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The Crystal Structure of Anilite

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(*Received* 1 *August* 1969)

Anilite, Cu_7S_4, is a new mineral first described from the Ani Mine, Akita, Japan. It is orthorhombic with space group *Pnma*, with $a=7{\cdot}89$, $b=7{\cdot}84$, $c=11{\cdot}01$ Å, $Z=4$, $D_x=5{\cdot}68$ g.cm^{-3}. Three-dimensional data (Cu $K\alpha$ radiation) were collected from integrating Weissenberg photographs taken from a synthetic crystal. The structure was determined by the Patterson method and refined by full-matrix least squares. The residual was $R=0{\cdot}144$ for the 450 reflexions observed. The sulphur atoms approximate a cubic face-centred arrangement and the copper atoms are ordered in the interstices. The ordered distribution of the copper atoms results in slight displacements of the sulphur atoms from the positions of cubic closest packing. The structure contains five kinds of copper atom, occurring in tetrahedral and triangular coordinations. In one case the copper atom is displaced toward an edge of the tetrahedron. Two kinds of layer parallel to (011) alternate with each other: in one layer the chains of edge-sharing octahedra of sulphur atoms, three of whose faces are occupied by copper atoms, extend parallei to the *a* axis; in the other, pairs of edge-sharing tetrahedra around copper atoms are linked into chains, which extend parallel to the *a* axis. The layers are linked by isolated octahedra, two faces of which are occupied by copper atoms.

Introduction

There are a number of compounds with apparently nonstoichiometric composition among sulphide minerals. Examples of such minerals in the Cu–S system are djurleite, $Cu_{1{\cdot}97}S$ (Djurle, 1958; Morimoto, 1962; Roseboom, 1962, 1966; Takeda, Donnay, Roseboom & Appleman, 1967) and anilite, $Cu_{1{\cdot}75}S$ or Cu_7S_4 (Morimoto, Koto & Shimazaki, 1969). Digenite, $(Cu, Fe)_{1{\cdot}8-x}S$, is also considered to be an example of this type, the composition being very close to the Cu–S system.

The crystal structures of the high-temperature forms of digenite and chalcocite have been studied (Morimoto & Kullerud, 1963; Wuensch & Buerger, 1963; Sadanaga, Ohmasa & Morimoto, 1965). In these structures the sulphur atoms are in cubic or hexagonal closest packing and the copper atoms statistically occupy the interstices.

Many crystallographic studies on the minerals mentioned above indicate that their structures are superstructures of the high-temperature forms of digenite or chalcocite (Buerger & Buerger, 1944; Morimoto & Kullerud, 1963). On the basis of the change in cell dimensions and lowering of symmetry relative to the high-temperature forms, the super-structures of these minerals are considered to result from ordered arrangements of copper atoms and slight displacements of sulphur atoms from the positions of closest packing.

In order to elucidate the relationships between apparent nonstoichiometry and crystal structure, especially in super-structures of sulphides, it was necessary to obtain accurate crystal structures of these minerals. Among these minerals, the structure of low chalcocite was recently reported (Evans, 1968). In this investigation the crystal structure of anilite has been determined. The results help towards an understanding of the transition or decomposition mechanisms of copper sulphides in general.

Experimental

Material

Natural crystals from the Ani Mine, Akita, Japan and synthetic crystals of composition $Cu_{1{\cdot}75}S$, give the same X-ray patterns and were considered to be identical in structure. Synthetic crystals were used in the present work.

Cell and space group

Anilite is orthorhombic. The cell dimensions were determined from precession photographs with Cu $K\alpha$ radiation (1·5418 Å) using quartz for calibration. They are: $a=7{\cdot}89$, $b=7{\cdot}84$ and $c=11{\cdot}01$ Å, all $\pm 0{\cdot}2\%$. There are 16 formula units of $Cu_{1{\cdot}75}S$ per cell, giving a calculated density $D_x=5{\cdot}68$ g.cm^{-3}.

The diffraction aspect is $Pn{*}a$ with possible space groups $Pnma$ and $Pn2_1a$. Because of their high conductivity it was not possible to detect by the piezoelectric test whether or not the crystals were centrosymmetric. The structure determination was started in both space groups. At the final stage, however, the space group was found to be $Pnma$.

Intensity measurements

Natural and synthetic specimens all contain a small amount of djurleite (Morimito & Koto, 1970) and all show twinning. Attempts to obtain single crystals were unsuccessful: a synthetic crystal was used for intensity measurements. The specimen is about $0{\cdot}1\times 0{\cdot}03\times 0{\cdot}15$ mm, with a very small amount of djurleite and some twinning.

The intensity data were collected from integrating Weissenberg photographs (levels 0 to 6) around the a and b axes using the multiple-film technique. Cu $K\alpha$ radiation was used. Lorentz and polarization factors were applied but no absorption correction was made. Of 677 b-axis reflexions observed on the photographs 114 had relative intensities less than unity on a full intensity scale of 650. As the intensity data around the a axis were considered to be seriously affected by absorption, only those of the zero-level were used; the others served only at the first stage of the structure refinement for correlating the different layers in the b-axis photographs.

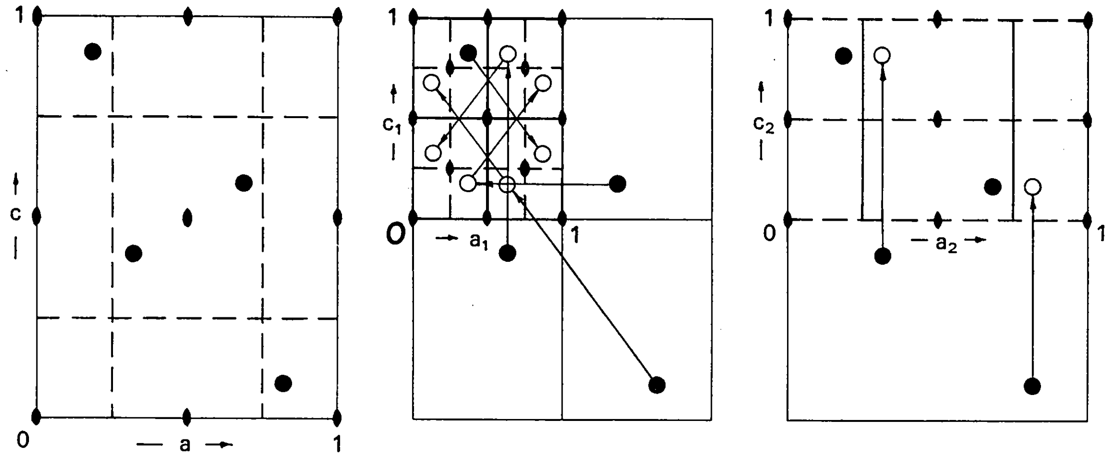
The specimen was twinned around the c axis by 90°, so that the **a** and **b** directions of one twin component coincide with the **b** and **a** directions respectively of the other. Because of the near equality of the a and b axes, the hkl reflexions of one component overlap with the khl reflexions of the other. Correction of intensities for twinning was made by using the volume ratio $p{:}q$ of the two components, which could be estimated by comparing the intensities of eight reflexions, *viz.* 014, 023, 025, 032, 034, 038, 041 and 043, from both components, because these reflexions do not overlap. The ratio $p{:}q$ was determined to be 40:1 and the intensities $I_{(hkl)}$ and $I_{(khl)}$ were obtained. Since the twinning correction was applied only to the intensity data in which both $I_{(hkl)}$ and $I_{(khl)}$ were obtained from b-axis photographs, 450 reflexions were corrected.

