.518
—S(1)	3.033	2.962	—Pb	3.167	3.136
Mean(4)	(2.902)	(2.894)			
Pb—S(3″)	3.102	3.260	S(3)—X	2.480	2.269
—S(2)	3.167	3.136	—Pb‴	2.877	2.799
Mean(2)	(3.135)	(3.198)	—Pb′	2.892	2.976
Mean(6)	(2.980)	(2.995)	—Ag	2.928	2.912
			—Pb″	3.102	3.260
Ag—S(2′)	2.522	2.473			
—S(2)	2.575	2.518	σ	≈ 0.004	≈ 0.014
Mean(2)	(2.549)	(2.496)			
Ag—S(1‴)	2.687	2.682			
Mean(3)	(2.595)	(2.558)			
Ag—S(3)	2.928	2.912			
Mean(4)	(2.678)	(2.646)			
σ	≈ 0.004	≈ 0.014			

NOWACKI and TAKÉUCHI, 1970), pyrostilpnite, Ag_3SbS_3 (KUTOGLU, 1968) and pyrargyrite, Ag_3SbS_3 (ENGEL and NOWACKI, 1966), respectively. The other three S atoms around Sb are far apart; the Sb—S distances are 3.239, 3.477 and 3.576(4) Å.
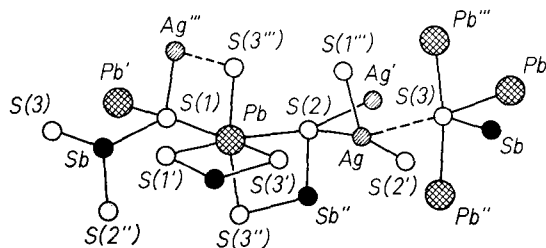
Fig. 4. Coordinations around the individual atoms in freieslebenite

Table 9. *Bond angles in freieslebenite and marrite*
(X = Sb or As respectively)

	Freieslebenite	Marrite
S(2″) —X　S(1)	94.5°	97.9°
—S(3)	98.5	99.3
S(1)　—X　—S(3)	93.3	97.3
Mean	(95.4)	(98.2)
S(1′)　—Pb—S(3‴)	84.4	81.3
—S(3′)	78.1	71.9
—S(1)	82.2	80.4
—S(3″)	103.1	110.0
—S(2)	160.1	—
S(3‴)—Pb—S(3′)	85.7	81.8
—S(1)	84.3	82.4
—S(3″)	166.9	—
—S(2)	96.5	98.3
S(3′)　—Pb—S(1)	158.6	—
—S(3″)	85.5	88.5
—S(2)	82.2	81.4
S(1)　—Pb—S(3″)	107.1	112.6
—S(2)	117.7	126.4
S(3″) —Pb—S(2)	72.8	65.3
S(2′)　—Ag—S(2)	157.3	152.7
—S(1‴)	111.6	116.0
S(2)　—Ag—S(1‴)	89.5	88.5
Sum	(358.4)	(357.2)
S(3)　—Ag—S(2′)	90.1	91.1
—S(2)	98.6	103.4
—S(1‴)	89.8	85.3
σ	≈ 0.1	≈ 0.3

The mean S—Sb—S bond angle and S···S contact distance in the SbS$_3$ pyramid are 95° and 3.63 Å, respectively; the corresponding values in the AsS$_3$ pyramid of marrite are 98° and 3.43 Å. If we consider an ideal model of XS$_3$ pyramids (X = As, Sb and Bi) in which S—X—S = 90° (p^3) and S...S = 3.70 Å (van der Waals distance), both the angle and the distance in the SbS$_3$ pyramid of freieslebenite are nearer to the ideal values than those in the AsS$_3$ pyramid of marrite.

