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The Crystal Structure Refinement of Chalcopyrite, $CuFeS_2$*

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The crystal structure of chalcopyrite, $CuFeS_2$, has been refined to an R value of 0·031 using multiple sets of 4-circle diffractometer data and full-matrix least-squares procedures. Spherical absorption corrections and anomalous dispersion data were applied in the refinement of the sulphur x coordinate at site 8d [0·2574 (2), $\frac{1}{4}$, $\frac{1}{8}$] and the anisotropic temperature factors. The thermal motion of all atoms is essentially isotropic and in excellent agreement with that of equivalent atoms in cubanite, $CuFe_2S_3$. The metal–sulphur distances of Cu–S = 2·302 (1) and Fe–S = 2·257 (1) Å are significantly closer than those reported previously. There is stereochemical evidence that the structure exists in a strong covalently-bonded configuration which has an effective ionic state between $Cu^+Fe^{3+}S_2^{2-}$ and $Cu^{2+}Fe^{2+}S_2^{2-}$.

Introduction

The crystal structure of chalcopyrite has been the subject of considerable study since it was first described by Burdick & Ellis in 1917. The currently accepted atomic and antiferromagnetic structures for chalcopyrite are those first reported by Pauling & Brockway (1932) and by Donnay, Corliss, Donnay, Elliott & Hastings (1958) respectively. This study was undertaken in order to provide more accurate structural parameters than those presently available and thus enable a meaningful comparison with those of the other chalcopyrite-like minerals, talnakhite $Cu_9Fe_8S_{16}$ (Hall & Gabe, 1972), mooihoekite $Cu_9Fe_9S_{16}$ and haycockite $Cu_{10}Fe_8S_{16}$ (Cabri & Hall, 1972). In particular, it is hoped that the more precise coordination and thermal motion information obtained from further study of structures such as chalcopyrite and cubanite, where the sites of the copper and iron atoms are unambiguously known, will aid in the identification of the metals in the more complex sulphide minerals.

Crystal data

Source: Western Mines, Vancouver Island, B.C., Canada.
Microprobe analysis in atomic % (Cabri & Hall, 1972)
Cu: 25·10 (12), Fe: 25·27 (15), S: 49·63 (25).
Chemical composition: $Cu_{1\cdot01(1)}Fe_{1\cdot02(1)}S_{2\cdot00}$.
Formula: $CuFeS_2$.
Space group: $I\bar{4}2d$ (No. 122).
Cell dimensions: a = 5·289 (1), c = 10·423 (1) Å,
Z = 4, D_{meas} = 4·23 (1), D_{calc} = 4·18 (3) g cm^{-3}.
Linear absorption coefficient μ(Mo $K\alpha$) = 136·6 cm^{-1}.
Crystal radius R = 0·0135 (5) cm, μR = 1·84.
Intensity data: 694 reflexions measured three times.

Experimental

A crystal from Western Mines, Vancouver Island, B.C., was ground to a sphere of radius 0·135 (5) mm using a Nonius grinder and diamond-impregnated paper. An X-ray photographic survey with a precession camera showed the crystal to be single and untwinned. The observed diffraction pattern complied with the previously reported space-group symmetry $I\bar{4}2d$. The crystal was mounted in a random orientation on the Mines Branch 4-circle Picker diffractometer and was automatically aligned using 20 independent reflexions. A least-squares refinement process was applied to the measured angles 2θ, φ, χ and ω of these reflexions assuming a triclinic cell, and a best fit was obtained for the cell dimensions $a=b=5{\cdot}289$ (1), $c=10{\cdot}423$ (1), $\alpha=\beta=\gamma=90{\cdot}00$ (1).

The intensities of a symmetric set of hkl reflexions were measured three times and those of $h\bar{k}l$ data set once, all to a 2θ limit of 128°. All measurements were made on the 4-circle diffractometer using graphite monochromatized Mo $K\alpha$ radiation and a $\theta/2\theta$ scan with a 2θ-width of 2·5 to 3·0°, according to the dispersion. Background counts were measured on each side of the scan for a total time approximating that of the scan (30 sec per degree of 2θ). The intensities of three reflexions were recorded every 25 measurements to monitor the crystal alignment and instrument stability.

The three independently measured sets of hkl intensities were compensated for spherical absorption effects and merged into one unique set of data. This was done in two ways. In the first merged data set a reflexion was considered 'observed' if its net intensity was significant at the 10% significance level [*i.e.* $I > 1{\cdot}65\sigma(I)$]. In the second all intensities were accepted as averaged, except for the negative values, which were set to zero. Structure factors of the merged data sets were obtained following the application of Lorentz and polarization factors. The average agreement index ob-

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tained for the first merged data set (432 'observed' reflexions only) was 0·029.

As the crystal grinding process tends to reduce secondary extinction effects, no *a priori* corrections of this kind were made but were applied empirically during the subsequent refinement process. The $hk\bar{l}$ intensities were reduced to structure factors separately and used only to confirm the correct application of anomalous dispersion components.