In addition to the overlapping of reflexions due to twinning, some djurleite reflexions are superposed with anilite reflexions because of an epitaxic relation between the two species. However, the amount of djurleite in the specimen was so small that the change in intensity of the reflexions was neglected.

Determination of the crystal structure

The structure of anilite may be considered to be a super-structure of the high-temperature digenite (Morimoto & Kullerud, 1966), because a pseudo-cubic subcell with cell edge of approximately 5·5 Å can be derived from the pseudo-tetragonal cell of anilite by the transformation matrix $\frac{1}{2}\bar{\frac{1}{2}}0/\frac{1}{2}\frac{1}{2}0/00\frac{1}{2}$.

The projection on (010) was first considered because



(*a*) (*b*) (*c*)

Fig. 1. (*a*) Plane groups *pgg* of the original structure, (*b*) *cmm* of the first hypothetical structure and (*c*) *pmg* of the second hypothetical structure. Black circles represent the atoms in the original structure, and open circles represent the atoms transferred to the hypothetical cell (indicated by the arrows).

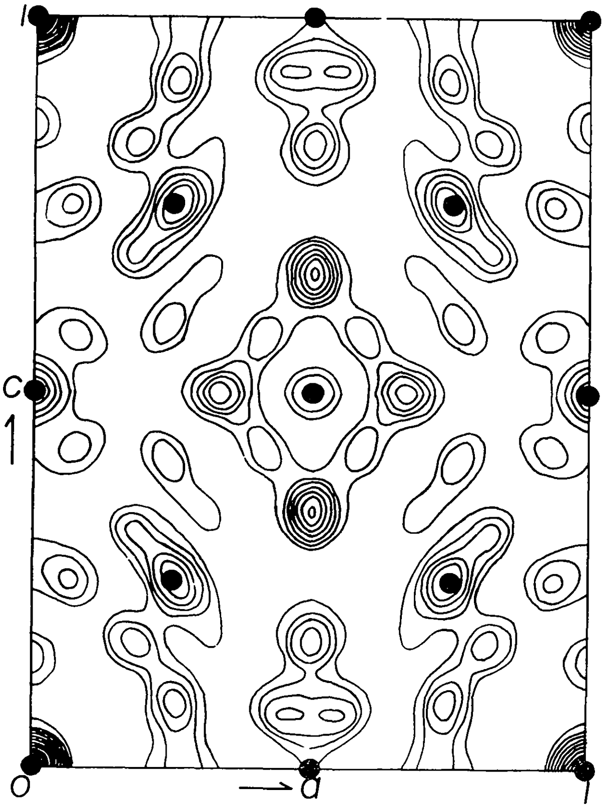


Fig. 2. Patterson projection $P(uw)$ on (010). Contours drawn at arbitrary intervals. Black circles represent predicted S-to-S peaks.

the plane group of this projection is *pgg* [Fig. 1(*a*)] for both *Pnma* and $Pn2_1a$. In the Patterson projection $P(uw)$ on (010) (Fig. 2), the predicted S-to-S peaks are indicated by the black circles, on the assumption that the S atoms are in cubic closest packing. As illustrated by the point ($\frac{1}{2}$,0), however, they are not all maxima. With the assuming that the structure contains a substructure of S atoms, it was determined as follows.

A Patterson projection $P'(uw)$ [Fig. 3(*a*)] was synthesized from only the reflexions to which the sulphur substructure contributes *i.e.* $h0l$ with h and l even and $h+l=4n$. This projection corresponds to that of a *hypothetical* structure with symmetry *cmm* [Fig. 1(*b*)] obtained by dividing the original structure into four parts by halving a and c, and then superimposing these four parts by means of translations $\mathbf{a}/2$, $\mathbf{c}/2$ and $(\mathbf{a}+\mathbf{c})/4$ (after division of the weight of each atom by eight).

The electron density of the S atoms in the *cmm* cell remains the same as in the *pgg* cell, because the S substructure is translated by $\mathbf{a}_1=\mathbf{a}/2$, $\mathbf{c}_1=\mathbf{c}/2$ and $(\mathbf{a}_1+\mathbf{c}_1)/4$ in the *pgg* cell. However, the electron density of the Cu atoms is reduced to $\frac{1}{8}$ of the original value because the Cu atoms do not form a sublattice in the *pgg* cell. Because S–S peaks in the Patterson map, $P'(uw)$, are enhanced about 64 times compared with the Cu–Cu peaks, the S–S peaks at (0,0) and ($\frac{1}{2}$,$\frac{1}{2}$) were easily located from the Patterson map. The Cu–S peaks are considered to be those near the centre of the sulphur tetrahedron (0,$\frac{1}{4}$) and at the centres of the sulphur triangles (0,$\frac{1}{3}$) and ($\frac{1}{6}$,$\frac{1}{6}$). Thus it became clear from this Pat-