Pb is coordinated with six S atoms in a distorted octahedral arrangement. The six Pb—S distances range from 2.806 to 3.167(4) Å; these values (the mean 2.98 Å) are quite normal for Pb with the coordi-

nation number of six (NOWACKI, 1969). If we look at them more closely, however, the six Pb—S distances can be grouped into the four shorter (the mean 2.90 Å) and the two longer (the mean 3.14 Å). The latter two, 3.102 and 3.167(4) Å, are longer than the sum (3.04 Å) of the ionic radii of Pb^{2+} and S^{2-}. Therefore, these two Pb—S bonds are very weak bonds. It is interesting to note that this 4 + 2 coordination of S around Pb (in a more exaggerated form) is quite common among Pb salts of dithioacids, a quite different class of compounds from sulfosalts (IWASAKI and HAGIHARA, 1972; ITO, 1972). The two smallest S—Pb—S angles, 72.8 and 78.1° (65.3 and 71.9° in marrite), belong to the two four-membered chelate rings around Pb, $X\diagdown_S^S\diagup Pb$ (X = Sb or As).

The smallest angle is also associated with the two longer Pb—S distances mentioned above.

Ag has three nearest S neighbours at the distances, 2.522, 2.575 and 2.687(4) Å. The AgS_3 group is almost planar; the sum of the three angles is 358.4°. A fourth S atom is at a distance of 2.928(4) Å; the corresponding Ag—S bond (shown in the figures with broken lines) is approximately perpendicular to the AgS_3 plane (Table 9). If we apply the PAULING's (1960) relation for fractional bonds, $D(n) = D(1) + 0.60 \log n$, to the four observed Ag—S distances, the corresponding bond numbers are: $n = 0.70$, 0.55, 0.37 and 0.15, respectively[4]. Therefore, the fourth bond (2.928 Å) is a weak bond, although it is shorter than the sum (3.10 Å) of the ionic radii of Ag^+ and S^{2-}.

Very similar 3 + 1 coordinations are also found in smithite, $AgAsS_2$, where Ag(1)—S = 2.51, 2.56, 2.68 and 2.84 Å, Ag(2)—S = 2.52, 2.55, 2.65 and 2.90 Å (HELLNER and BURZLAFF, 1964) and in hatchite, $PbTlAgAs_2S_5$, where Ag—S = 2.48, 2.52, 2.54 and 2.93 Å (MARUMO and NOWACKI, 1967). The other two S atoms around Ag in freieslebnite are far apart; the Ag—S distances are 3.288 and 3.349 Å.

Thermal vibrations

The root-mean-square amplitudes of the atoms along the principal axes of the vibration ellipsoids are given in Table 10. The most interesting feature of the thermal vibrations in freieslebenite is the large amplitudes of Ag compared to those of the other atoms. In fact, this feature is common among sulfosalts containing Ag (Table 11). In these structures the B values of Ag are more than twice as large as those of

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[4] The single bond distance, $D(1)$, of Ag—S was taken as the sum (2.43 Å) of the covalent radius of S (1.04 Å) and that of Ag in linear bonds (1.39 Å).

Table 10. *Root-mean-square amplitudes of the atoms of freieslebenite along the principal axes of the vibration ellipsoids and the direction cosines* $(\times 10^3)$ *of the axes with respect to a, b and c**

	B_{equiv}	B	$\sqrt{\bar{u}^2}$	l	m	n
Sb	1.2 Å²	1.33 Å²	0.130 Å	— 211	581	786
		1.19	0.123	— 220	755	— 617
		1.01	0.113	952	304	32
Pb	1.7	1.95	0.157	100	789	606
		1.74	0.148	— 6	— 609	793
		1.52	0.139	995	— 83	— 56
Ag	2.9	3.91	0.223	690	— 706	— 163
		3.09	0.198	264	35	964
		1.57	0.141	674	708	— 211
S(1)	1.4	2.02	0.160	170	— 172	970
		1.11	0.119	822	— 518	— 236
		0.99	0.112	543	838	53
S(2)	1.4	1.76	0.149	574	808	130
		1.29	0.128	479	— 461	747
		1.04	0.115	664	— 367	— 652
S(3)	1.2	1.56	0.140	467	44	883
		1.16	0.121	— 571	777	263
		0.84	0.103	675	628	— 389

the other atoms; only in miargyrite the differences between them are not significant. This means that the Ag atoms are less tightly bound than the other atoms in these structures.

