THE CRYSTAL STRUCTURE OF ARGENTIAN PENTLANDITE (Fe,Ni)$_8$AgS$_8$, COMPARED WITH THE REFINED STRUCTURE OF PENTLANDITE (Fe,Ni)$_9$S$_8$*.

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ABSTRACT

The crystal structure of argentian pentlandite (Fe,Ni)$_8$ AgS$_8$ has been determined by single crystal x-ray diffraction methods. The crystal data are: $a = 10.521(3)$Å, $Z = 4$, space group is $Fm3m$, and the composition is (Fe$_{4.83}$Ni$_{3.17}$)Ag$_{0.99}$S$_{8.00}$. The crystal structure of a natural pentlandite (Fe,Ni,Co)$_9$S$_8$ has been refined using single crystal data. The crystal data are: $a = 10.044(3)$Å, $Z = 4$, space group is $Fm3m$, and the composition is (Fe$_{4.15}$Ni$_{4.74}$Co$_{0.15}$) S$_{8.00}$.

Multiple data sets were collected with a 4-circle diffractometer using MoKα radiation and a graphite monochromator. Generalized Gaussian and spherical absorption corrections were applied and the structures were refined by means of full-matrix least-squares procedures. Final R-values for argentian pentlandite are 0.109 (all data) and 0.039 (obs. data only) and, for pentlandite are 0.047 (all data) and 0.040 (obs. data only). There is strong structural and compositional evidence that the octahedrally-coordinated sites in argentian pentlandite are occupied exclusively by Ag atoms. Placement of the Ag atoms at the 4b sites, and (Fe,Ni) atoms at the 32f sites, gives interatomic distances of Ag — S = 2.676(2)Å, (Fe,Ni) — S = 2.264(2), 2.243(2)Å, and (Fe,Ni) — (Fe,Ni) = 2.670(2)Å. The corresponding distances in pentlandite are (Fe,Ni) — S = 2.382(2)Å, (Fe,Ni) — S = 2.257(2), 2.156(1)Å, and (Fe,Ni) — (Fe,Ni) = 2.533(2)Å.

INTRODUCTION

The occurrence of argentian pentlandite in the Ore Fault claims of the Bird River Mines, Manitoba, has been described by Scott & Gasparrini (1973) in a preceding paper. The crystal used in this analysis was supplied by Dr. D. C. Harris of this laboratory, who investigated samples from the Ore Fault claims after the preliminary reports by Scott & Gasparrini. The polished section of argentian pentlandite has been deposited with the Royal Ontario Museum (ROM M32672). The compositions obtained from electron probe measurements agree closely with those of Scott & Gasparrini (1973) and are consistent stoichiometrically with the proposal of Shishkin *et al.*

(1971) that the Ag atoms in argentian pentlandite occupy the octahedrally-coordinated site in a pentlandite-type structure. The structures of pentlandite (Fe,Ni)$_9$S$_8$ and Co$_9$S$_8$ were determined as being isostructural by Lindqvist *et al.* (1936) by means of powder data. These structures were confirmed subsequently by Pearson & Buerger (1956) and by Geller (1962) with single-crystal methods. Although the basic $Fm3m$ pentlandite-type structure appeared well substantiated (Fig. 1), the precision of the atomic coordinates determined by Lindqvist *et al.* (1936) was not high by present-day standards and it was desirable to obtain more precise values in order to make a suitable comparison with the argentian pentlandite structure.

It has long been assumed by workers in this area that the reason why the pentlandite structure had not been refined was due to the microcrystallinity of this mineral. It was therefore surprising that an examination of a −65 to +100
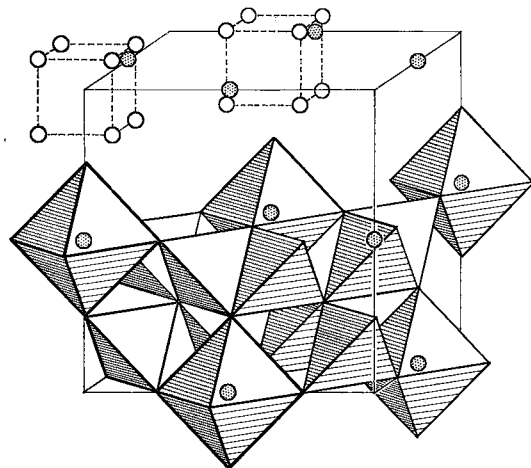

FIG. 1. A crystal cell model of a pentlandite-like structure, showing the octahedral and tetrahedral coordination of sulphur atoms about metal atoms. Also shown are the close approach distances of the 32f metal atoms which form a "cubic" arrangement. The 4b metal atoms are dotted. (Based on a figure of Hulliger 1968).

mesh concentrate of pentlandite, prepared for neutron diffraction studies from a hand specimen obtained from the Geological Survey of Canada, showed that virtually all fragments were single crystals. A few milligrams of this concentrate have been deposited with the Royal Ontario Museum collection (ROM M32676). The composition of this material was consistent for the twelve grains analyzed by electron probe methods (Table 1). The crystal structure was therefore refined to provide a basis for comparison with the argentian pentlandite structure. It was subsequently learned, at a conference where the preliminary results of this analysis were being presented (Hall & Stewart 1973a), that other workers (Rajamani & Prewitt 1973a) had also refined the structure of a natural pentlandite from the same area. It was agreed that these independent analyses should be published together to facilitate ready comparison. Our analyses of argentian pentlandite and pentlandite were therefore amalgamated in this article and the work of Rajamani & Prewitt (1973b) on two pentlandite structures appears in the following paper of this issue.

EXPERIMENTAL

Argentian pentlandite

A crystal fragment of argentian pentlandite, approximately $0.02 \times 0.08 \times 0.12$ mm, was examined to ensure a single phase by means of a Gandolfi x-ray camera. Several levels of reciprocal space were surveyed by means of precession camera techniques and these showed the crystal to be single and untwinned. The observed systematic absences, $h + k, h + l = 2n + 1$, satisfy the requirements of the space groups $Fm3m$, $F\bar{4}3m$, and $F432$. However, if it is assumed that the site occupancies in this structure approach unity, the atoms in pentlandite must occupy only certain equivalent sites, and these are the same for the space groups $Fm3m$ and $F432$. The

difference between the centric space group $Fm3m$ and the acentric space group $F\bar{4}3m$ will be discussed later.