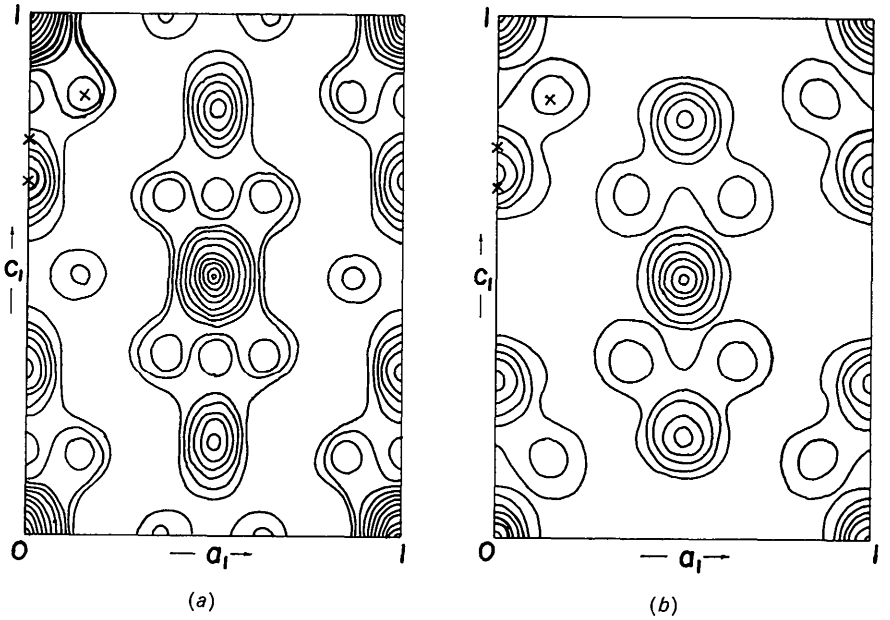


Fig. 3. (*a*) A two-dimensional Patterson synthesis $P'(uw)$, a special projection synthesized by using the reflexion $h0l$ with h and l even and $h+l=4n$ and (*b*) the corresponding Fourier synthesis. Crosses represent copper atoms at the centres of triangles and tetrahedra of sulphur atoms which are at (0,0) and ($\frac{1}{2}$,$\frac{1}{2}$).

terson projection that the Cu atoms occupy the centres of triangles and tetrahedra of S atoms at the nodes of a pseudocubic face-centred lattice. From the Fourier synthesis [Fig. 3(*b*)], the *x* and *z* coordinates and the number of Cu atoms were determined.

In the *cmm* structure the Cu atom, which occupied one position in the original structure, is distributed over eight equivalent sites, so one of these eight *cmm* sites must be selected in order to derive the original structure. On the other hand, a number of different atoms in the original structure are superposed in the *cmm* structure, making it difficult to select possible combinations of atoms.

An intermediate hypothetical cell translated by $\mathbf{a}_2=\mathbf{a}$ and $\mathbf{c}_2=\mathbf{c}/2$ was considered, which gives rise to only reflexions corresponding to $l=2n$ of the original structure. It gives the plane group *pmg* [Fig. 1(*c*)]. The sites for the Cu atoms in an asymmetric unit of the *pmg* structure can be obtained by selecting one of four equivalent sites in the *cmm* cell. The combinations of sites for Cu atoms possible in the *pmg* cell were found by application of the relationship between the two plane groups. The correct structure was determined by comparison of F_o with F_c based on structures with these possible combinations.

Finally, all the observed reflexions were taken into account to obtain the projection on (010). In a procedure similar to that described above, all possible combinations of Cu sites were considered. The resulting structure gave an *R* value of 0·32 and the others, more than 0·40. The F_o and F_o-F_c syntheses were carried out with this structure. The final *R* value was 0·21. The displacements of the S atoms from the nodes of the cubic face-centred lattice were revealed at this stage.

The Patterson projection on (100) was interpreted on the basis of the information obtained from the (010) projection. The final *R* value from the 0*kl* data dropped to 0·24.

Refinement

All computations in the present investigation were carried out on the HITAC 5020E computer of the University of Tokyo using the *UNICS System* (1967).

Refinement was carried out by the full-matrix least-squares method using the program *ORFLS* of Busing, Martin & Levy (1962), modified by Sakurai to the *UNICS System*. The centrosymmetric space group *Pnma* was adopted during the structure refinement and successful refinement of the structure confirmed this choice.

In the least-squares refinement, unit weight was given to all 450 three-dimensional observed reflexions. The function minimized in the least-squares refinement was $\sum ||F_o|-|F_c||^2$. Scattering factors for non-ionized atoms and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1962). After one cycle of refinement in which the coordinates, individual isotropic temperature factors and scale factors were varied simultaneously, the *R* value dropped from 0·236 to 0·159. Several cycles were carried out and the final *R* value was 0·144 for the 450 observed reflexions. Attempts to refine the structure further with aniso-

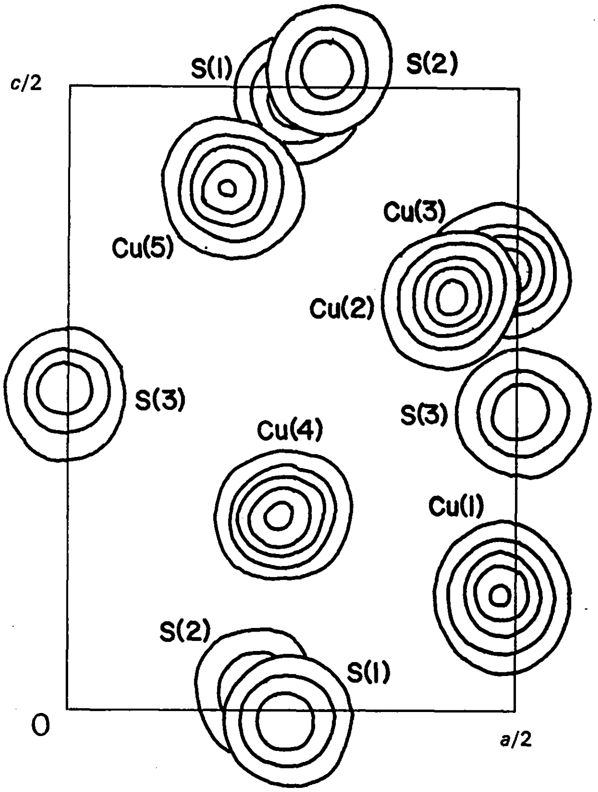


Fig. 4. Projection of the crystal structure of anilite on to the (010) composite section of three-dimensional electron-density map, each section cutting the centre of an atom.