Structure refinement

All calculations used in the refinement of chalcopyrite were performed on a CDC 6400 computer with the X-ray System of crystallographic programs (Stewart, Kruger, Ammon, Dickenson & Hall, 1972). For the most part, refinement of the coordinate and thermal parameters involved the full-matrix structure-factor least-squares program *CRYLSQ* (written for the X-ray System by F. Kundell) applied to the data set that included observed and unobserved reflexions. In order that the start of the refinement process would be largely independent of previously reported determinations, all atoms were placed initially at the idealized tetrahedral sites; Cu atoms at the 4(*a*) (0,0,0) sites, Fe atoms at the 4(*b*) (0,0,$\frac{1}{2}$) sites, and S atoms at the 8(*d*) (0·25,$\frac{1}{4}$,$\frac{1}{8}$) sites. An isotropic temperature factor of 1·0 Å^2 was used, along with the neutral atomic scattering factors of Cromer & Waber (1965). Unit least-squares weights were used throughout the refinement process, but several schemes that down-weighted the subcell (a_0 = 5·3 Å) reflexions were also tested (this is discussed below). The least-squares process converged rapidly to an R value of 0·067 and resulted in Cu, Fe and S temperature factors of 0·93, 1·32, and 0·96 Å^2 respectively and a sulphur x coordinate (x_S) of 0·2484. Considering the relatively low R value, and the apparent independent nature of the refinement,

Table 1. *Final atomic parameters and standard deviations* (*in parentheses*)

The anisotropic temperature factors are expressed in the form $T = \exp\left[-2\pi(U_{11}a^{*2}h^2 + 2U_{12}a^*b^*hk + \ldots) \times 10^4\right]$.

	Site	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	4*a*	0	0	0	184 (2)	184 (2)	197 (1)	0	0	0
Fe	4*b*	0	0	$\frac{1}{2}$	117 (1)	117 (1)	118 (1)	0	0	0
S	8*d*	0·2574 (2)	$\frac{1}{4}$	$\frac{1}{8}$	113 (6)	132 (6)	136 (1)	0	0	14 (1)

Table 2. *Observed and calculated structure factors*

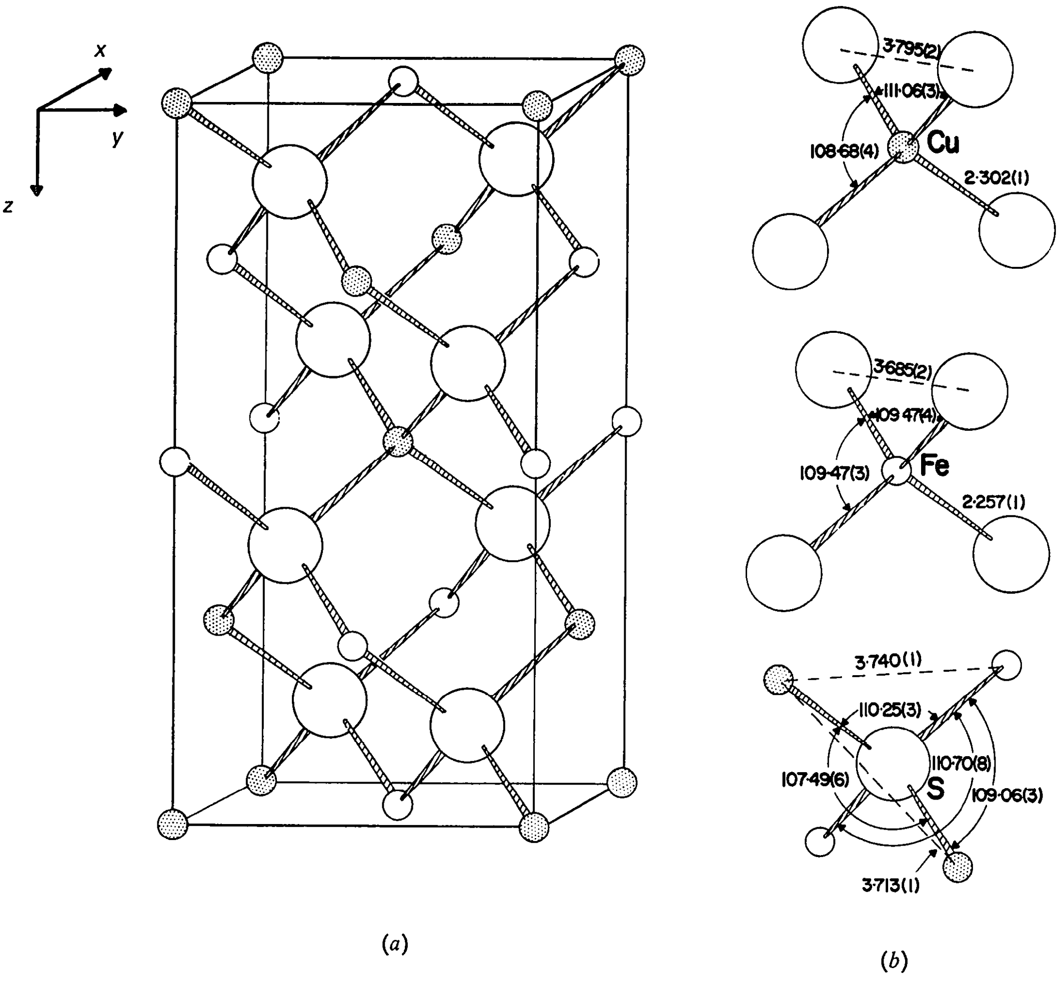
Structure factors are listed in blocks of constant *hk* in columns of *l*, $[F_o] \times 10$ and $[F_c] \times 10$. The asterisk (*) denotes reflexions considered 'unobserved' at the 10% significance level, and an *E* denotes reflexions corrected for secondary extinction and omitted from the final refinement.