The crystal was mounted in a random orientation on a 4-circle diffractometer and aligned by means of the 12 equivalents of the 12,12,0 reflection. The cell dimensions at room temperature were determined by a least-squares fit of the diffractometer angles 2θ, χ, and ω for these reflections, assuming a triclinic cell. The best fit was obtained for the cell dimensions $a = b = c = 10.521(3)$ Å and $\alpha = \beta = \gamma = 90.00(1)$ Å.

The intensities of an asymmetric set of hkl reflections were measured five times, to a 2θ limit of 120°. All measurements were made on a 4-circle Picker diffractometer, using graphite-monochromatized MoKα radiation and a $\theta/2\theta$ scan rate of two degrees per minute with the width adjusted for dispersion. Background counts were measured for 45 seconds on each side of the peak scan, and intensities of three linearly-independent reflections were recorded every 50 measurements to monitor crystal alignment and instrument stability.

The five independently measured sets of hkl intensity data were merged into a unique set using two different procedures. In the first, a reflection was coded as "observed" if at least three of the five equivalent reflections had net intensities above the 15% significance level, i.e., $I(\text{net}) > 1.4\sigma(I)$. Reflections coded as "unobserved" were set at a threshold intensity of $1.4\sigma(I)$. Using this criterion, 246 of the 509 reflections were considered as "observed" and the average agreement factor

$$\Sigma < \triangle I_{\text{obs}} > / \Sigma < I_{\text{obs}} > \text{ was } 0.015.$$

In the second procedure, all intensities were set at the mean net count, except for negative values which were set at zero. During the averaging process, specific equivalent reflections were excluded from the final mean intensity if they differed from a preliminary mean by more than 1.4 times the RMS deviation. The average agreement factor $\Sigma < \triangle I_{\text{all}} > / \Sigma < I_{\text{all}} >$ for this data set was 0.021.

No a priori corrections were made for secondary extinction and there was no evidence of this effect during subsequent refinement. Both merged data sets were corrected for absorption effects by a generalized Gaussian procedure (Gabe & O'Byrne 1970), and the structure factors were calculated with the application of Lorentz and polarization factors.

Pentlandite

Several fragments from a pentlandite concentrate were ground in a Nonius grinder using

TABLE 1. CRYSTAL DATA FOR ARGENTIAN PENTLANDITE AND PENTLANDITE

	Argentian Pentlandite	Pentlandite
Locality	Ore Fault claims, Bird River Mines, Manitoba	Exact locality unknown Sudbury area, Ontario
Microprobe anal., wt. %	Fe:33.0(5) Ni:22.7(2) Ag:13.1(4) S:31.3(4)	Fe:30.0(3) Ni:36.1(3) Co:1.1(1) S:33.0(3)
Chemical composition	$Fe_{4.83}Ni_{3.17}Ag_{0.99}S_{8.00}$	$Fe_{4.15}Ni_{4.74}Co_{0.15}S_{8.00}$
Space group	$Fm3m$ (No. 225)	$Fm3m$ (No. 225)
Cell dimen.	a=10.521(3)Å	a=10.044(2)Å
Calc. density (Z=4)	4.69 g/cm³	5.08 g/cm³
Linear abs. coefficient μ(MoKα)	139.8 cm⁻¹	161.9 cm⁻¹
Intensity data	509 reflections measured five times	446 reflections measured twice

diamond-impregnated paper. A sphere of radius 0.067 mm was examined on Gandolfi and precession cameras and found to be a single-phase pentlandite crystal. The same procedures used for argentian pentlandite to establish the space group and cell parameters were repeated for this crystal. The cell dimensions were determined as $a = b = c = 10.044(3)$ Å and $\alpha = \beta = \gamma = 90.00(1)$.

Similar procedures to those described for argentian pentlandite were then used to merge and process the two independently measured sets of hkl intensity data. 382 of the 446 reflections were considered as "observed" and the average agreement factor $\Sigma < \triangle I_{obs} > / \Sigma < I_{obs} >$ was 0.016. The average agreement factor $\Sigma < \triangle I_{all} > / \Sigma < I_{all} >$ for all data was 0.017. No a priori corrections were made for secondary extinction but four reflections were excluded during the subsequent refinement process because of this effect. Spherical absorption corrections were applied to both data sets and the structure factors were calculated with the application of Lorentz and polarization factors.

STRUCTURE SOLUTION AND REFINEMENT

Argentian pentlandite

The close similarity of the diffraction patterns of argentian pentlandite and pentlandite indicated that these two minerals were close to being isostructural. Accordingly, the first structure factors were calculated assuming the space group $Fm3m$ with metal atoms at the sites $4b$ $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and $32f$ $(.125,.125,.125)$ and with sulphur atoms at the sites $8c$ $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and $24e$ $(.25,0,0)$. The over-all isotropic temperature factor was set at 1.0 Å². The atomic scattering factors used for the metal atoms were averaged from the Fe, Ni, and Ag curves Cromer & Mann (1968), according to the composition. The S scattering curve was taken from the same source. The observed/unobserved data were used for this calculation, and the resulting structure factor agreement R-value $(\Sigma \mid \triangle F_{obs} \mid / \Sigma \mid F_{obs} \mid)$ was 0.29. A subsequent electron-density difference map showed two distinct features: large maxima of up to 110 eÅ⁻³ at the metal $4b$ sites and minima of -38 eÅ⁻³ at the metal $32f$ sites, with a significant shift indicated for the $24e$ sulphur atoms away from the $4b$ sites. These residuals were clearly consistent with the placing of the Ag atoms at the $4b$ sites. Further refinement was continued, therefore, on this basis, although tests for mixed (Ag,Fe,Ni) occupancy were made in the later stages of refinement (discussed below) metal ordering with Ag and (Fe,Ni) atoms occupying the $4b$ and $32f$ sites, respectively, proved eventually to be the correct one.

All calculations used in the analysis were performed on a CDC 6400 computer with the X-RAY system of crystallographic programs (Stewart et al. 1972). A scattering curve with $0.60f(Fe^{2+}) + 0.40f(Ni^{2+})$ was prepared from the values of Cromer & Mann (1968) and the S^{2-} curve of Tomiie & Stam (1958) was used for the sulphur atoms. The average anomalous scattering factors $\triangle f'(Ag) = -1.09e$, $\triangle f''(Ag) = 1.10e$, $\triangle f'(Fe,Ni) = 0.30e$, $\triangle f''(Fe,Ni) = 0.95e$, $\triangle f'(S) = 0.11e$ and $\triangle f''(S) = 0.12e$ (Cromer & Libermann 1970) were also included. Isotropic full-matrix least-squares refinement, employing $F(obs)$ weights derived from the RMS deviation of $I(net)$ during the averaging of the multiple data sets, was applied initially to the observed/unobserved data set. The structural parameters converged in 5 cycles, with an R-value of 0.045. Anisotropic temperature factors were introduced, and a further 3 cycles of least-squares refinement reduced the R-value to 0.041.