Table 1. *Final atomic coordinates and isotropic temperature factors of anilite*

The standard deviations given in parentheses are expressed in units of the last digit. $R=0·144$ for the 450 observed reflexions.

	x	*y*	*z*	*B*
S(1)	0·2460 (20)	0·2500 (0)	0·9873 (11)	0·25 (23)
S(2)	0·7850 (21)	0·2500 (0)	0·9841 (12)	0·41 (25)
S(3)	0·9988 (12)	0·9980 (15)	0·2611 (7)	0·31 (17)
Cu(1)	0·4832 (13)	0·7500 (0)	0·0942 (8)	0·94 (18)
Cu(2)	0·4258 (13)	0·2500 (0)	0·3335 (8)	0·77 (18)
Cu(3)	0·4790 (13)	0·7500 (0)	0·3545 (8)	0·74 (18)
Cu(4)	0·2371 (10)	0·4303 (12)	0·1553 (6)	1·35 (15)
Cu(5)	0·1770 (10)	0·4767 (12)	0·4186 (6)	1·52 (16)

tropic temperature factors were unsuccessful, showing that the experimental data were not sufficiently accurate for this purpose.

Finally, three-dimensional Fourier (Fig. 4) and difference syntheses were carried out. Non-observed reflexions about the *b* axis were included in the difference synthesis.

The atomic coordinates and the individual isotropic temperature factors are given in Table 1. F_o and F_c values are compared in Table 2.

Description

The structure of anilite projected on (100) is shown in Fig. 5. The bond distances and angles (Tables 3 and 4) were computed using Sakurai's program of the *UNICS system* (1967) *RSDA*-4. The standard deviations of the atomic coordinates were used to compute the errors in the distances and angles.

Sulphur atoms occupy the approximate nodes of a cubic face-centred lattice and copper atoms are regularly arranged in the interstices. The ordered distribution of the copper atoms results in slight displacements of the sulphur atoms from the positions of cubic closest packing: these displacements are 0·10, 0·12 and 0·33 Å for S(1), S(2) and S(3) respectively.

Coordination of copper atoms

Copper atoms are coordinated by sulphur atoms in two different ways: tetrahedral coordination of Cu(1)

Table 2. *Observed and calculated structure factors*

The three columns in each group contain the values, reading from left to right, of *l*, $10|F_o|$ and $10|F_c|$.

l	$10\lvert F_o\rvert$	$10\lvert F_c\rvert$
h=0, k=0		
2	114	-90
4	1809	-1994
6	455	418
8	511	517
10	618	-764
12	1480	1988
14	182	336
h=1, k=0		
1	334	-397
2	105	75
3	1206	-1311
4	1849	1979
5	1308	1352
6	506	562
7	2023	2149
8	1216	-1430
9	965	-1206
10	442	-518
11	217	-312
12	269	261
h=2, k=0		
2	2149	-2029
3	1158	-1185
4	224	130
5	997	-1115
6	1216	-1362
7	444	505
8	412	494
9	505	518
10	564	-400
12	209	-152
h=3, k=0		
1	549	686
2	1894	1932
3	255	-337
4	2334	-2079
5	1033	-953
6	434	-585
7	231	0129
8	1974	1726
9	803	-846
10	501	-372
12	587	-552
h=4, k=0		
1	2168	2151
2	693	-621
3	1856	1783
4	449	-275
5	494	-389
6	808	718
7	246	179
8	1526	1277
9	253	-289
10	632	-685
11	634	-650
12	705	746
h=5, k=0		
1	508	-555
2	1296	-1129
4	657	-595
5	1021	903
7	1876	1653
8	357	463
9	408	-315
10	613	455
11	423	-382
12	258	174
h=6, k=0		
2	336	65
4	146	87
6	2845	-2536
7	249	-263
8	231	152
11	325	-50
h=7, k=0		
2	1199	1212
4	309	-184
6	337	-408
8	386	284
10	429	-482
h=8, k=0		
1	489	447
3	289	184
5	528	-418
7	119.	54
h=9, k=0		
2	679	-678
4	171	70
6	204	153
h=1, k=1		
2	638	-631
3	436	402
4	163	-162
5	167	-186
7	513	-561
8	428	541
9	119	67
10	430	598
11	169	230
12	367	-472
13	169	-162
h=2, k=1		
0	142	168
1	1316	1362
2	243	-245
3	1136	1159
5	1079	-997
6	661	696
7	658	-879
9	238	-201
11	619	-635
12	137	159
13	317	-414
h=3, k=1		
1	895	850
2	194	-202
3	1312	-1027
4	1157	-1050
5	354	357
6	340	-361
7	426	429
8	788	807
9	421	-454
11	316	368
12	516	-641
13	209	296
h=4, k=1		
0	151	158
1	659	667
2	613	-566
3	1157	900
4	308	-247
5	223	135
6	368	338
8	467	-510
9	59	169
10	271	-259
h=5, k=1		
1	252	-291
2	300	342
3	80	78
4	650	-527
5	329	-170
6	122	115
7	540	-555
8	803	853
10	142	151
11	102	282
12	25	-109
h=6, k=1		
0	465	-496
1	1420	1159
2	185	180
3	399	367
4	857	762
5	1186	-1087
6	175	236
10	114	169
11	522	-613
h=0, k=1		
1	175	-241
3	1070	1083
5	968	915
7	649	-769
9	356	404
11	685	938
13	88	213
h=0, k=2		
2	1157	-1200
4	343	294
6	2325	-2242
8	405	-460
10	551	-715
12	121	278
h=1, k=2		
1	852	-1024
3	1313	1320
4	2106	2249
5	777	-763
6	476	465
7	412	-439
8	1348	-1536
9	488	444
10	311	-243
11	498	590
12	313	268
13	767	-817
h=2, k=2		
0	2172	-2394
1	1376	-1606
3	1358	-1393
4	3714	3836
5	280	298
6	310	-315
8	962	1112
9	576	575
10	304	303
11	632	673
12	122	-300
13	88	-222
h=3, k=2		
1	1411	1417
2	201	-100
3	1452	1266
4	282	94
5	1524	-1507
6	187	-194
7	1337	-1232
9	125	239
10	211	219
11	1284	1331
13	185	-206
h=4, k=2		
0	346	-405
1	155	-195
2	2289	-1915
3	807	674
4	510	513
5	1177	926
6	354	1
7	782	-631
9	681	-687
10	921	-1080
11	172	-199
12	150	119
h=5, k=2		
1	537	-567
2	1741	-1614
3	571	-527
4	580	495
7	285	292
8	914	-751
9	604	-509
10	397	368
11	297	432
h=6, k=2		
0	965	986
1	965	-921
3	989	-705
4	1728	1232
5	856	592
6	750	-683
7	366	149
9	104	187
10	125	83
11	234	483
h=0, k=3		
1	1860	-2104
3	2096	-2234
5	608	591
9	520	-584
13	298	-353
h=1, k=3		
1	432	-511
2	672	689
3	1552	1684
4	537	558
5	721	-651
7	1187	-1136
8	659	-740
9	690	750
10	527	-685
12	325	474
13	200	-236
h=2, k=3		
0	1285	-1162
1	773	862
4	213	234
5	432	-465
6	266	-360
7	1141	1314
8	304	325
9	536	578
12	387	-417
13	423	525
h=3, k=3		
1	198	169
3	839	-774
7	665	703
9	428	-319
11	500	-561
12	438	535
h=4, k=3		
0	927	1048
1	1872	-1759
2	651	636
3	967	-969
4	450	-359
5	1495	1216
6	426	-404
7	758	-523
8	190	266
9	708	-721
11	156	224
h=5, k=3		
1	957	-781
2	625	-462
3	1415	1105
4	1386	1134
5	299	237
8	1377	-1309
9	656	593
10	154	-252
h=6, k=3		
0	304	-305
1	350	-353
3	682	-543
4	268	-273
5	180	-23
6	600	-467
7	567	427
9	640	613
h=0, k=4		
2	437	398
4	694	-294
6	626	-575
8	571	571
12	814	1273
h=1, k=4		
1	159	-237
2	1141	1341
3	867	-839
4	634	276
5	899	904
7	1375	1569
8	267	-73
9	681	-957
10	527	-557
h=2, k=4		
0	1394	1349
1	251	307
2	1890	-1914
3	192	-626
4	735	-936
5	843	-960
6	399	-251
7	313	417
8	197	388
9	258	386
10	989	-1029
12	295	267
h=3, k=4		
1	464	492
2	558	233
3	585	-581
4	865	-716
5	630	-571
7	159	248
8	622	552
9	883	-864
h=4, k=4		
0	1610	1610
1	1220	1206
2	115	-24
3	1378	1103
4	678	631
6	513	-290
8	1312	1071
9	176	-241
11	289	-334
h=5, k=4		
1	583	-521
2	420	125
3	656	504
4	1218	-973
5	645	569
6	195	-121
7	1093	1063
8	1017	944
h=6, k=4		
0	1265	1125
1	473	441
2	502	-420
4	365	-370
5	491	-567
6	1737	-1480
h=0, k=5		
1	627	-768
3	143	20
5	687	749
7	212	-490
9	529	543
11	855	1050
h=1, k=5		
1	280	194
2	215	-210
3	525	652
4	133	127
5	507	-534
7	1008	-944
8	178	266
10	277	340
11	464	368
12	296	-353
h=2, k=5		
1	1131	1384
2	345	-351
3	1099	1097
4	407	405
5	758	-853
6	863	767
7	772	-650
8	60	53
9	115	-218
11	718	-787
h=3, k=5		
1	702	682
2	621	-460
3	971	-1007
4	1393	-1149
5	368	378
6	385	-341
7	592	588
8	782	876
9	481	-477
10	347	301
h=4, k=5		
1	483	288
2	192	-230
3	785	650
4	580	-438
5	578	455
8	512	-543
0	600	621
h=5, k=5		
1	614	-599
2	489	389
3	153	259
4	220	-57
6	210	143
7	399	-433
8	539	462
9	210	112
h=6, k=5		
0	546	-563
1	941	893
2	267	143
4	829	709
5	1232	-1120
6	326	210
7	167	179
h=0, k=6		
2	391	-411
4	1302	1286
6	2090	-2343
8	278	-198
h=1, k=6		
1	408	-512
2	967	977
3	878	896
4	360	172
5	679	-633
6	137	-185
7	349	-414
9	364	282
10	307	-256
11	354	529
h=2, k=6		
0	398	368
1	633	-596
2	541	-395
3	570	-505
4	1437	1529
6	627	572
8	819	854
9	348	326
10	352	-395
h=3, k=6		
1	795	746
2	1207	-1147
3	694	531
4	958	883
5	752	-682
6	337	281
7	473	-347
8	865	-837
h=4, k=6		
0	1141	-1255
1	609	-568
2	961	-948
3	282	67
4	926	1027
5	852	764
6	1037	-1006
h=5, k=6		
1	625	-484
2	281	-56
3	139	10
4	153	-127
5	334	-331
6	355	-165
7	227	-161
h=6, k=6		
0	1411	1394
1	269	-221
2	462	-371
3	450	-302
4	806	552
5	231	124
6	357	214
7	350	248