0,0,L		
4	842	848
8	1577E	1619
12	236	230
16	573	565
20	68	81
24	164	166
0,1,L		
1	79	95
3	109	121
5	83	82
7	31	23
9	29*	7
11	30*	8
13	33*	14
15	38	36
17	38	35
19	35*	29
21	36	31
23	41	32
25	30*	26
0,2,L		
0	836	851
2	22*	0
4	2011E	2123
6	26*	0
8	435	430
10	29*	0
12	873	904
14	34*	0
16	113	116
18	35*	0
20	235	295
22	33*	0
24	48	50
0,3,L		
1	136	105
3	25*	8
5	31*	7
7	55	57
9	37	25
11	42	45
13	33	38
15	35*	10
17	35	26
19	41	45
21	35*	35
23	31*	22
25	29*	23
0,4,L		
0	1547E	1654
2	27*	1
4	444	440
6	28*	1
8	1040	1095
10	31*	1
12	148	154
14	36*	0
16	429	435
18	34*	0
20	62	69
22	32*	0
24	132	135
0,5,L		
1	39	43
3	64	66
5	48	46
7	58	59
9	39	48
11	32*	15
13	34*	10
15	60	58
17	45	42
19	34*	16
21	33*	24
23	30	34
0,6,L		
0	255	243
2	29*	2
4	901	937
6	31*	2
8	159	158
10	33*	1
12	510	508
14	34*	1
16	69	82
18	33*	0
20	187	191
22	29*	0
0,7,L		
1	39	35
3	62	71
5	56	62
7	33*	23
9	34*	2
11	60	66
13	46	45
15	33*	7
17	33*	21
19	38	43
21	29	30
0,8,L		
0	633	601
2	37*	2
4	123	122
6	36*	2
8	451	455
10	33*	1
12	78	84
14	33*	1
16	215	219
18	41*	0
20	44	45
0,9,L		
1	65	66
3	33*	12
5	33*	3
7	60	66
9	57	53
11	33*	2
13	32*	15
15	46	47
17	35	33
19	27*	10
0,10,L		
0	81	86
2	32*	2
4	316	320
6	32*	1
8	63	73
10	32*	1
12	200	201
14	30*	0
16	43	45
0,11,L		
1	31*	2
3	49	54
5	51	49
7	31*	3
9	34*	11
11	45	44
13	30	34
0,12,L		
0	166	186
2	30*	1
4	53	55
6	29*	1
8	147	149
10	28*	1
0,13,L		
1	37	37
3	27*	5
5	26*	8
1,1,L		
2	1972E	1994
6	1430E	1443
10	866	862
14	540	542
18	248	283
22	169	172
26	79	83
1,2,L		
1	110	111
3	67	65
5	48	43
7	50	43
9	37	34
11	30	27
13	36	31
15	34*	23
17	37	32
19	39*	39
21	41*	34
23	37	27
25	41	25
1,3,L		
0	24*	1
2	1402E	1461
4	26*	1
6	1056	1089
8	29*	0
10	752	762
12	32*	0
14	429	432
16	35*	0
18	258	276
20	34*	0
22	138	141
24	30*	0
1,4,L		
1	50	59
3	51	55
5	53	61
7	39	41
9	37	42
11	32*	23
13	34	39
15	35	39
17	38	40
19	34*	33
21	33*	31
23	31	29
1,5,L		
0	28*	2
2	873	888
4	29*	1
6	764	776
8	30*	1
10	502	513
12	33*	1
14	365	362
16	34*	0
18	194	200
20	33*	0
22	125	126
24	28*	0
1,6,L		
1	61	60
3	52	56
5	53	54
7	34	36
9	55	50
11	50	42
13	41	46
15	39	31
17	38	36
19	39	33
21	34	30
23	28*	22
1,7,L		
0	31*	2
2	562	570
4	32*	2
6	446	449
8	35*	1
10	379	370
12	33*	1
14	224	230
16	33*	0
18	157	160
20	30*	0
22	81	86
1,8,L		
1	59	54
3	40	44
5	55	51
7	49	40
9	51	49
11	36	34
13	36	39
15	36	34
17	32	34
19	31*	25
1,9,L		
0	33*	2
2	304	304
4	34*	2
6	290	294
8	33*	1
10	202	209
12	32*	1
14	167	164
16	30*	0
18	96	97
1,10,L		
1	37	41
3	48	43
5	41	45
7	39	35
9	40	37
11	44	33
13	38	35
15	31	25
17	29	25
1,11,L		
0	32*	1
2	188	189
4	31*	1
6	158	154
8	31*	1
10	136	136
12	28*	1
14	89	90
1,12,L		
1	39*	34
3	34	30
5	30	30
7	34	29
9	35	30
11	27	23
1,13,L		
0	27*	1
2	92	94
4	27*	1
2,2,L		
0	2122E	2138
4	640	640
8	1280	1318
12	192	185
16	505	495
20	71	75
24	151	150
2,3,L		
1	26	21
3	92	80
5	67	65
7	40	37
9	33	34
11	31*	15
13	33*	21
15	63	50
17	44	41
19	34*	22
21	33*	28
23	35	34
25	28	25
2,4,L		
0	471	444
2	27*	1
4	1278	1337
6	29*	1
8	247	237
10	31*	0
12	658	667
14	34*	0
16	92	96
18	34*	0
20	238	237
22	31*	0
24	35	44
2,5,L		
1	59	62
3	56	56
5	43	49
7	40	37
9	32*	21
11	64	63
13	48	48
15	34*	9
17	34*	24
19	39	45
21	36	33
23	29*	17
2,6,L		
0	932	941
2	30*	2
4	203	193
6	31*	1
8	669	681
10	36*	1
12	108	107
14	34*	0
16	302	304
18	33*	0
20	57	56
22	29*	0
2,7,L		
1	63	67
3	35*	31
5	35*	22
7	72	70
9	64	56
11	34*	7
13	33*	16
15	54	54
17	43	39
19	31*	13
21	29*	20
2,8,L		
0	122	122
2	34*	2
4	540	523
6	33*	1
8	98	99
10	33*	1
12	304	311
14	37*	0
16	57	61
18	30*	0
20	126	127
2,9,L		
1	33*	11
3	69	66
5	56	59