While the treatment of data in terms of "observed" and "unobserved" reflections can considerably reduce calculation times, it can also have an unpredictable effect on the refined parameters. Refinement was, therefore, repeated with the second data set where all intensities were set at their average net value. Although this resulted in a higher final R-value of 0.111, the standard deviations of all parameters were significantly smaller.

Before the refinement could be considered complete, it was necessary to determine whether the acentric space group, rather than the centric one, was correct for this structure. To do this, the refinement process was repeated with the space group $F\bar{4}3m$. However, this resulted in a lack of convergence in the thermal parameters for the sulphur $4c(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and $4d(\frac{3}{4},\frac{3}{4},\frac{3}{4})$ sites plus non-positive definite errors in the least-squares calculation for x derivatives of the (Fe, Ni) sites, $16e(x,0,0,)$ and $16e(x,0,0)$. These appeared to be due to least-squares correlation effects (some coefficients were in excess of $+0.9$) between S sites $4c$ and $4d$, and between the two (Fe,Ni) sites in the space group $F\bar{4}3m$. This, in conjunction with successful refinement of the $Fm3m$ structure, was considered to be strong evidence that the crystal structure is centric.

One further test was required in order to establish the occupancy of the metal sites. Further least-squares refinement, in which the population parameters of the Ag and (Fe,Ni) atoms at the $4b$ and $32f$ sites, respectively, were varied within the compositional and symmetry constraints, was now performed. Again, this calculation did not converge due to the high correlation between population parameters and individual tempera-

ture factors, neither of which can be conveniently, or for that matter legitimately, fixed. After several attempts to minimize the correlation effects it was decided to attempt a "bootstrap" process in which various proportions of Ag and (Fe,Ni) atoms were assigned to both the 4b and 32f sites and then the least-squares process was applied in the usual way. The proportions of 0.9 Ag + 0.1 (Fe,Ni) at site 4b and 0.0125 Ag + 0.9875 (Fe,Ni) at site 32f provided a higher final R-value of 0.118. The proportions 0.8 Ag + 0.2 (Fe,Ni) at site 4b, and the remainder in site 32f, further increased the final R-value to 0.127. This cannot be considered a particularly sensitive method of determining occupancies, but it does provide a result which is consistent with the coordination about the metal positions, that is, that the Ag atoms occupy almost exclusively the 4b sites and the (Fe,Ni) atoms the 32f sites.

In the subsequent refinement of pentlandite, it was found that the application of neutral metal form factors, in the final cycle of least-squares refinement, significantly improved the structure factor agreement of the low-angle reflections. A similar improvement was obtained in the refinement of argentian pentlandite, using the scattering curve $0.60f(Fe) + 0.40f(Ni)$. Possible reasons for this are discussed briefly below.

The final atomic parameters are listed in Table 2 and provide R-values of 0.109 (all data) and 0.039 (obs. data only). The final structure factors are listed in Table 3a.

Pentlandite

A similar but more direct refinement process was performed with the two sets of pentlandite data. Using the data set where all reflections were considered at their measured values, a full-matrix least-squares anisotropic refinement was performed. In this calculation, the curve $0.47f (Fe^{2+}) + 0.53f(Ni^{2+})$ was prepared from the values of Cromer & Mann (1968) for the metal atom sites 4b and 32f, and the S^{2-} curve of Tomiie & Stam (1958) was used for the sulphur atom sites 8c and 24e. The least-squares weights for F(obs.) were derived from the RMS deviation of I(net) during the averaging of the two data sets. The average anomalous scattering factors $\triangle f'(Fe,Ni) = 0.29e$, $\triangle f''(Fe,Ni) = 0.99e$, $\triangle f'(S) = 0.11e$, and $\triangle f''(S) = 0.12e$ (Cromer & Libermann 1970) were also included. In four cycles of least-squares refinement, the agreement R-value (all data) was reduced to 0.058.

Two aspects of the data were apparent at this stage. First, the calculated structure factors for the most intense reflections were consistently larger than the measured values, indicating secondary extinction effects. These reflections showed a linear relationship of the type $I_c/I_o = \varepsilon I_c + K^2$ where $\varepsilon = 8.3 \times 10^{-7}$ and $K = 1.0$, but no attempt was made to increase the F(obs.) on this basis. Instead, the four reflections that were most affected (i.e., 440, 800, 844, 880) were excluded from further refinement.

The other noticeable feature of the structure factor agreement was that the calculated structure factors for the three reflections with $\sin \theta/\lambda$ values less then 0.15 (i.e., 111, 200, 220) were all significantly less then the measured values. The most obvious explanation for this was that the ionized form factors used do not describe the scattering of the metals as adequately as in the semi-conducting sulphides chalcopyrite (Hall & Stewart 1973b) and cubanite (Szymanski 1973). The refinement process was repeated with the neutral curve $0.47f(Fe) + 0.53f(Ni)$ of Cromer & Mann (1968) for the metals, and the structural parameters converged to R-values of 0.040 (all data) and 0.047 (obs. data only). This suggested that the effective charge is less than the +2 expected, and/or the charge is not distributed spherically in the outer orbitals.

No attempt was made to test if the acentric space group $F\bar{4}3m$ rather than $Fm3m$ was the correct space group, or if the Fe and Ni atoms were preferentially ordered in the 4b or 32f sites, because this was considered beyond the scope or intent of this investigation. However, the experience with the argentian pentlandite analysis described above and the similarity of the thermal parameters at the metal sites in this analysis suggest that this pentlandite is centric and that the metals are essentially disordered between both sites.

The final atomic parameters are given in Table 2 and the structure factors are listed in Table 3b.