Table 3. *Bond distances* (Å) *in anilite*

Standard deviations are given in parentheses in units of the last digit.

(*a*) Copper–sulphur distances in the sulphur tetrahedron

	S(1)	S(2)	S(3)
Cu(1)	2·317 (18)	2·285 (19)	2·517 (12) 2·517 (12)
Cu(2)	3·206 (17)	2·295 (17)	2·306 (12) 2·306 (12)
Cu(3)	2·300 (17)	2·346 (18)	2·329 (12) 2·329 (12)
Cu(4)	2·329 (12)	2·944 (11)	2·282 (12) 2·329 (12)
Cu(5)	2·352 (11)	2·243 (12)	2·241 (11) 3·225 (12)

Table 3 (*cont.*)

(*b*) Copper–copper distances

	Cu(1)	Cu(2)	Cu(3)	Cu(4)	Cu(5)
Cu(1)			2·866 (12) 3·952 (14) 4·018 (14)	3·241 (11) 3·241 (11) 3·797 (12) 3·797 (12)	2·636 (11) 2·638 (11) 2·915 (11) 2·915 (11)
Cu(2)			3·516 (13) 3·949 (2) 3·949 (2)	2·837 (12) 2·837 (12) 2·840 (11) 2·840 (11)	2·809 (11) 2·809 (11) 3·845 (11) 3·846 (11)
Cu(3)	2·866 (12) 3·952 (14) 4·018 (14)	3·516 (13) 3·949 (2) 3·949 (2)		3·231 (11) 3·231 (11) 3·839 (11) 3·839 (11) 3·984 (11) 3·984 (11)	3·281 (11) 3·281 (11) 4·009 (11) 4·010 (11)
Cu(4)	3·241 (11) 3·797 (12)	2·837 (12) 2·840 (11)	3·231 (11) 3·839 (11) 3·984 (11)	2·827 (13)	2·790 (10) 2·960 (9) 3·583 (11)
Cu(5)	2·636 (11) 2·915 (11)	2·809 (11) 3·846 (11)	3·281 (11) 4·009 (11)	2·790 (10) 2·960 (9) 3·583 (11)	3·339 (11) 3·555 (13)

