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THE CRYSTAL STRUCTURE OF MAWSONITE, $Cu_6Fe_2SnS_8$

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ABSTRACT

The crystal structure of mawsonite, $Cu_6Fe_2SnS_8$, has been determined and refined to an *R*-value of 0.049 (all 1426 data) and 0.037 (1004 "observed" data only) from multiple sets of four-circle diffractometer X-ray intensity data. Microprobe analysis indicates that the formula is stoichiometric in terms of the metals, but with 1.5% of the sulfur replaced by selenium in the specimen examined. The structure is tetragonal, *a* 7.603(2), *c* 5.358(1)Å, space group $P\bar{4}m2$, and is based on a nearly *ccp* sulfur matrix with metals filling half of the tetrahedral interstices and an extra interstitial Fe atom at the (½,½,½) position. The latter gives rise to close Fe . . . Fe . . . Fe contacts (2.679(1)Å) in the *z* direction, but no close Fe . . . Fe contacts normal to this. The deviations from an ideal *ccp* structure are due to the large Sn atom at the origin, and the extra Fe atom at ½,½,½. The bond lengths, angles and thermal parameters are in close agreement with those found in stannite, $Cu_2(Fe,Zn)SnS_4$, and kesterite, $Cu_2(Zn,Fe)SnS_4$.

SOMMAIRE

La structure cristalline de la mawsonite, $Cu_6Fe_2SnS_8$, a été déterminée et affinée jusqu'à un indice *R* de 0.049 (pour toutes les 1426 données) et de 0.037 (pour les 1004 données "observées", seulement) au moyen de plusieurs séries de données d'intensité recueillies sur diffractomètre aux rayons X à quatre cercles. L'analyse à la microsonde indique que la formule est stoechiométrique en ce qui concerne les métaux, mais que 1.5% du soufre contenu dans l'échantillon étudié est remplacé par du sélénium. La structure est tétragonale, *a* 7.603(8), *c* 5.358(1)Å, dans le groupe spatial $P\bar{4}m2$; elle consiste en un assemblage quasi-cubique compact d'atomes de soufre, dont les interstices tétraédriques sont remplis pour moitié par les métaux tandis qu'un atome de fer supplémentaire est interstitiel en position (½,½,½). Celui-ci donne lieu à de courtes distances Fe . . . Fe . . . Fe (2.679(1)Å) dans la direction *z*, mais non perpendiculairement à cette direction. La structure s'écarte de la structure idéale à empilement cubique compact; deux atomes en sont la cause: le gros atome Sn à l'origine et l'atome Fe en ½,½,½. Les valeurs des longueurs de liaison, des angles et des paramètres thermiques concordent avec celles que l'on observe dans la stannite $Cu_2(Fe,Zn)SnS_4$ et la kestérite $Cu_2(Zn,Fe)SnS_4$.

INTRODUCTION

Mawsonite, $Cu_6Fe_2SnS_8$, was first described by Markham & Lawrence (1965), and identified by them as being present in the material described as "orange bornite" by Murdock (1916). The chemical composition has been variously reported as $Cu_7Fe_2SnS_{10}$ (Markham & Lawrence 1965), $Cu_{5.91}Fe_{1.89}Sn_{0.98}S_{8.20}$ (Lévy 1967), $Cu_6Fe_2SnS_8$ (Springer 1968), and $Cu_{2.86}FeSn_{0.55}S_{4.06}$ (Kachalovskaya *et al.* 1973). The more recent analyses of Petruk (1973) and of Yamanaka & Kato (1976) are in agreement with the present analyses and with the present structural determination.

Mawsonite powder patterns generally have been indexed on a pseudo-cubic cell, *a* 10.74± .01Å, but because of its anisotropic optical properties, mawsonite cannot be truly cubic (Markham & Lawrence 1965). Recently, Yamanaka & Kato (1976) have indexed the mawsonite pattern using a tetragonal cell, *a* 10.745, *c* 10.711Å.