TABLE 2. FINAL ATOMIC PARAMETERS AND STANDARD DEVIATIONS*

		Ag-pentlandite	Pentlandite
Metal (4b)		Ag	Fe,Ni
	x/a	1/2	1/2
	$U_{11} \times 10^2 (A^2)$	1.73(2)	0.77(2)
Metal (32f)		Fe,Ni	Fe,Ni
	x/a	0.1269(1)	0.1261(1)
	$U_{11} \times 10^2$	1.21(1)	0.75(1)
	$U_{12} \times 10^2$	0.07(1)	0.04(1)
Sulphur (8c)		S	S
	x/a	1/4	1/4
	$U_{11} \times 10^2$	1.44(4)	0.95(3)
Sulphur (24e)		S	S
	x/a	0.2456(2)	0.2629(2)
	$U_{11} \times 10^2$	1.02(5)	0.68(3)
	$U_{22} \times 10^2$	1.26(3)	0.80(2)

*s.d. in parentheses. The anisotropic temperature factors are expressed in the form $T=\exp[-2\pi(U_{11}a^{*2}h^2 + 2U_{12}a^*b^*hk + ...)]$

TABLE 3. OBSERVED AND CALCULATED STRUCTURE FACTORS *

a. *Argentian pentlandite*

b. *Pentlandite*

(The following are structure-factor data listed in blocks of constant hk, in columns of l, $[F_o] \times 10$, and $[F_c] \times 10$. The dense numerical tables are reproduced below.)