(*c*) Sulphur–sulphur distances in six different sulphur-atom tetrahedra

Cu(1) tetrahedron

	S(2)	(3)	S(3′)
S(1)	4·253 (23)	3·747 (15)	3·747 (15)
S(2)		3·850 (16)	3·850 (16)
S(3)			3·889 (17)

Cu(2) tetrahedron

	S(2)	S(3)	S(3′)
S(1)	3·637 (23)	4·098 (15)	4·098 (15)
S(2)		4·006 (15)	4·006 (15)
S(3)			3·951 (17)

Cu(3) tetrahedron

	S(2)	S(3)	S(3′)
S(1)	3·637 (23)	3·872 (15)	3·872 (15)
S(2)		3·739 (15)	3·739 (15)
S(3)			3·889 (17)

Cu(4) tetrahedron

	S(2)	S(3)	S(3′)
S(1)	3·940 (2)	3·944 (15)	4·098 (15)
S(2)		3·850 (16)	3·739 (15)
S(3)			3·953 (13)

Cu(5) tetrahedron

	S(2)	S(3)	S(3′)
S(1)	3·940 (2)	3·872 (15)	3·747 (15)
S(2)		4·006 (15)	4·108 (16)
S(3)			3·953 (13)

Vacant tetrahedron

	S(2)	S(3)	S(3′)
S(1)	4·253 (23)	3·944 (15)	3·944 (15)
S(2)		4·108 (16)	4·108 (16)
S(3)			3·951 (17)

and Cu(3) and triangular coordination of Cu(2), Cu(4) and Cu(5) (Fig. 6).

The tetrahedron around Cu(1) is distorted in that two Cu–S distances [Cu(1)–S(1) and Cu(1)–S(2)] are shorter than the others [two Cu(1)–S(3)]. The bond angle S(1)–Cu(1)–S(2) of 135·1° is much larger than the normal tetrahedral angle, and Cu(1) is displaced so as to be close to the line connecting S(1) and S(2) in the tetrahedron. The tetrahedron around Cu(3) is nearly regular and the mean value of the four Cu–S

Table 4. *Bond angles* (°) *in anilite*

Standard deviations are given in parentheses in units of the last digit.

S(1)–Cu(1)–S(2)	135·1 (6)
S(1)–Cu(1)–S(3)	101·5 (4)
S(1)–Cu(1)–S(3′)	101·5 (4)
S(2)–Cu(1)–S(3)	106·5 (4)
S(2)–Cu(1)–S(3′)	106·5 (4)
S(3)–Cu(1)–S(3′)	101·2 (4)
S(2)–Cu(2)–S(3)	121·1 (3)
S(2)–Cu(2)–S(3′)	121·1 (3)
S(3)–Cu(2)–S(3′)	117·9 (5)
S(1)–Cu(3)–S(2)	103·1 (6)
S(1)–Cu(3)–S(3)	113·5 (4)
S(1)–Cu(3)–S(3′)	113·5 (4)
S(2)–Cu(3)–S(3)	106·2 (4)
S(2)–Cu(3)–S(3′)	106·2 (4)
S(3)–Cu(3)–S(3′)	113·2 (4)
S(1)–Cu(4)–S(3)	115·7 (5)
S(1)–Cu(4)–S(3′)	125·4 (6)
S(3)–Cu(4)–S(3′)	118·0 (4)
S(1)–Cu(5)–S(2)	118·0 (5)
S(1)–Cu(5)–S(3)	109·3 (6)
S(2)–Cu(5)–S(3)	132·7 (6)

distances is 2·33 Å. The triangles around Cu(2) and Cu(4) are almost equilateral, while the triangle around Cu(5) is distorted: the mean Cu–S distances are 2·30, 2·31 and 2·28 Å for the triangles around Cu(2), Cu(4) and Cu(5) respectively. The mean distances in anilite are in agreement with those obtained in other sulphide minerals except for the Cu(1)–S distance. For example, the mean Cu–S distances in tetrahedrite (Wuensch, 1964) are 2·342 and 2·259 Å for copper atoms with tetrahedral and triangular coordinations respectively.

Vacant tetrahedra of sulphur atoms

The approximately closest-packed sulphur atoms form 32 tetrahedra in the unit cell. If it is considered that each copper atom coordinated by three sulphur atoms belongs to the tetrahedron having the sulphur triangle, four tetrahedra must remain vacant. Thus there are six different sulphur-atom tetrahedra in the structure: tetrahedra for Cu(1), Cu(2), Cu(3), Cu(4) and Cu(5) and a vacant tetrahedron (Table 3).

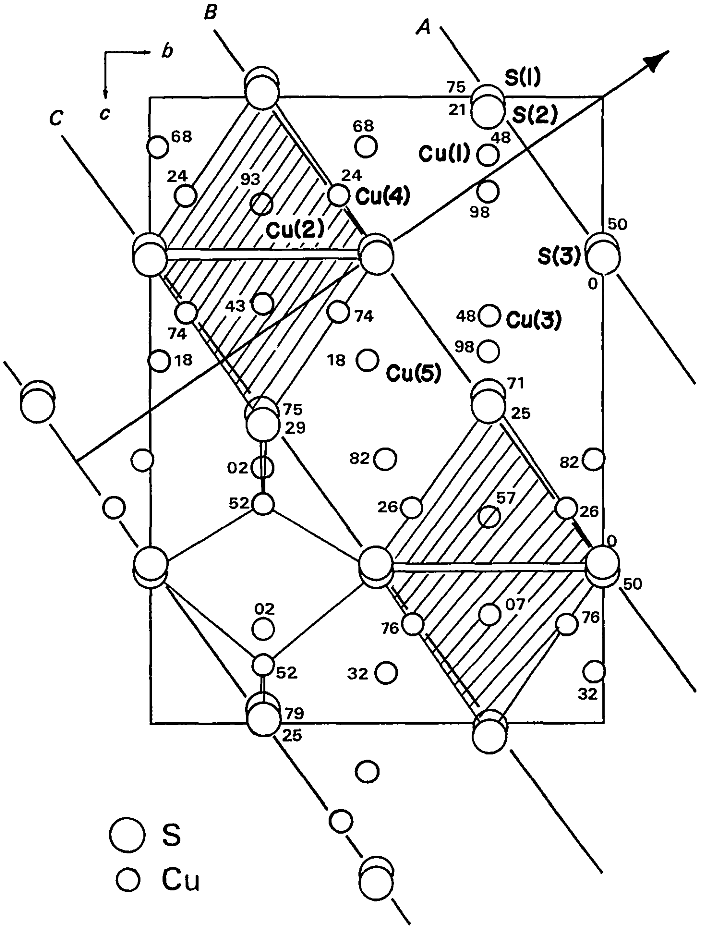


Fig. 5. Projection of the crystal structure of anilite on to (100) with the *x* parameters of the atoms indicated. *A*, *B* and *C* represent the almost cubic closest-packed layers of sulphur atoms; the direction of stacking is shown by the arrow. Vacant sulphur atom tetrahedra are hatched.