7	33*	7
9	33*	10
11	48	56
13	32	42
15	31*	9
17	29*	17
2,10,L		
0	322	321
2	36*	1
4	73	80
6	32*	1
8	251	253
10	32*	1
12	47	58
14	29*	0
16	130	130
2,11,L		
1	55	52
3	31*	5
5	31*	8
7	36	49
9	34	41
11	29*	7
13	29*	13
2,12,L		
0	49	55
2	29*	1
4	168	167
6	28*	1
8	47	47
10	26*	1
2,13,L		
1	27*	7
3	28	36
3,3,L		
2	1106	1100
6	938	930
10	600	600
14	420	412
18	222	223
22	137	140
3,4,L		
1	67	68
3	56	52
5	46	47
7	32	35
9	42	39
11	50	51
13	46	47
15	34*	20
17	39	31
19	48	41
21	39	33
23	29*	21
3,5,L		
0	29*	1
2	796	783
4	29*	1
6	614	611
8	31*	1
10	486	483
12	34*	0
14	287	290
16	33*	0
18	203	198
20	33*	0
22	99	104
3,6,L		
1	56	58
3	38	41
5	57	49
7	60	55
9	60	54
11	34*	24
13	37	36
15	38	44
17	38	39
19	32*	23
21	38*	25
3,7,L		
0	31*	1
2	458	453
4	34*	1
6	453	428
8	32*	1
10	296	296
12	35*	1
14	227	227
16	32*	0
18	125	131
20	26*	0
3,8,L		
1	47	43
3	56	55
5	56	55
7	33	32
9	35	39
11	49	44
13	44	43
15	33*	24
17	35	28
19	33	29
3,9,L		
0	32*	1
2	296	296
4	33*	1
6	231	237
8	35*	1
10	206	207
12	32*	1
14	130	134
16	29*	0
18	97	97
3,10,L		
1	53	46
3	38	33
5	36	35
7	44	40
9	47	40
11	35*	25
13	34*	23
15	31	28
3,11,L		
0	31*	1
2	150	155
4	31*	1
6	152	153
8	30*	1
10	107	111
12	29*	0
3,12,L		
1	33*	27
3	37	32
5	34	33
7	28*	24
9	28	24
4,4,L		
0	1126	1115
4	297	242
8	787	790
12	128	119
16	337	341
20	58	60
4,5,L		
1	58	59
3	34	41
5	40	40
7	69	64
9	52	55
11	34*	14
13	37	26
15	49	52
17	40	41
19	31*	18
21	33*	23
4,6,L		
0	168	161
2	31*	1
4	688	689
6	32*	1
8	127	121
10	34*	0
12	392	395
14	33*	0
16	67	71
18	32*	0
20	151	155
4,7,L		
1	34	27
3	70	68
5	60	61
7	33*	16
9	33*	20
11	61	59
13	51	40
15	32*	12
17	31*	22
19	48	37
4,8,L		
0	474	461
2	32*	1
4	100	100
6	34*	1
8	350	356
10	32*	1
12	74	72
14	31*	0
16	175	177
18	29*	0
4,9,L		
1	59	60
3	32*	12
5	32*	13
7	54	57
9	43	48
11	31*	9
13	32*	17
15	40	41
17	32	30
4,10,L		
0	71	74
2	34*	1
4	256	256
6	32*	1
8	59	63
10	30*	1
12	164	163
14	23*	0
4,11,L		
1	30*	9
3	48	47
5	32	43
7	30*	9
9	31*	13
11	40	39
4,12,L		
0	151	151
2	28*	1
4	46	47
6	27*	1
8	121	122
5,5,L		
2	540	526
6	503	491
10	346	336
14	259	254
18	143	144
22	94	94
5,6,L		
1	43	38
3	64	65
5	58	54
7	33*	24
9	33	32
11	49	54
13	39	46
15	32*	19
17	38*	26
19	34	35
21	27	27
5,7,L		
0	34*	1
2	402	379
4	35*	1
6	305	301
8	33*	0
10	255	259
12	32*	0
14	163	164
16	31*	0
18	113	119
5,8,L		
1	52	55
3	36	29
5	36	33
7	52	51
9	43	47
11	32*	22
13	37*	29
15	39	37
17	29	31
5,9,L		
0	32*	1
2	213	213
4	33*	1
6	212	210
8	31*	1
10	145	151
12	30*	0
14	125	122
16	27*	0
5,10,L		
1	36*	21
3	37	42
5	43	42
7	32*	24
9	30*	26
11	34	34
13	28	31
5,11,L		
0	39*	1
2	149	139
4	29*	1
6	109	113
8	29*	0
10	100	101
5,12,L		
1	31	31
3	31	21
5	26*	21
6,6,L		
0	557	525
4	119	110
8	407	402
12	79	79
16	195	197
20	39	42
6,7,L		
1	59	60
3	33*	21
5	33	24
7	61	57
9	49	50
11	32*	15
13	32*	23
15	39	42
17	32	32
6,8,L		
0	84	86
2	32*	0
4	321	320
6	33*	0
8	73	73
10	31*	9
12	204	201
14	29*	0
16	49	46
6,9,L		
1	31*	15
3	53	52
5	48	48
7	31*	13
9	31*	19
11	44	42
13	35	34
15	27*	12
6,10,L		
0	209	207
2	30*	1
4	56	59
6	29*	0
8	167	166
10	28*	0
12	42	43
6,11,L		
1	34	39
3	30*	11
5	38*	12
7	36	37
7,7,L		
2	240	239
6	241	234
10	165	167
14	140	135
7,8,L		
1	32*	23
3	57	50
5	51	47
7	31*	19
9	33	24
11	42	40
13	35	34
15	27*	15
7,9,L		
0	31*	0
2	173	170
4	30*	0
6	138	138
8	29*	0
10	129	124
12	27*	0
7,10,L		
1	45	38
3	37*	20
5	29*	21
7	35	34
9	33	32
7,11,L		
0	27*	0
2	92	93
4	26*	0
8,8,L		
0	234	230
4	66	64
8	184	184
12	43	46
8,9,L		
1	40	41
3	29*	16
5	32*	17
7	40	38
9	36	33
11	27*	13
8,10,L		
0	44	47
2	27*	0
4	131	136
6	23*	0
9,9,L		
2	101	103
6	105	102