a. Argentian pentlandite

1,1,L		
1	1185	1152

2,0,L		
0	1496	1502

2,2,L		
0	1675	1615
2	2479	2277

3,1,L		
1	4137	4093

3,3,L		
1	961	913
3	3932	3777

4,0,L		
0	1692	1778

4,2,L		
0	1523	1525
2	1300	1292

4,4,L		
0	9502	9553
2	1057	1030
4	1410	1418

5,1,L		
1	3324	3044

5,3,L		
1	767	747
3	2944	2694

5,5,L		
1	682	644
3	2348	2263
5	1864	1787

6,2,L		
0	1540	1545

6,2,L		
0	1072	1073
2	1546	1423

6,4,L		
0	689	664
2	972	969
4	1203	1176

6,6,L		
0	687	687
2	1394	1326
4	690	690
6	1211	1167

7,1,L		
1	701	686

7,3,L		
1	2836	2828
3	683	698

7,5,L		
1	2262	2233
3	949	926
5	462	461

7,7,L		
1	522	503
3	2342	2277
5	1678	1634
7	373	407

8,0,L		
0	7320	7416

8,2,L		
0	784	766
2	645	640

8,4,L		
0	948	931
2	882	877
4	6029	6051

8,6,L		
0	989	942
2	674	651
4	439	437
6	969	983

8,8,L		
0	5074	5068
2	575	532
4	563	614
6	722	667
8	3643	3706

9,1,L		
1	933	933

9,3,L		
1	1749	1771
3	493	456

9,5,L		
1	1414	1420
3	465	440

9,7,L		
1	315	374
3	1905	1930
5	1220	1227
7	264	282

9,9,L		
1	394	375
3	988	963
5	887	806
7	703	647
9	354	309

10,0,L		
0	383	312

10,2,L		
0	561	599
7	340	181
9	115	166
11	534	531

10,4,L		
0	666	688
2	2122	2170

10,4,L		
0	1012	1005
2	579	577
4	301	256

10,6,L		
0	519	463
2	1035	1034
4	994	599
6	917	919

10,8,L		
0	222	231
2	466	476
4	747	720
6	364	345
8	165	177

10,10,L		
0	516	463
2	279	793
4	275	269
6	762	674
8	310	344
10	597	529

11,1,L		
1	1794	1841

11,3,L		
1	376	396
3	1674	1699

11,5,L		
1	326	339
3	1537	1542
5	1243	1262

11,7,L		
1	1960	1605
3	397	326
5	372	275
7	1434	1448

11,9,L		
1	1096	1079
3	199	244
5	389	239
7	1092	1069
9	712	662

11,11,L		
1	279	296
3	1275	1264
5	1263	1269
7	264	259
9	129	179
11	921	924

12,0,L		
0	526	485

12,2,L		
0	999	606
2	522	498

12,4,L		
0	4210	4386
2	466	454
4	444	398

12,6,L		
0	301	321
2	434	434
4	586	574
6	379	338

12,8,L		
0	368	349
2	387	450
4	3237	3216
6	242	244
8	284	310

12,10,L		
0	591	542
2	277	299
4	65	194
6	442	415
8	152	203

12,12,L		
0	2460	2476
2	19	261
4	343	303
6	414	337
8	1985	1948
10	16	65
12	203	284

13,1,L		
1	950	976

13,3,L		
1	233	308
3	987	1015

13,5,L		
1	345	323
3	839	837
5	655	691

13,7,L		
1	870	878
3	248	231
5	272	234
7	826	806

13,9,L		
1	619	643
3	228	253
5	392	272
7	557	563
9	368	395

13,11,L		
1	211	166
3	738	713
5	661	696

13,13,L		
1	291	223
3	389	417
5	197	391
7	17	175
9	258	201
11	371	328
13	19	195

14,0,L		
0	715	756

14,2,L		
0	396	367
2	760	767

14,4,L		
0	266	93
2	402	379
4	657	667

14,6,L		
0	427	386
2	684	687
4	495	512
6	623	586

14,8,L		
0	879	583
2	290	371
4	66	70
6	259	291
8	490	493

14,10,L		
0	199	174
2	495	512
4	908	499
6	128	128
8	376	328

14,12,L		
0	79	36
2	236	212
4	324	402
6	17	142
8	234	289
10	28	179
12	363	293

14,14,L		
0	269	235
2	440	346
4	266	79
6	309	260
8	247	162
10	137	251
12	167	39
14	312	193

15,1,L		
1	145	242

15,3,L		
1	1172	1203
3	243	296

15,5,L		
1	1009	997
3	220	216
5	192	196

15,7,L		
1	166	236
3	1102	1113
5	879	929
7	207	238

15,9,L		
1	235	112
3	397	318
5	249	272
7	19	100
9	222	121
11	162	151

15,11,L		
1	239	136
3	277	165
5	254	181
7	14	110
9	138	121
11	294	209

15,13,L		
1	475	505
3	17	142
5	296	140
7	199	477
9	323	343
11	278	120
13	163	110

15,15,L		
1	163	181
3	565	662
5	14	699
7	218	159
9	243	131
11	13	24
13	262	300

16,0,L		
6	247	232

16,2,L		
2	2199	2191
2	322	229
4	445	266
6	375	298
8	1775	1735

16,4,L		
0	16	101
2	303	195
4	312	327
6	190	142
8	137	74

16,6,L		
0	237	25
2	18	77
4	217	199
6	14	41
8	167	24

16,8,L		
0	319	298
2	213	207
4	1979	1992
6	223	188
8	240	276
10	314	289
12	1031	1019

16,10,L		
0	389	283
2	173	119
4	89	21
6	36	129
8	255	226
10	13	90
12	259	7

16,12,L		
0	319	290
2	18	77
4	14	41
6	167	24

16,14,L		
0	1136	1126
2	117	106
4	371	288
6	346	146
8	949	921
10	14	48
12	13	216

16,16,L		
0	69	158
2	633	684
6	513	590

17,1,L		
1	188	224

17,3,L		
1	573	550
3	83	189

17,5,L		
1	490	462
3	244	204
5	15	221

17,7,L		
1	67	174
3	415	516
5	494	437
7	16	143

17,9,L		
1	202	283
3	399	369
5	211	106
7	71	160
9	212	184

17,11,L		
1	437	435
3	15	199
5	196	138
7	406	421

17,13,L		
1	113	281
3	46	150
5	220	170
7	14	173
9	14	132

17,15,L		
1	235	112
3	397	318
5	249	272
7	15	100
9	222	121
11	17	246

17,17,L		
1	239	136
3	14	207
5	270	106

18,0,L		
0	217	20

18,2,L		
0	14	231
2	444	449

18,4,L		
0	528	466
2	15	184
4	158	21

18,6,L		
0	151	140
2	436	389
4	414	346

18,8,L		
0	120	22
2	266	178
4	407	366
6	17	104
8	146	24

18,10,L		
0	207	102
2	220	384
4	17	71
6	163	387
8	17	156
10	212	222

18,12,L		
0	262	308

2,2,L		
0	90	26
2	293	207
4	16	148
6	231	197
8	90	15
10	14	137

2,17,L		
2	17	104
4	17	26
6	17	127
8	353	247
10	73	35
12	121	25

18,14,L		
0	14	112
2	139	137

19,1,L		
1	682	735

19,3,L		
1	23	163
3	663	768

19,5,L		
1	69	158
3	633	684
5	513	590

19,7,L		
1	645	695
3	337	193
5	89	160
7	669	664

19,9,L		
1	928	490
3	17	139
5	229	128
7	439	466
9	223	334

19,11,L		
1	252	170
3	626	597
5	936	500
7	89	182
9	108	123
11	537	466

19,13,L		
1	223	112
3	319	349
5	257	197
7	16	13

19,15,L		
1	437	435
3	15	199
5	196	138

20,0,L		
1	299	288

20,2,L		
0	186	206
2	16	152

20,4,L		
0	1561	1549
2	16	185
4	148	262

20,6,L		
0	249	108
2	16	207
4	17	246

20,8,L		
2	299	244
4	15	95
6	305	44
8	50	100
10	16	163
12	15	47

20,10,L		
0	1041	1017
2	18	93
4	312	247
6	639	130
8	841	482
10	79	204

20,12,L		
2	118	70
4	244	214
6	53	162
8	180	4

20,14,L		
0	126	215
2	129	79

21,1,L		
1	375	300

21,5,L		
1	215	156
3	236	297
5	16	228

21,7,L		
1	351	271
3	140	117
5	109	129
7	229	256

21,9,L		
1	177	199
3	15	139
5	217	144
7	111	190
9	104	140

21,11,L		
1	228	103
3	197	231
5	219	200
7	29	67
9	40	96

21,13,L		
1	16	124
3	274	147
5	14	127
7	14	101

22,0,L		
0	343	335

22,2,L		
0	14	93
2	141	235

22,4,L		
2	15	66
4	196	111
6	280	300

22,6,L		
0	188	21
2	198	169
4	243	118
6	267	197

22,8,L		
0	196	126
2	317	212
4	15	93