The observed anisotropy of vibration of Ag in freieslebenite gives us hints for the explanation of the larger amplitudes of the atom. The principal axis with the largest amplitude ($B = 3.91$ Å²) is almost perpendicular ($90° \pm$ ca $8°$) to the AgS$_3$ plane and parallel ($7.9°$) to the weakest bond with Ag—S $= 2.928$ Å. The other two axes lie in the AgS$_3$ plane; the axis with the smallest amplitude ($B = 1.57$ Å²) is parallel ($8.5°$) to the strongest bond with Ag—S $= 2.522$ Å, whereas the third axis with the intermediate amplitude ($B = 3.09$ Å²) is directed between the two remaining bonds but roughly along ($24.0°$) the weaker bond with Ag—S $= 2.687$ Å. In other words, Ag vibrates most out of the AgS$_3$ plane along the weakest Ag—S bond, next along the weaker bond within the plane, and least along the strongest bond.

Table 11. *Temperature factors of the atoms in sulfosalts containing* Ag

Crystal	Atom	B	Crystal	Atom	B
Proustite[1]	Ag	6.1 Å²	Freieslebenite[5]	Ag	2.9
Ag₃AsS₃	As	2.0	PbAgSbS₃	Sb	1.2
	S	2.3		Pb	1.7
				<3S>	1.3
Pyrargyrite[1]	Ag	4.7			
Ag₃SbS₃	Sb	1.1	Hatchite[6]	Ag	4.0
	S	1.2	PbTlAgAs₂S₅	<2As>	2.4
				<5S>	2.8
Xanthoconite[2]	Ag(1)	4.3		(Pb, Tl)	2.6
Ag₃AsS₃	Ag(2)	4.2		(Tl, Pb)	4.2
	Ag(3)	4.6			
	As	2.1	Smithite[7]	Ag(1)	3.1
	<3S>*	2.1	AgAsS₂	Ag(2)	3.9
				Ag(3)	3.4
Pyrostilpnite[3]	Ag(1)	4.6		Ag(4)	3.1
Ag₃SbS₃	Ag(2)	5.6		<3As>	1.0
	Ag(3)	4.3		<6S>	1.4
	Sb	2.9			
	<3S>	3.8	Trechmannite[8]	Ag	2.4
			AgAsS₂	As	1.7
Marrite[4]	Ag	2.4		<2S>	1.4
PbAgAsS₃	As	0.9			
	Pb	1.1	Miargyrite[9]	Ag(1)	1.2
	<3S>	1.2	AgSbS₂	Ag(2)	1.2
				<2Sb>	0.9
				<4S>	1.1

[1] ENGEL and NOWACKI (1966).
[2] ENGEL and NOWACKI (1968).
[3] KUTOGLU (1968).
[4] WUENSCH and NOWACKI (1967).
[5] Present work.

[6] MARUMO and NOWACKI (1967).
[7] HELLNER and BURZLAFF (1964).
[8] MATSUMOTO and NOWACKI (1969).
[9] KNOWLES (1964).

* < > denotes the mean value; for example, <3S> is the mean of the three S atoms.

It should be noted that the least amplitude ($B = 1.57$ Å²) is of the same order of magnitude as those of the other atoms (the mean $B = 1.4$ Å²). It may be concluded from these observations that Ag vibrates more than the other atoms because it is tightly bound only within a plane (or almost linearly) in the structure. The above conclusion seems to be valid also for the other sulfosalts listed in Table 11.

In contrast to the vibration of Ag, that of Sb is quite normal with less anisotropy and less amplitudes. This is probably because that the

SbS_3 pyramid vibrates as an almost rigid unit of a large volume and, therefore, it has less freedom to move in the structure. The observed anisotropies of the three S atoms can, at least qualitatively, be explained by a larger libration of the SbS_3 pyramid around the approximate threefold symmetry axis passing through Sb.

Calculations

The main part of the numerical calculations was performed on the Bull-Gamma 30 S computer and the IBM 370/155 computer at Rechenzentrum der Universität Bern with the program system, "Kristallographische Programme, 1970 and 1972" written by P. ENGEL (Bern).

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