the reversal of shift x_S from that previously determined (Pauling & Brockway, 1932; Donnay *et al.*, 1958) appeared to have some validity. However, examination of the structure factors that are particularly sensitive to the contribution of the sulphur atoms (*i.e.* *hkl* with $l=2n+1$) showed these to have a much higher R value (0·231) than the rest (0·053). A calculation of the separate metal and sulphur structure factor components showed that, to improve agreement for these reflexions, x_S must exceed $\frac{1}{4}$. The least-squares refinement process was therefore repeated starting with the x_S value of 0·27 previously reported by Pauling & Brockway (1932). The refinement converged to an R value of 0·059, giving Cu, Fe, and S temperature factors of 1·25, 0·93, and 0·89 Å^2; and $x_S=0{\cdot}2576$. This clearly demonstrated that, because of minima on each side of $x_S=\frac{1}{4}$, the least-squares process alone need not provide a reliable initial shift from a special position, though it should be pointed out that this inadequacy is probably compounded in chalcopyrite by the one-dimensional nature of the shift.

At this stage in the refinement, it was necessary to consider the effect of anomalous dispersion. Both enantiomorphic structures in the non-centrosymmetrical space group $I\bar{4}2d$ may be described with right-handed sets of axes and are both present in chalcopyrite. It follows that the choice of a right-hand set of axes at data-collection time, as a basis for indexing reflexions, is arbitrary, provided that the anomalous dispersion corrections are made accordingly. This is because the imaginary anomalous scattering factor $\Delta f''$ reverses in phase for the two possible enantiomorphic structures, and consequently the intensities of the Friedel-equivalent reflexions are different. Since the imaginary components $\Delta f''(\mathrm{Cu}) = 1{\cdot}36\mathrm{e}$ and $\Delta f''(\mathrm{Fe}) = 0{\cdot}92\mathrm{e}$ (Cromer, 1965), do provide a measurable difference between the Friedel-equivalent intensities in this structure it is important to ensure their correct application.

Two methods were employed in order to ensure the correct application of anomalous dispersion corrections. The first was to apply the least-squares refinement process, involving the $\Delta f'$ and $\Delta f''$ components,



(*a*) (*b*)

Fig. 1. (*a*) Unit-cell model showing the crystal structure of chalcopyrite in the configuration specific to the data set listed in Table 2. (*b*) Interatomic bond lengths and angles of each atom in chalcopyrite.

to the $+h$, $+k$, $+l$ data set for both configurations $+x_S$ and $-x_S$. This resulted in agreement values of $R(+x_S)=0{\cdot}035$ and $R(-x_S)=0{\cdot}055$, thus indicating that the configuration with $+x_S$ is correct for the choice of axes in this analysis. The second method is to match the structure factors calculated for $+x_S$ and $-x_S$, to the measured data sets hkl and $\bar{h}\bar{k}\bar{l}$. In chalcopyrite, the anomalous dispersion differences are enhanced for the reflexions with $h, k=2n+1$ and $l=4n+2$ because the sulphur atom contribution to these structure factors is large, and $\pi/2$ out of phase with that of the metals. 85 out of 88 of these reflexions had $F_c(+x_S)$ closer to $F_o(hkl)$ and $F_c(-x_S)$ closer to $F_o(\bar{h}\bar{k}\bar{l})$, than *vice-versa*. This confirmed that the enantiomorphic structure with $+x_S$ was the correct one for the specified right-handed axial system.

The large structure factors showed a systematic error that indicated secondary extinction effects. A plot of I_c/I_o *versus* I_c was consistent with the empirical relationship $I_c/I_o=\varepsilon I_c+K^2$, where the secondary extinction coefficient $\varepsilon=0{\cdot}37\times10^{-7}$ and F_o scale $K=0{\cdot}975$. Appropriate corrections were made to seven observed structure factors (see Table 2) and these reflexions were excluded from subsequent refinement. Further least-squares refinement, using isotropic temperature factors, resulted in a significant improvement of the overall structure factor agreement of the lower intensity reflexions, and an R value of 0·034. Examination of the difference map showed essentially spherical shells of negative residual about the atomic sites, similar to that observed in the study of talnakhite (Hall & Gabe, 1972). This type of residual can arise from deficiencies in the scattering factor curves being used. In previous studies it has been suggested that chalcopyrite exists in the ionic configurations $Cu^{2+}Fe^{2+}S_2^{2-}$ and/or $Cu^{+}Fe^{3+}S_2^{2-}$. The ionized scattering factors for Cu^{+} and Fe^{3+} (Cromer & Waber, 1965) and for S^{2-} (Tomiie & Stam, 1958) were therefore used in further least-squares refinement, and this finally resulted in an R value of 0·031. This value approached that of the observed structure factors $[R(F_{\text{obs}})=0{\cdot}029]$ and in dicated that further refinement was not warranted.

To ensure that the unit weights used in the least-squares refinement provided sufficient weight to the weak 'superlattice' structure factors (*i.e.* those reflexions not present in the sphalerite-like structure), the refinement process was repeated with these reflexions at double weight. No significant changes in parameters resulted. To further ensure that the use of an 'unobserved' reflexion criteria did not influence the refinement process, least-squares refinement using unit weights was repeated with the data set in which all intensities were as measured (except for the negative values which were set to zero). This resulted in a final R value of 0·086 and an x_S value of 0·2578 (2). The change in x_S from the 'observed–unobserved' data set is not considered significant, particularly as the standard deviations calculated from the least-squares matrix tend to be underestimated.

The final refined atomic parameters are shown in Table 1, and the structure factor magnitudes are listed in Table 2. (The final difference electron density map is shown in Fig. 4.)