Two closely packed sheets of sulphur atoms parallel to (011) (for example, *B* and *C* in Fig. 5) form a layer of tetrahedra for copper atoms. The layers containing vacant tetrahedra alternate with those containing tetrahedra all filled with copper atoms along [021], [0$\bar{2}$1], [201] and [$\bar{2}$01]. The distribution of vacant tetrahedra

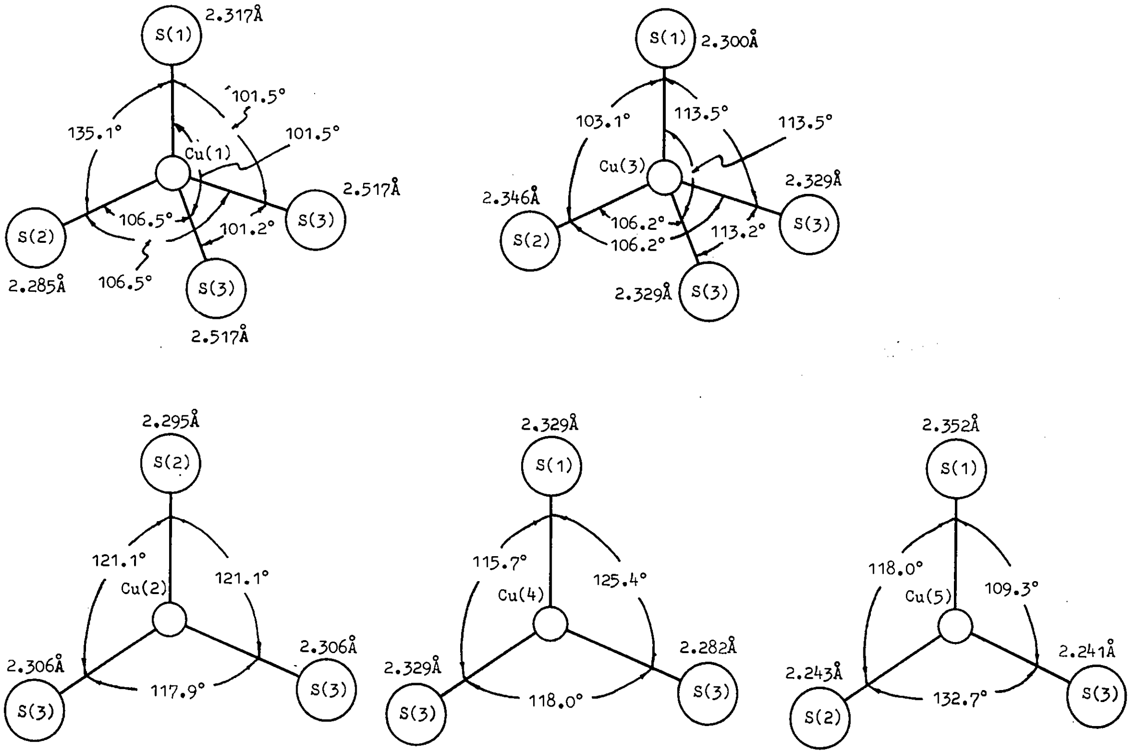


Fig. 6. The coordinations, bond distances and angles in anilite.

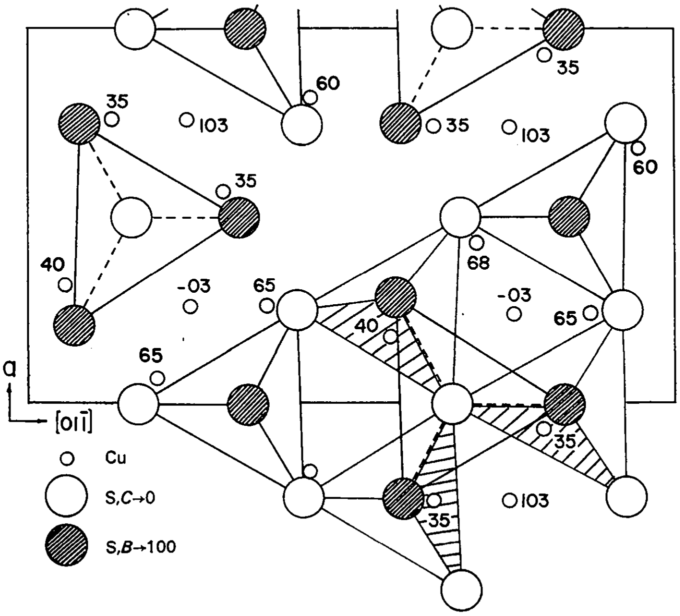


Fig. 7. Projection of the crystal structure of anilite between sulphur layers *B* and *C* (Fig. 5) along [021] with the parameters normal to the projection, normalized $C \rightarrow 0$, $B \rightarrow 100$. Cu atoms on the hatched triangle of S atoms are displaced towards the vacant tetrahedron.

in the layer is ordered so that the tetrahedra are separated as far as possible by filled tetrahedra (Fig. 7). In order to avoid the influence of these vacant tetrahedra and to distribute the copper atoms as evenly as possible, copper atoms in adjacent tetrahedra move to the centres of the triangles which share their edges with the vacant tetrahedra (Fig. 7).

The mean S–S distance in the tetrahedra is least (3·79 Å) for the regular tetrahedron of Cu(3). The Cu atom tetrahedra with coordination number 4 are generally smaller than those with coordination number 3. The mean S–S distance in the vacant tetrahedron (4·05 Å) is larger than in any filled tetrahedron. This is explained by sulphur repulsion in the vacant tetrahedron.