Structural examination of mawsonite was undertaken in our laboratory, to provide accurate information on a metal-rich copper-iron-tin sulfide mineral, for comparison with the related non metal-rich minerals, stannite and kesterite (Hall *et al.* 1975), in the same way that the chalcopyrite series of minerals was investigated (Hall 1975). In the latter series, two metal-rich copper-iron sulfides, haycockite, $Cu_4Fe_5S_8$, and mooihoekite, $Cu_9Fe_9S_{16}$, were both believed to have iron atoms filling additional tetrahedral interstices, though it was difficult to prove this unequivocally. It was hoped that the present investigation would indicate more clearly the preference of iron over copper to occupy additional interstitial sites.

EXPERIMENTAL

Three single-crystal fragments of mawsonite were successively examined by microprobe analysis and crystal structure determination. The first two fragments proved to be too small for an accurate parameter refinement, though the structure was solved using these data. The results of the third crystal structure determination,

TABLE 1. MICROPROBE ANALYSES FOR MAWSONITE

Element	Specimen 1		Specimen 2		Specimen 3	
	Wt.%	Formula	Wt.%	Formula	Wt.%	Formula
Cu	43.2	5.89	42.8	5.89	44.0	6.02
Sn	13.8	1.01	13.8	1.01	13.7	1.01
Fe	13.1	2.02	13.0	2.03	12.9	2.02
S	29.8	8.07	29.2	7.95	28.8	7.83
Se	-	-	1.0	0.11	1.1	0.12
Total	99.9		99.8		100.5	

Specimen 1. Hotuko vein, Kanagase 1 Kuno mine, Hyogo Prefecture, Japan (Smithsonian Institute, Specimen #122102).

Specimens 2, 3: Kidd Creek mine, Timmins, Ontario.

TABLE 2. CRYSTAL DATA FOR MAWSONITE, $Cu_6Fe_2SnS_8$

Composition: (microprobe analysis given in Table 1)

Source: Kidd Creek mine, Timmins, Ontario

Formula weight: 868.1

Crystal system: tetragonal

Systematic absences: none

Space group: (possibly) $P422$(#89), $P4mm$(#99), $P\bar{4}2m$(#111), $P\bar{4}m2$(#115), $P4/mmm$(#123)
$P\bar{4}m2$(#115) confirmed by structure analysis.

Cell dimensions: a = 7.603(2), c = 5.358(1)Å at 20°C using $\lambda(MoK\alpha_1)$ = 0.70926Å

Linear absorption coefficient: $\mu(MoK\alpha)$ = 160.3 cm^{-1}

Density: D_{calc} = 4.65g/cm^{-3}; Z = 1
(Density not measured)

on a mawsonite specimen from the Kidd Creek mine, Timmins, Ontario, are reported here.

The microprobe analyses for the three mawsonite specimens examined are listed in Table 1. The second and third were found to have a small but significant quantity of selenium replacing sulfur. This appears to be the first established occurrence of selenium in mawsonite.

The third specimen of mawsonite, after extraction from a polished section, was cut with a knife, to provide more regular "faces" so as to facilitate subsequent absorption corrections. The resultant fragment was an irregular hexagonal tablet 0.3×0.2×0.005 mm. Gandolfi powder photographs of the single crystal were the same as those previously published for mawsonite (Markham & Lawrence 1965), and contained no additional lines that could be attributed to impurities.

The crystal was mounted on a four-circle automatic diffractometer in a general orientation. The cell dimensions were determined from a least-squares refinement of the 2θ, χ and ω angles (Busing 1970) for 90 reflections in the range $55° < 2\theta < 93°$. The parameters were refined on a triclinic cell. The difference between the a and b cell edges was less than 0.2σ, and the maximum deviation from orthogonality was less than 1′ of arc. The errors quoted in the Table 2 represent 3σ as derived from the least-squares matrix. Long-exposure precession photographs, and diffractometer traces of weak axial reflections showed that there were no systematic absences. Comparison of absorption-corrected intensities of symmetry-related reflections showed that the Laue symmetry of the lattice was $4/mmm$ and not $4/m$.