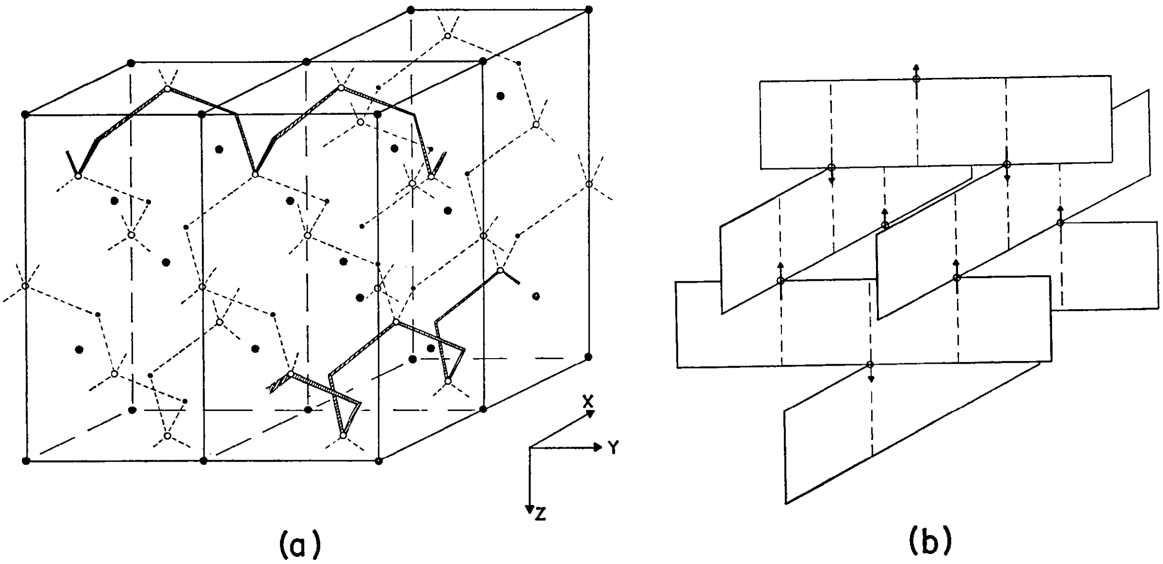


Fig. 2. (*a*) Diagrammatic representation of three chalcopyrite unit cells with the iron atoms as ○, the copper atoms as ● and the sulphur atoms as •. Most of the iron–sulphur bonds are shown dashed (---) but some appear in shaded tabular form to emphasize the antiferromagnetically coupled –Fe–S–Fe–S– chains running through the structure in the **x** and **y** directions. (*b*) Another representation of the interconnecting bands of antiferromagnetically-arranged iron atoms showing the directions of the magnetic moments as arrows.

Description of the structure

The nature of bonding between atoms in chalcopyrite is still a matter of some conjecture. Pauling & Brockway (1932) considered the bonding interactions in chalcopyrite to be essentially covalent with the atoms fluctuating between the two ionic states $Cu^+Fe^{3+}S_2^{2-}$ and $Cu^{2+}Fe^{2+}S_2^{2-}$. This conclusion was based largely on a comparison of the Cu–S and Fe–S distances [2·32 (3) and 2·20 (3) Å, respectively] and tetrahedral electron-pair bond radii deduced from other structures. Strong covalent bonding was also deduced by Donnay *et al.* (1958) in their study of the magnetic structure of chalcopyrite. The spins were coupled antiferromagnetically and the magnetic moments (μ) were 0·02 and 3·85 B.M. for copper and iron atoms, respectively. They proposed that this was consistent with the ionic configuration $Cu^+Fe^{3+}S_2^{2-}$ [$\mu(Cu^+)=0{\cdot}0, \mu(Fe^{3+}) = 5{\cdot}9$ B.M.] and with covalent sp^3-hybrid bonding which reduces the *d*-electron contribution to the iron magnetic moment. The electrical and magnetic measurements by Teranishi (1961), on the semi-conductor properties of chalcopyrite appeared to confirm the dominant covalent bonding but were not consistent with a mixture of ionic states. The reader should be reminded at this stage that, although specific ionic configurations are usually cited in the discussions of chalcopyrite bonding interactions, this has been for convenience rather than accuracy. It is now well recognized by workers in this field, that the effective changes associated with ions in chalcopyrite are almost certainly not integral, both because of the exchange interactions (covalent, electrostatic and magnetic) and the presence of electrons in the conduction band. These can have a range of delocalization effects on the charge distribution and thus provide equally convincing arguments for balanced ionic configurations such as $Cu^+Fe^{2+}S_2^{1\cdot5-}$.

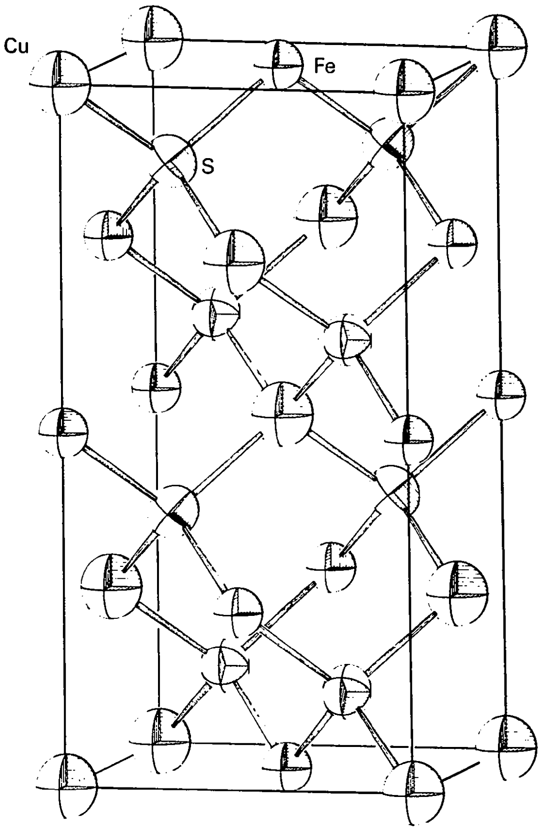


Fig. 3. Unit-cell model of chalcopyrite showing the thermal ellipsoids of the atoms, plotted at the 99% probability level.