The resulting structure can be described as follows. Two kinds of layers parallel to (011) alternate with each other. Two sheets of closely packed sulphur

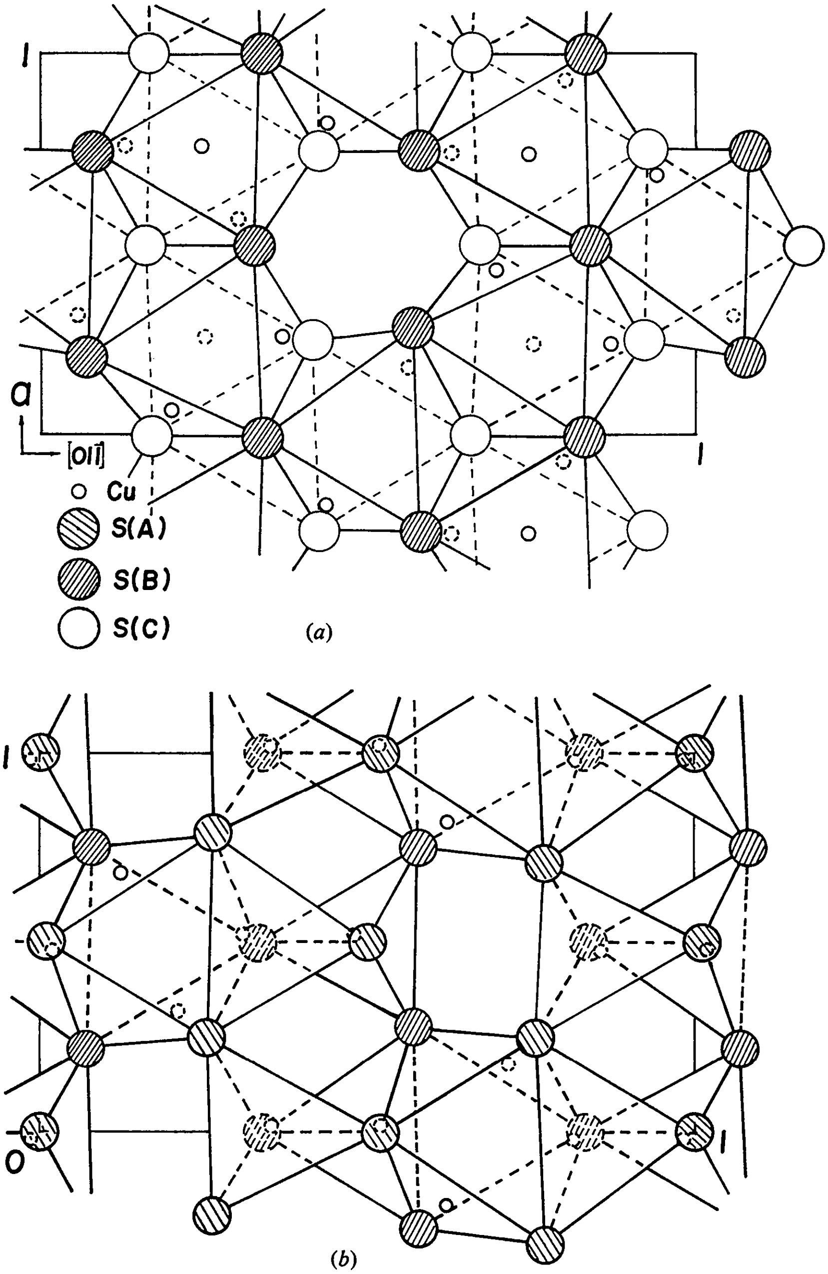


Fig. 8. Projection of the crystal structure of anilite between sulphur layers (*a*) *B* and *C* (Fig. 5) and (*b*) *A* and *B*, along [021]. (*a*) Two kinds of chains of octahedra, three faces of which are occupied by copper atoms, and (*b*) two kinds of edge-sharing tetrahedra around copper atoms, are shown. Both chains extend along the *a* axis and isolated octahedra, with only two faces occupied by copper atoms, serve to connect the chains in both layers.

atoms parallel to (011) form one type of layer of octahedra [Fig. 8(*a*)]. The chains of edge-sharing octahedra, three faces of which are occupied by copper atoms, extend parallel to the *a* axis, and isolated octahedra, with only two faces occupied by copper atoms, connect the chains. The second type of layer [Fig. 8(*b*)] is also made up from two sheets of closely packed sulphur atoms (*A* and *B* in Fig. 5). Pairs of tetrahedra around copper atoms, which share an edge, are linked into chains which extend parallel to the *a* axis, and isolated octahedra, two faces of which are occupied by copper atoms, serve to tie the chains together [Fig. 8(*b*)].

Discussion

The high-temperature form of the bornite solid solution has the antifluorite-type structure (Morimoto & Kullerud, 1966), in which sulphur atoms are in the ideal cubic closest packing arrangement and metal atoms are distributed statistically inside the sulphur tetrahedra according to the cubic symmetry (Morimoto & Kullerud, 1963) so that the number of metal atoms in each tetrahedron becomes a fraction. The structure of high-temperature anilite is similar. In low-temperature anilite, copper atoms are not statistically distributed but are in ordered positions. This results in some sulphur tetrahedra containing no Cu atoms. The vacant tetrahedra are regularly distributed according to the orthorhombic symmetry and separated from each other by filled tetrahedra. Sulphur atoms are slightly displaced from the positions of ideal closest packing in order to adapt to the ordered arrangement of the copper atoms.

The structure of anilite seems to be characteristic of apparently nonstoichiometric compounds of sulphides stable at low temperatures which should be considered to be stoichiometric because the atoms in the structure occupy crystallographic positions in a definite space group. No cation disorder is observed. The ordered arrangement of metal atoms and the concomitant displacement of sulphur atoms result in a super-structure of the high-temperature form, which is truly nonstoichiometric.

A wide solid-solution range of a high-temperature form of bornite solid solution transforms to a number of, or to mixtures of, low-temperature forms, which are super-structures of the high-temperature form and to narrow-range solid solutions such as chalcocite, djurleite, anilite, digenite and bornite.

According to the ratio of metal to sulphur atoms, the sulphur atoms adopt the hexagonal closest packing (chalcocite and djurleite) or the cubic closest packing (anilite, digenite and bornite). Some synthetic crystals of anilite show diffuse streaks along the direction of stacking of the closest-packed planes of sulphur atoms, indicating the existence of some mistakes in the stacking of the sulphur planes.

The authors are indebted to Professor J. D. H. Donnay and Dr G. Donnay for reviewing the manuscript and making numerous suggestions for its improvement.

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