Five Friedel-equivalent segments of data, each 1/16 of the Ewald sphere, were collected using monochromatized Mo$K\alpha$ radiation to a limit of $2\theta = 120°$. The scan range was 1.9° plus the α_1–α_2 dispersion, and the background counts were measured on either side of the peak for a total time approximately equal to the average scan time. Three standards were measured after every 50 reflections to maintain a check on crystal alignment and instrument stability. A uniform systematic decrease of about 4% of the intensity of the standards was noted over the period of data collection, and as the crystal alignment was found to be unchanged at the end, a linear scaling procedure was applied to the data to account for this decrease.

Absorption corrections were applied to the intensity data using a Gaussian integration procedure, and the five equivalent segments were averaged and reduced to a single data set which contained 1426 independent intensities, of which 1004 can be considered as observed at the 10% significance level, i.e. $I(\text{net}) \geqq 1.65\sigma(I)$. The discrepancy factor $(\Sigma\Delta I/\Sigma I)$ among the five data sets was 0.031.

STRUCTURE SOLUTION AND REFINEMENT

Examination of the cell dimensions suggested that the structure was based on two sphalerite-type 5.3Å "cubes", with the tetragonal cell dimension a, representing the face diagonal of the "cube". This reasoning imposed the condition that the nearly *ccp* sulfur lattice would be approximately c-centred and would have $\bar{4}$ symmetry about the c-axis (and hence about a line through the mid-point of the c-face). An added condition for limiting the choice of space group was that, based upon the probable value of $Z=1$ (i.e. one formula unit per unit cell to account for a reasonable value of D_{calc}), the space group chosen would have to have a site with an equivalent–position multiplicity of 1, where tin could be assigned. Examination of the seven possible space groups for equivalent position sites that would yield an approximately *ccp* sulfur lattice with normal S . . . S distances of about 3.8Å, eliminated all except $P\bar{4}m2$, and this choice led to a successful solution of the structure.

The sulfur atoms were assigned to sites *4j* (~¼,0,~¼) and *4k* (~¼,½,~¼) and various combinations were tried in assigning the metals to the tetrahedral interstices of the sulfur matrix. The tin atom was arbitrarily assigned to the origin, and an "average" metal (¾Cu+¼Fe) was assigned to fill the tetrahedral vacancies at sites *4i* (~¼,~¼,½), *2g* (0,½,~0) and *1b* (½,½,0). This model refined successfully, but the difference synthesis indicated that an extra interstitial atom was required at site *1c* (½,½,½). Bearing in mind the multiplicities of these sites and the stoichiometry of the formula (6Cu+2Fe), site *4i* was assigned as copper. This left two copper and two iron atoms to be assigned to the four sites *2g*, *1b* and *1c*. Better agreement was observed when copper was placed at site *2g* and two iron atoms at sites *1b* and *1c*, than when the metal types were reversed.

The final correct model refined anisotropically to R=0.037 for the 1004 observed reflections (see above) and to R=0.049 when all 1426 were treated as observed. There was no significant difference in the final parameters between these two refinements, and the parameters quoted in Table 3 are those for the latter case. An isotropic extinction parameter (Larsen 1970) was included in the refinement. The scattering curves used were those for the neutral atomic species Cu,Fe,Sn,Se and S, taken from Cromer & Mann (1968) and the anomalous dispersion corrections were those of Cromer & Libermann (1970). Better agreement was obtained using the curves for the neutral atomic species than for the ionized species. This is opposite to what was found in the refinement of chalcopyrite (Hall & Stewart 1973), but the same as that found in the refinements of stannite and kesterite (Hall & Stewart 1975). In the final stages of refinement, a composite curve ($0.985f_S$ $0.015f_{Se}$) was used to account for the 1.5% selenium replacement of sulfur in the sample. The anomalous scattering was also modified to take this into account. The resultant improvement in the agreement factor was 0.001, but it appears to be significant. In the least-squares procedure, refinement using unit weights and calculated weights was tried, (calculated weight = $1/\sigma^2(F)$, where $\sigma(F)$ is based on the relative agreement of the five observations of the intensity and on counting statistics. No significant difference was observed between these refinements, and the results quoted are based on the unit–weight refinement.