This study is not intended to resolve the uncertainties of ionic configurations or bonding in chalcopyrite but it should contribute, through more precise parameters, towards their better understanding. The final atomic coordinates, listed in Table 1, show the x parameter of sulphur to be significantly closer to the idealized sphalerite-like site than that previously determined. This results in similar, but significantly different Cu–S and Fe–S distances of 2·302 (1) and 2·257 (1) Å, respectively [see Fig. 1(*b*)]. Based on this information alone, the effective ionic configuration in chalcopyrite would appear to be closer to $Cu^{2+}Fe^{2+}S_2^{2-}$ than to $Cu^+Fe^{3+}S_2^{2-}$. In a sense, this may be anticipated from the delocalization effects of covalent bonding on the ionic configuration $Cu^+Fe^{3+}S_2^{2-}$. However, stereochemical arguments of this type, which make inferences about the bonding interactions, must be used with caution both because of the range of forces possible in the structure and the complexity of their interrelationships. In particular, the Anderson super-exchange magnetic coupling is present in this structure between the antiferromagnetically-arranged iron atoms. Although this is a relatively weak interaction, small changes in stereochemistry could result, directly or indirectly, from such coupling forces. One of the more important stereochemical features to be considered in this structure, is the angle that the sulphur atoms subtend with the metals. Fig. 1(*b*) shows that the two independent S–Fe–S angles of the iron tetrahedron are 109·47 (4) and 109·47 (3)°, while the S–Cu–S angles in the copper tetrahedron are 111·06 (3) and 108·68 (4)°. The iron coordination is, therefore, *perfectly* tetrahedral (the ideal tetrahedral angle is 109·47°) and the copper coordination is that of a tetrahedron 'flattened' in the **z** direction of the cell.

The 'expected' coordination of iron and copper atoms in this type of structure, is of interest here. Both Fe^{2+} and Fe^{3+} ions can have tetrahedral coordination, though this is not common, and are in general regular in shape. On the other hand, the coordination of the Cu^+ and Cu^{2+} ions are expected to be different. Cu^+ is commonly regular-tetrahedral, while Cu^{2+} is only rarely (usually it is octahedral or square planar), and then generally distorted. This distortion is similar to the 'flattening' of the copper tetrahedron observed in this study. The regularity of the iron tetrahedron reinforces the significance of this distortion, though it cannot be assumed yet that this is strictly a result of ionic–covalent bonding. The Anderson super-exchange coupling, between iron atoms of opposite spin, is at a maximum when the moments are directly opposed. As a consequence, the iron atoms attempt to subtend an angle approaching 180°, in order to minimize the energy of the interaction. One expects, therefore, that the Fe–S–Fe angle in this structure will be greater than the tetrahedral angle. This is the case [110·70 (8)°], but only by +0·96°, a value which is consistent with the covalent bonding being the more dominant interaction. Even so, an examination of the –Fe–S–Fe–S– inter-meshing chains that run in the **x** and **y** directions of the structure (see Fig. 2) suggests that, while the magnetic coupling causes little distortion to the tetrahedral coordination, it may be an important factor in determining the metal-ordering in the structure. This proposal is supported by the existence of similar, but more complex, chalcopyrite-like (pseudo-polytypic) structures that are largely antiferromagnetic. If the magnetic interaction is important in the ordering of metal atoms at the interstitial sites of the sulphur *fcc* matrix, during the formation of chalcopyrite, then the dominant role of ionic–covalent bonding in the stereochemistry of this structure may be clearer. The increase of Fe–S–Fe angles beyond the ideal value results, *via* the –Fe–S–Fe–S– chains, in an increase of the *a* and *b* cell dimensions over *c*/2. This distortion of the sulphur matrix is best accommodated, and in a sense controlled, by the combination of regular tetrahedrally-coordinated iron atoms and distorted tetrahedrally-coordinated copper atoms. Although this argument is largely intuitive, it is consistent with the qualitative stereochemical results. It is not possible to make firm conclusions based on this bonding hierarchy but all indications are that the structure exists in a strongly covalent configuration with an effective ionic state between $Cu^+Fe^{3+}S_2^{2-}$ and $Cu^{2+}Fe^{2+}S_2^{2-}$.

The anisotropic temperature factors, listed in Table 1 and displayed as thermal ellipsoids in Fig. 3, show that the thermal motion of all atoms is essentially isotropic. This observation is supported by the reduction of the *R* value to 0·038 using isotropic temperature factors in the least-squares refinement process. Table 3 compares the mean isotropic temperature factor $\langle B\rangle$ $(=8\pi^2\langle U\rangle)$ of each atom with those of a recent refinement of cubanite, $CuFe_2S_3$ (Szymanski, 1972). The agreement between equivalent values is quite remarkable and from observations with other chalcopyrite-like minerals, apparently consistent with the atom species for this type of structure. For this reason, the isotropic temperature factors should prove to be an important parameter in identifying metal atoms in other Cu–Fe sulphide minerals. One explanation for the relative magnitude of these temperature factors is that the antiferromagnetic coupling restricts the thermal motion of the iron atoms and has a successively smaller effect on the sulphur and copper atoms. Alternatively, this may also be explained in terms of a stronger ionic–covalent bond between the iron and sulphur atoms than between the copper and sulphur atoms.