6	94	153

22,8,L		
0	313	270
2	226	70
4	15	60
6	55	94
8	238	218

22,10,L		
0	15	93
2	15	65
4	319	196

22,12,L		
0	15	93
2	15	65
4	319	196

23,1,L		
1	15	134

23,3,L		
1	441	496
3	178	149

23,5,L		
1	392	385
3	148	129
5	89	110

23,7,L		
1	15	139
3	458	439
5	383	369
7	203	148

23,9,L		
1	129	102
3	421	318
5	197	263
7	14	102
9	14	21

23,11,L		
1	364	337
3	70	138

24,0,L		
0	892	916

24,2,L		
0	15	82
2	15	71

24,4,L		
0	234	99
2	234	314
4	171	164

24,6,L		
2	234	99
4	305	45

25,1,L		
1	163	104

25,3,L		
1	229	144
3	14	89

25,5,L		
1	235	125
3	166	97

b. Pentlandite

1,1,L		
1	1562	1498

2,0,L		
0	933	905

2,2,L		
0	972	962
2	2631	2502

3,1,L		
1	3271	3364

3,3,L		
1	1937	1568
3	2446	2484

4,0,L		
0	2555	2537

4,2,L		
0	584	566
2	743	742

4,4,L		
0	7353	9046
2	590	562
4	1998	1976

5,1,L		
1	3157	3167

5,3,L		
1	1109	1066
3	2401	2429

5,5,L		
1	474	496
3	2482	2433
5	2464	2483

6,0,L		
0	1827	995

6,2,L		
0	726	722
2	1914	1790

6,4,L		
0	435	448
2	687	626
4	732	729

6,6,L		
0	698	699
2	1546	1568
4	490	517
6	1368	1396

7,1,L		
1	1455	1399

7,3,L		
1	1896	1873
3	1781	1725

7,5,L		
1	1921	1915
3	1169	1133
5	665	642

7,7,L		
1	1447	1429
3	1128	1116
5	1215	1227
7	1464	1471

8,0,L		
0	6488	7150

8,2,L		
0	245	227
2	146	199

8,4,L		
0	4130	4281
2	100	129
4	674	652

8,6,L		
0	1514	1428
2	427	424
4	5454E	5846

8,6,L		
0	90	186
2	280	173
4	343	266
6	167	163

8,8,L		
0	4769E	4976
2	167	181
4	975	953
6	311	332
8	3629	3737

9,1,L		
1	402	336

9,3,L		
1	1963	1963
3	718	666

9,5,L		
1	2092	2059
3	367	257
5	134	101

9,7,L		
1	569	546
3	1313	1306
5	1423	1424
7	731	710

9,9,L		
1	128	89
3	1512	1517
5	1630	1626
7	166	164
9	221	242

10,0,L		
0	349	396

10,2,L		
0	570	575
2	1362	1362

10,4,L		
0	765	749
2	479	481
4	284	268

10,6,L		
0	478	464
2	1154	1165
4	487	491
6	976	989

10,8,L		
0	216	201
2	371	347
4	519	498
6	290	322
8	58	106

10,10,L		
0	509	496
2	650	641
4	402	371
6	720	703
8	377	341
10	498	503

11,1,L		
1	1244	1243

11,3,L		
1	1220	1199
3	951	942

11,5,L		
1	813	783
3	1047	1054
5	1167	1170

11,7,L		
1	818	815
3	1256	1269
5	921	907
7	561	552

11,9,L		
1	1092	1020
3	516	513
5	339	349
7	703	733
9	891	909

11,11,L		
1	979	978
3	531	518
5	614	606
7	1028	1034
9	957	967
11	391	367

12,0,L		
0	946	948

12,2,L		
0	348	373
2	279	259

12,4,L		
0	348	373
2	279	259
4	259	239

12,6,L		
0	805	795
2	198	121
4	329	307

12,8,L		
0	598	40
2	667	739

12,10,L		
0	363	351
2	237	175
4	101	77
6	293	249
8	272	262
10	236	107

12,12,L		
0	2981	2613
2	31	19
4	710	714
6	73	903
9	195	213

13,1,L		
1	1142	1496

13,3,L		
1	235	207
3	1182	1204

13,5,L		
1	172	65
3	1323	1317
5	1419	1422

13,7,L		
1	1095	1076
3	419	392
5	185	165
7	793	785

13,9,L		
1	1268	1262
3	118	39
5	217	194
7	958	952
9	1126	1093

13,11,L		
1	300	307
3	723	728
5	615	610
7	428	421
9	22	128
11	495	490

13,13,L		
1	185	121
3	938	916
5	1007	983
7	113	36
9	172	170
11	668	615
13	774	724

14,0,L		
0	684	703

14,2,L		
0	431	435
2	840	846

14,4,L		
0	257	241
2	415	416
4	591	600

14,6,L		
0	466	456
2	727	713
4	33	396
6	627	595

14,8,L		
0	919	516
2	302	293
4	294	145
6	348	320
8	402	346

14,10,L		
0	242	240
2	44	24
4	174	123
6	337	393
8	181	169
10	343	284

14,12,L		
0	130	89
2	243	198
4	18	46
6	32	170
8	174	47
10	189	217
12	198	209

14,14,L		
0	1395	1379
2	110	39
4	558	583
6	46	34
8	1192	1172

15,1,L		
1	472	455
3	824	822
5	641	626
7	337	363
9	493	445
11	725	711

15,3,L		
1	608	595
3	349	336
5	115	207
7	472	468
9	588	564
11	328	339
13	136	93

15,9,L		
1	618	697
3	361	347
5	363	360
7	656	645
9	379	397

15,11,L		
1	178	185
3	429	424
5	229	241
9	91	95

15,13,L		
1	1266	1262
3	110	39
5	558	583

15,15,L		
1	732	729
3	30	72
5	2624	2619

16,2,L		
0	330	306
2	380	357
4	399	338
6	289	300

16,4,L		
0	151	38
2	30	31

16,6,L		
0	31	148
2	4	31
4	31	19
6	32	76

16,8,L		
0	2355	2359
2	139	17
4	708	698
6	32	101
8	1995	1941

16,10,L		
0	334	342
2	163	170
4	222	194
6	271	275
8	60	153

16,12,L		
0	679	664
2	33	21
4	1780	1779
6	32	32
8	514	628
10	127	111
12	1381	1268

16,14,L		
0	130	89
2	16	113
4	219	225

17,1,L		
1	176	34

17,3,L		
1	945	914
3	185	182

17,5,L		
1	1005	996
3	198	37
5	94	113

17,7,L		
1	192	168
3	558	564
5	771	765
7	290	765

17,9,L		
1	38	52
3	822	822
5	927	883
7	79	47
9	193	137

17,11,L		
1	432	432
3	663	659
5	515	502
7	331	393

17,13,L		
1	799	733
3	19	37
5	100	112
7	592	584
9	714	699

18,4,L		
0	652	544
2	334	314
4	171	164

18,6,L		
0	404	346
2	283	250
4	196	244
6	144	203
8	317	256
10	138	146

18,8,L		
0	334	342
2	163	170
4	222	194

18,16,L		
0	134	32
2	16	113
4	219	225

19,1,L		
1	523	543

19,3,L		
1	601	682
3	457	454

19,5,L		
1	421	432
3	913	505
5	559	595

19,7,L		
1	432	432
3	663	659
5	515	502
7	331	393

19,13,L		
1	240	225
3	421	406
5	498	456
7	322	276

19,15,L		
1	263	306
3	473	485

20,5,L		
0	599	618
2	35	17
4	1502	1503
6	31	32
8	571	679

20,6,L		
0	32	22
2	33	26
6	131	67
8	32	14

20,8,L		
0	226	241
9	81	95

20,10,L		
0	146	119
2	31	23
4	107	45
6	25	45
8	196	91
10	27	34

20,12,L		
0	1294	1275
2	89	33
4	936	957
6	32	32

20,14,L		
0	99	4
2	146	91

21,1,L		
1	684	660

21,3,L		
1	110	76
3	535	558

21,5,L		
1	142	27
3	583	609
5	669	697

21,7,L		
1	503	520
3	100	153
5	31	71
7	429	411

21,9,L		
1	998	603
3	302	254
5	33	68
7	513	463

21,11,L		
1	157	129
3	415	386
5	190	152
7	407	423

22,0,L		
0	405	496

22,2,L		
0	300	294
2	165	194

22,4,L		
0	143	128
2	302	264
4	414	411

22,6,L		
0	276	276
4	290	212
6	129	122

22,8,L		
0	373	371
2	163	194
4	214	63
6	237	215

22,10,L		
0	298	192
2	158	100
4	235	248

23,1,L		
1	348	361

23,3,L		
1	358	376
3	456	440

23,9,L		
1	403	400
3	330	334
5	261	241

23,7,L		
1	405	404
3	322	318

24,0,L		
0	1188	1189

24,2,L		
0	28	22
2	72	37

24,4,L		
2	49	524
4	27	13

* The structure factors are listed in blocks of constant hk in columns of $l[F_o] \times 10$, and $[F_c] \times 10$.