The calculations were carried out using the X-ray system of programs (Stewart *et al.* 1972). The bond lengths and angles are given in Table 4. The observed ($10\times F_o$) and calculated ($10\times F_c$) structure factors are given in Table 5*, for the refinement treating all data as "observed", though reflections which can be considered "unobserved" (see above) are marked with an asterisk.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The structure of mawsonite is based upon the compounding of two sphalerite-like cubes (Fig. 1). Kesterite and stannite (Hall & Stewart 1975) also have "two cube" structures, but in these the doubling of the cell occurs along the *z*-direction. In mawsonite, the expansion is accomplished by considering the face diagonals of two adjacent sphalerite–like cubes as the a_1, a_2 directions of the tetragonal cell. The sulfur matrix is approximately cubic close-packed, with metal atoms occupying half of the available tetrahedral interstices, and an additional metal atom (Fe2) occupying the interstice at the (½,½,½) position of the cell. This results in a coordination scheme in which each metal is in contact with four sulfur atoms (Fig. 2, a-e),

TABLE 3. ATOMIC POSITIONAL AND THERMAL PARAMETERS.

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$\bar{B}$(equiv.)
Sn	*1a*	0	0	0	84(1)	84(1)	91(1)	0	0	0	0.68
Cu1	*2g*	½	0	0.0002(6)	165(3)	247(4)	186(3)	0	0	0	1.57
Cu2	*4i*	0.2463(1)	0.2463(1)	½	165(1)	165(1)	182(2)	-27(2)	12(4)	-12(4)	1.35
Fe1	*1b*	½	½	0	114(2)	114(2)	51(2)	0	0	0	0.73
Fe2	*1c*	½	½	½	83(2)	83(2)	54(2)	0	0	0	0.58
S1	*4j*	0.2615(2)	0	0.2538(3)	95(3)	106(3)	115(4)	0	-26(3)	0	0.83
S2	*4k*	0.2597(2)	½	0.2490(2)	92(3)	132(4)	84(3)	0	-18(3)	0	0.81

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*Table 5 is available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada, K1A 0S2.

TABLE 4. BOND DISTANCES AND ANGLES WITH STANDARD DEVIATIONS

(a) Bond distances (Å)

Sn - S1	2.409(1)
Cu1 - S1	2.266(2)
Cu1 - S2	2.384(2)
Cu2 - S1	2.293(1)
Cu2 - S2	2.354(1)
Fe1 - S2	2.262(1)
Fe2 - S2	2.269(1)

(b) Non-bonded short metal-metal distances (Å)

Cu2...Fe2	2.728(1)
Fe1...Fe2	2.679(1)

(c) Sulfur tetrahedra (Å)

1. Around Sn	
S1 ... S1^{9}	3.977(2)
S1 ... S1^{23}	3.912(2)
2. Around Cu1	
S1 ... S1^{7}	3.626(2)
S2^{23}... S2^{28}	3.949(2)
S1 ... S2^{23}	3.801(2)
3. Around Cu2	
S1 ... S2	3.802(1)
S1 ... S2^{22}	3.779(2)
S1 ... S1^{22}	3.856(2)
S2 ... S2^{22}	3.730(2)
4. Around Fe1, Fe2	
S2 ... S2^{7}	3.654(2)
S2 ... S2^{23}	3.714(2)

(d) Bond Angles (°)

S1 - Sn - S1^{9}	111.26(5)
S1 - Sn - S1^{23}	108.59(3)
S1 - Cu1 - S1^{7}	106.30(13)
S1 - Cu1 - S2^{23}	109.63(3)
S2^{23} - Cu1 - S2^{28}	111.86(13)
S1 - Cu2 - S2	109.78(5)
S1 - Cu2 - S1^{22}	114.41(5)
S1 - Cu2 - S2^{22}	108.82(5)
S2 - Cu2 - S2^{22}	104.81(4)
S2 - Fe1 - S2^{7}	107.73(5)
S2 - Fe1 - S2^{26}	110.35(3)
S2 - Fe2 - S2^{7}	107.28(5)
S2 - Fe2 - S2^{25}	110.58(3)
Sn - S1 - Cu1	108.78(9)
Sn - S1 - Cu2	106.44(4)
Cu1 - S1 - Cu2	112.67(5)
Cu2 - S1 - Cu2^{23}	109.48(6)
Fe1 - S2 - Cu1^{23}	109.80(8)
Fe1 - S2 - Cu2	111.84(4)
Fe1 - S2 - Fe2	72.50(4)
Fe2 - S2 - Cu2	72.31(3)
Fe2 - S2 - Cu1^{23}	177.71(8)
Cu2 - S2 - Cu2^{11}	110.07(6)
Cu2 - S2 - Cu1^{23}	106.51(5)

List of superscripts, indicating symmetry operations, used in text, Table, and Fig. 2.