Table 3. *Mean isotropic temperature factors* $\langle \mathbf{B}\rangle$

	Chalcopyrite, $CuFeS_2$ (This study)	Cubanite, $CuFe_2S_3$ (Szymanski, 1972)
Cu	1·48 (2) Å^2	1·44 (2) Å^2
Fe	0·92 (1)	0·92 (1)
S	1·00 (4)	1·02 (3)

Several anisotropic distortions of the spherical thermal motion appear to be significant. The thermal el-

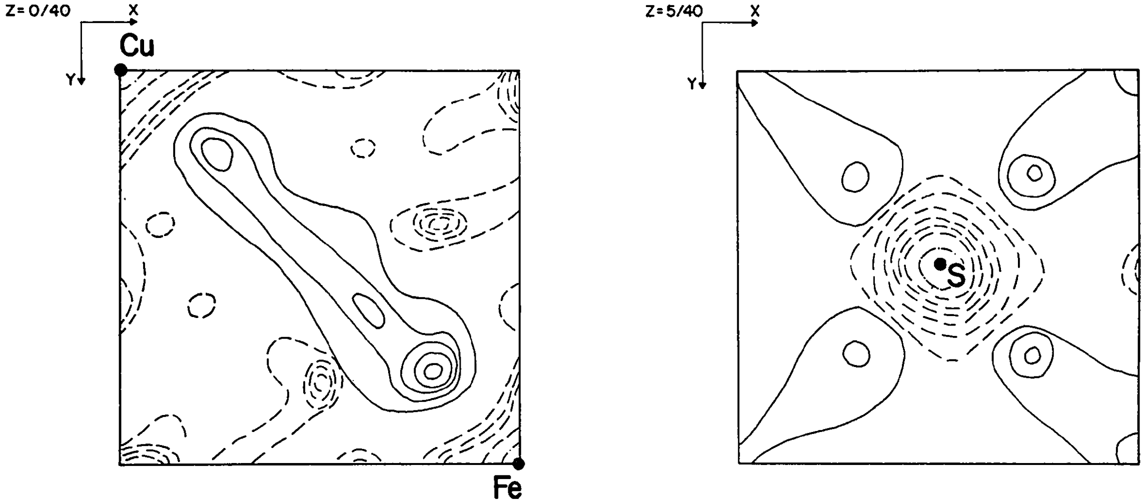


Fig. 4. Sections at $z/c=0$ and $\frac{1}{8}$ of the final difference electron-density map showing positive contours as full lines, negative contours as dashed lines (---) and re-entrant negative contours as dot-dash lines (–·–·). All contours are in intervals of 0·2 e Å^{-3}. The zero contour is not shown.

lipsoid of the sulphur is flattened in the direction of the iron–iron edge of the sulphur tetrahedron. This may be because this is the direction of least freedom due to magnetic coupling through the sulphur. However, it also agrees with the effective boundary between the two thermally-active copper atoms and the less active iron atoms, to which the sulphur is bonded. Another distortion to the isotropic temperature factors that appears real, is the elongation of the copper thermal ellipsoid along the **z** direction. This is the direction of least steric interference from the sulphurs in the 'flattened' copper tetrahedron.

The concept of a strong ionic-covalent bonding is also supported by residuals in the final difference electron-density map displayed, in part, in Fig. 4. This shows distinct positive maxima in line with the metal–sulphur contact directions and near the atom sites. These features are similar to those observed in residual maps of other accurate structure analyses where spherical scattering factors had been used to describe strong covalently bonded atoms. The positive maxima in this structure are largest along the iron–sulphur directions and, in particular, close to the sulphur and iron sites. This indicates a larger distortion of the sulphur electron-density distribution in this direction, consistent with a stronger bonding interaction between the iron and sulphur atoms. For this reason, future refinements of the chalcopyrite structure will almost certainly require the use of aspherical scattering factors in order to describe more accurately the electron-density distribution of the atoms.

There are also features in the final difference map that may not be attributable to asymmetric electron-density distributions alone. In particular, the pronounced negative residuals at the atomic centres could be due wholly to a F_o-scale shift to compensate for the bonding electrons, but it would appear likely that a significant proportion results from other symmetric differences between the measured data and the structural model. This could be due to still unaccounted for systematic absorption or extinction effects, but these should be relatively small. Alternatively, the correlation of such symmetric parameters as site occupancy, temperature factors, state of ionization and F_o scale in the least-squares process, when applied to experimental data, can result in this type of residual. This explanation is considered probable in view of similar effects in the study of talnakhite (Hall & Gabe, 1972). On the other hand these results, and those on cubanite (Szymanski, 1972), suggest that it is entirely possible that these features arise from inaccuracies in the presently-available spherical atomic scattering factors, and these become evident only at this level of refinement.

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References

BURDICK, C. L. & ELLIS, J. H. (1917). *J. Amer. Chem. Soc.* **39**, 2518.

CABRI, L. J. & HALL, S. R. (1972). *Amer. Min.* **57**, 689–708.

CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

DONNAY, G., CORLISS, L. M., DONNAY, J. D. H., ELLIOTT, N. & HASTINGS, J. M. (1958). *Phys. Rev.* **112**, 1917–1923.

HALL, S. R. & GABE, E. J. (1972). *Amer. Min.* **57**, 368–380.

PAULING, L. & BROCKWAY, L. O. (1932). *Z. Kristallogr.* **82**, 188–194.

STEWART, J. M., KRUGER, G., AMMON, H., DICKINSON, C. H. & HALL, S. R. (1972). Univ. of Maryland Comput. Sci. Tech. Rep. TR-192.

SZYMANSKI, J. T. (1972). Private communication.

TERANISHI, T. (1961). *J. Phys. Soc. Japan*, **16**, 1881–1887.

TOMIIE, Y. & STAM, C. H. (1958). *Acta Cryst.* **11**, 126–127.