DESCRIPTION OF STRUCTURE

The structure of argentian pentlandite (Fe, Ni)$_8$AgS$_8$ is essentially that of the original pentlandite-like structure determined by Lindqvist *et al.* (1936), but with Ag atoms located at the octahedrally co-ordinated 4b sites. Argentian pentlandite does exist in nature with an Ag content of *less* than one atom per formula weight (Ag : 0.77-0.85, Vuorelainen *et al.* 1972), but has not been found to date with a value significantly greater than one *. It seems reasonable therefore, to assume that these minerals having compositions with less than one Ag per formula

weight, should have a structure that is identical to that determined here, except that some of the Fe and Ni atoms occupy the 4b site in a disordered arrangement with the Ag atoms. Because of stereochemical reasons discussed below, it seems unlikely that Ag atoms will occupy to a

* The slight excess of one Ag per formula weight reported by Scott & Gasparrini (1973) of 1.01-1.08 and by Shishkin *et al.* (1971) of 1.05-1.16 cannot be considered significant because of limitations in micriprobe accuracy. This also applies to the argentian pentlandites from the Sudbury area (Karpenkov *et al.* 1973).
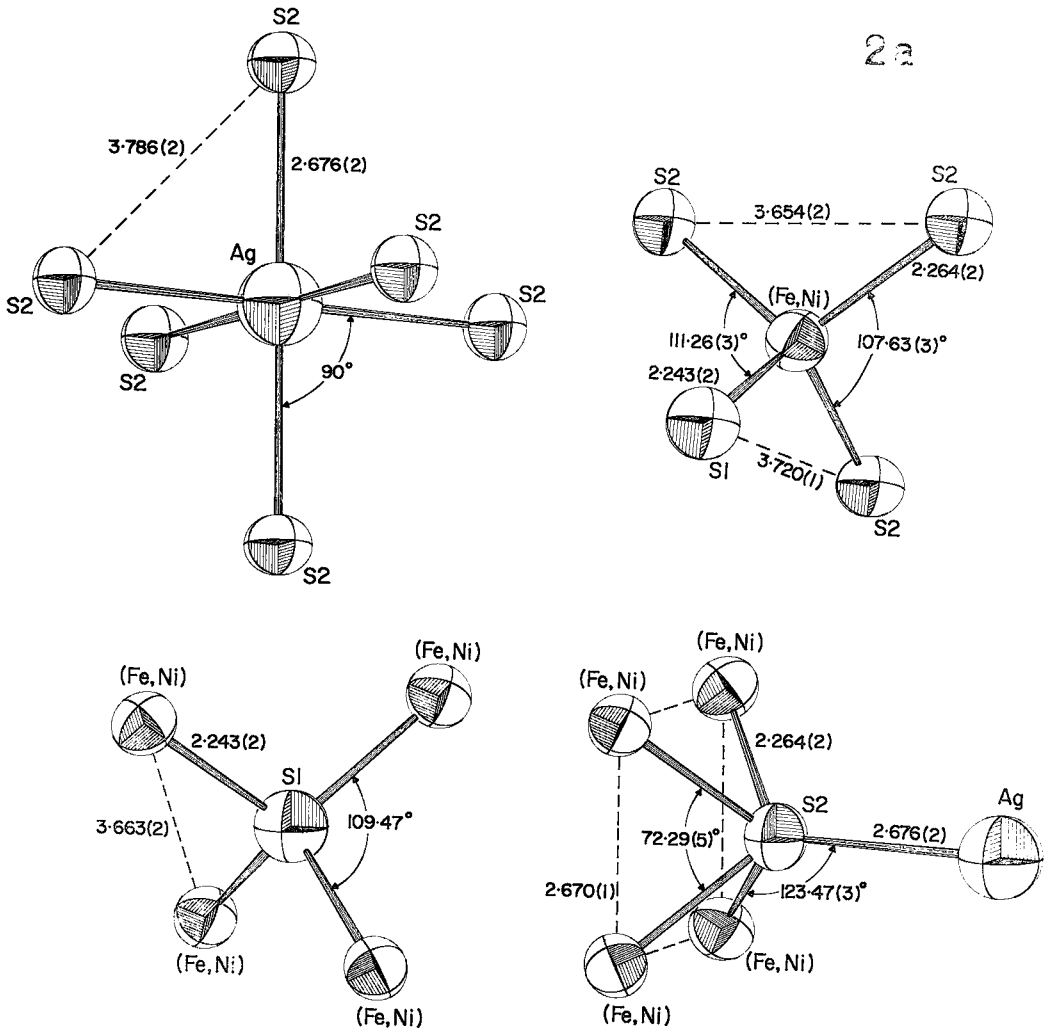
FIG. 2. The coordination of each atom type in argentian pentlandite (a) and pentlandite (b), showing the interatomic distances (in Angstroms) and angles (in degrees). The estimated standard deviations are given in parentheses. The atoms are shown as thermal ellipsoids, plotted at the 99% probability limit (Johnson 1965).

significant extent the tetrahedrally-coordinated 32f sites for any of the known argentian pentlandite compositions. Consistent with the argument that it is energetically favourable for the octahedrally-coordinated 4b site to be occupied by an atom of larger ionic radius, is the mineralogical observation that argentian pentlandite seems to occur in mineral deposits in preference to other silver sulphides *if* both Ag and pentlandite are present (D. C. Harris pers. comm. 1973).

The atomic parameters of argentian pentlandite and pentlandite, listed in Table 1, and bond lengths and angles, given in Table 4 and Figures 2a and 2b, show clearly that, although these two structures are similar, there are significant differences which arise primarily from the presence of the Ag atom at the 4b site.

In pentlandite the S(24e) atoms are 0.3Å closer to the 4b metal octahedral site than in argentian pentlandite, consistent with the much larger effective ionic radius of Ag ($\sim$ 1.3Å) over that of Fe and Ni ($\sim$ 0.7Å). This argument is supported by the much closer agreement of the distances between the S atoms about the metal tetrahedral site for the two structures, though

TABLE 4. COMPARISON OF SELECTED INTERATOMIC DISTANCES AND ANGLES IN PENTLANDITE AND Ag-PENTLANDITE

	Ag-pentlandite	Pentlandite
$M(4b)$-S(24e)	2.676(2) Å	2.382(2) Å
$M(32f)$-S(24e)	2.264(2)	2.257(2)
$M(32f)$-S(8c)	2.243(2)	2.156(2)
$M(32f)$-$M(32f)$	2.670(2)	2.533(2)
S(8c)-$M(32f)$-S(24e)	111.26(3)°	107.24(3)°
S(24e)-$M(32f)$-S(24e)	107.63(3)	111.61(3)
$M(4b)$-S(24e)-$M(32f)$	123.47(3)	127.50(2)
$M(32f)$-S(24e)-$M(32f)$	72.29(5)	68.25(5)

2b
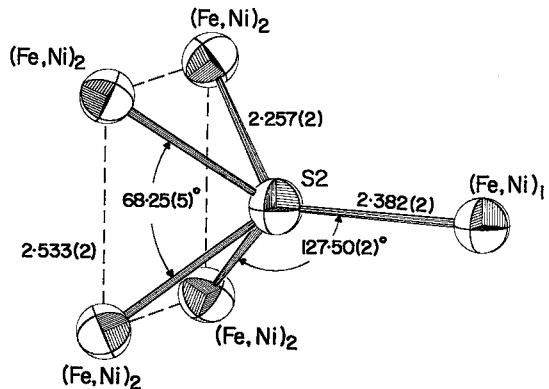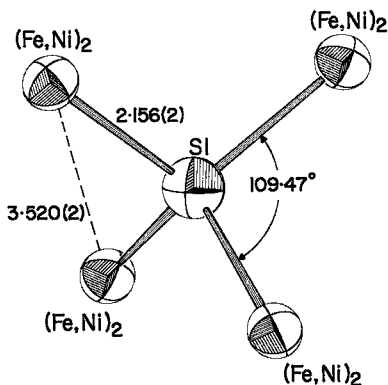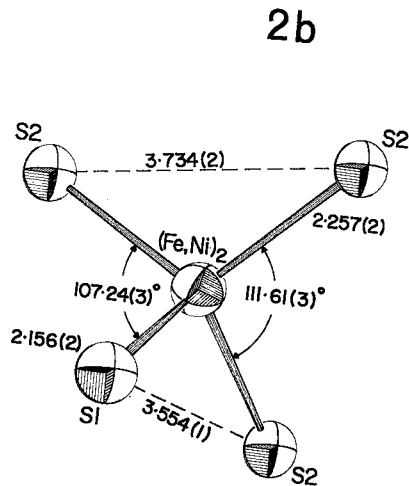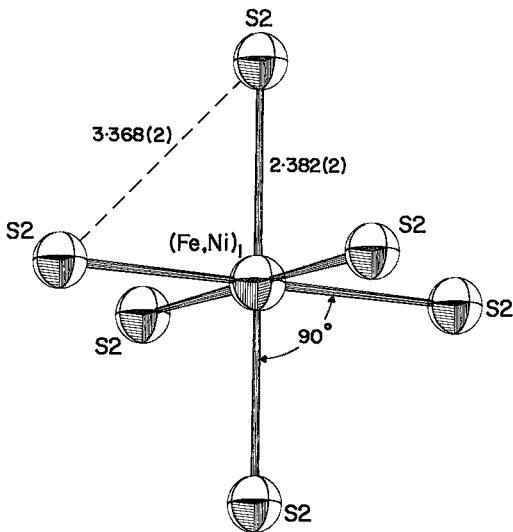
the argentian pentlandite values are significantly larger. These, and the larger metal-metal distance between the 32f sites (Fig. 3), may be expected in argentian pentlandite because of the expansion of the sulphur octahedron due to the Ag atom. As a result, the shortest $M(32f)$-$M(32f)$ distance of 2.670(2) in argentian pentlandite is significantly longer than both the distance of 2.533 (2) Å in pentlandite, and the metallic Fe-Fe and Ni-Ni distances of ~2.5Å. This, coupled with the weaker (Fe,Ni)-Sl-(Fe,Ni) ligand configuration ((Fe,Ni)-Sl = 2.243(2), (Fe,Ni) − (Fe,Ni) = 3.663(2) Å compared to 2.156(2) and 3.520(2) in pentlandite), suggests that argentian pentlandite may have significantly different electrical properties from those of pentlandite.

The anisotropic thermal parameters of argentian pentlandite and of pentlandite are listed in Table 2, and are plotted as thermal ellipsoids in Figure 2. The thermal motion of all atoms is essential isotropic. However, in both structures, the S(8c) atoms show a slight decrease in vibrational amplitude along the $M(4b)$-S(8c) bond direction. This is consistent with the anisotropic environment of this atom. The average temperature factors are, however, significantly lower in pentlandite than in argentian pentlandite, consistent with the closer packing in the former structure and its higher density. The similarity

of the temperature factors for sites 4b and 32f in pentlandite supports the view that the Fe and Ni atoms are disordered throughout these sites. The temperature factor of the Ag atom is higher than that for (Fe,Ni) atoms and may well reflect a discrepancy in the high-angle region of the silver form factors. The temperature factors in these two structures are similar to those observed in other structures with sulphur cubic close-packing such as chalcopyrite (Hall & Stewart 1973b) and cubanite (Szymanski 1973).

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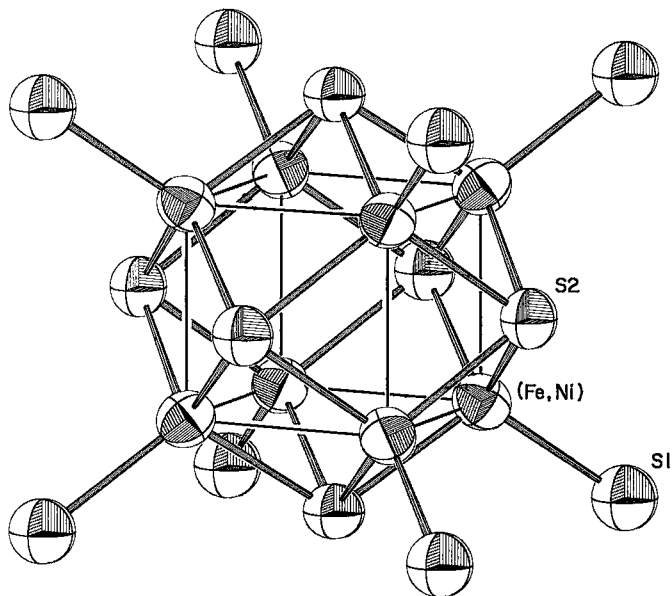

FIG. 3. Part of the structures of argentian pentlandite and pentlandite, showing the close-approach distances of the (Fe,Ni) atoms as heavy black lines. These are in a cubic arrangement with S2 atoms at the face of the cube and Sl atoms at the corners. The atoms are plotted as thermal ellipsoids at the 99% probability limit (Johnson 1965).

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