7.	1-x, y, z
9.	-x, y, z
11.	x, 1-y, z
13.	x, -y, z
22.	y, x, 1-z
23.	y, x, -z
25.	y, 1-x, 1-z
26.	y, 1-x, -z
28.	y, -x, -z

one of the sulfur atoms (S1) is coordinated to four metals (Fig. 2f), and the other sulfur atom (S2), is coordinated to five metals, due to the presence of the extra metal (Fe2), (Fig. 2g).

The additional iron atom (Fe2) has four coordinating sulfur atoms (S2) in a distorted tetrahedron at a distance of 2.269Å (Fig. 2e), and has six metal atoms at close distances. The Fe1 atom is directly above and below it at 2.679Å, and four Cu2 atoms at 2.728Å complete the flattened octahedron of metal nearest-neighbors. Such an environment is common in the "stuffed derivatives" (structures with extra interstitial metals) in the chalcopyrite series (Hall 1975). The structure of mooihoekite (Hall & Rowland 1973) is very similar to that of mawsonite. Like mawsonite, mooihoekite ($Cu_9Fe_9S_{16}$) has a metal/sulfur ratio of 9/8, but because the cell is approximately twice that of mawsonite, it contains two extra atoms. Both of these extra metal sites are filled by iron atoms, but these sites are not equivalent. In one case they give rise to infinite chains in the *z*-direction of Fe . . . Fe . . . Fe . . . atoms 2.69Å apart, and in the second case the chains are . . Cu . . . Fe . . . Cu . . . Fe . . ., also 2.69Å apart. In mawsonite, the single extra iron atom gives rise to infinite chains . . Fe1 . . . Fe2 . . . Fe1 . . . Fe2 . . . 2.68Å apart.

Mawsonite was originally reported as being "magnetic", (Markham & Lawrence), and the largest crystal specimen used here was tested with iron wire, and a strong bar magnet. The crystal was unaffected by the iron wire, but was attracted weakly by the magnet. The iron atoms in the structure are close enough for magnetic

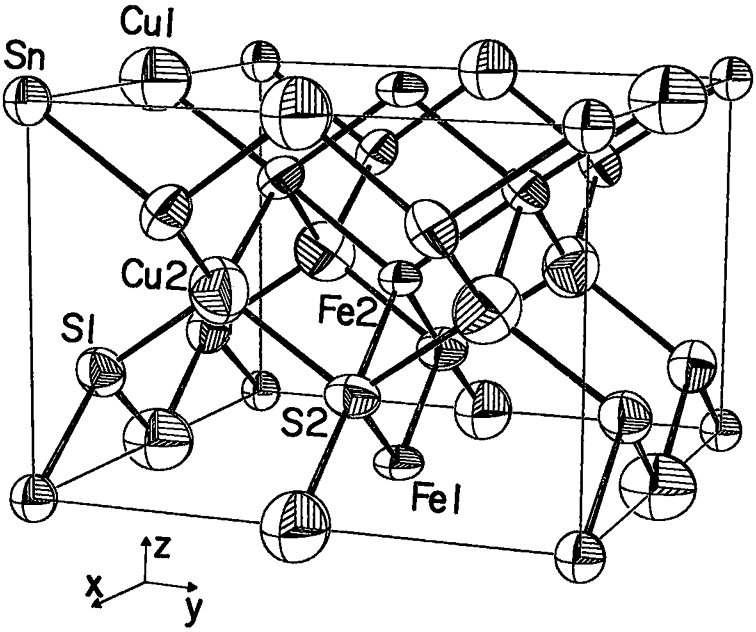

FIG. 1. The unit cell of mawsonite. Thermal ellipsoids are drawn to include 99% probability.

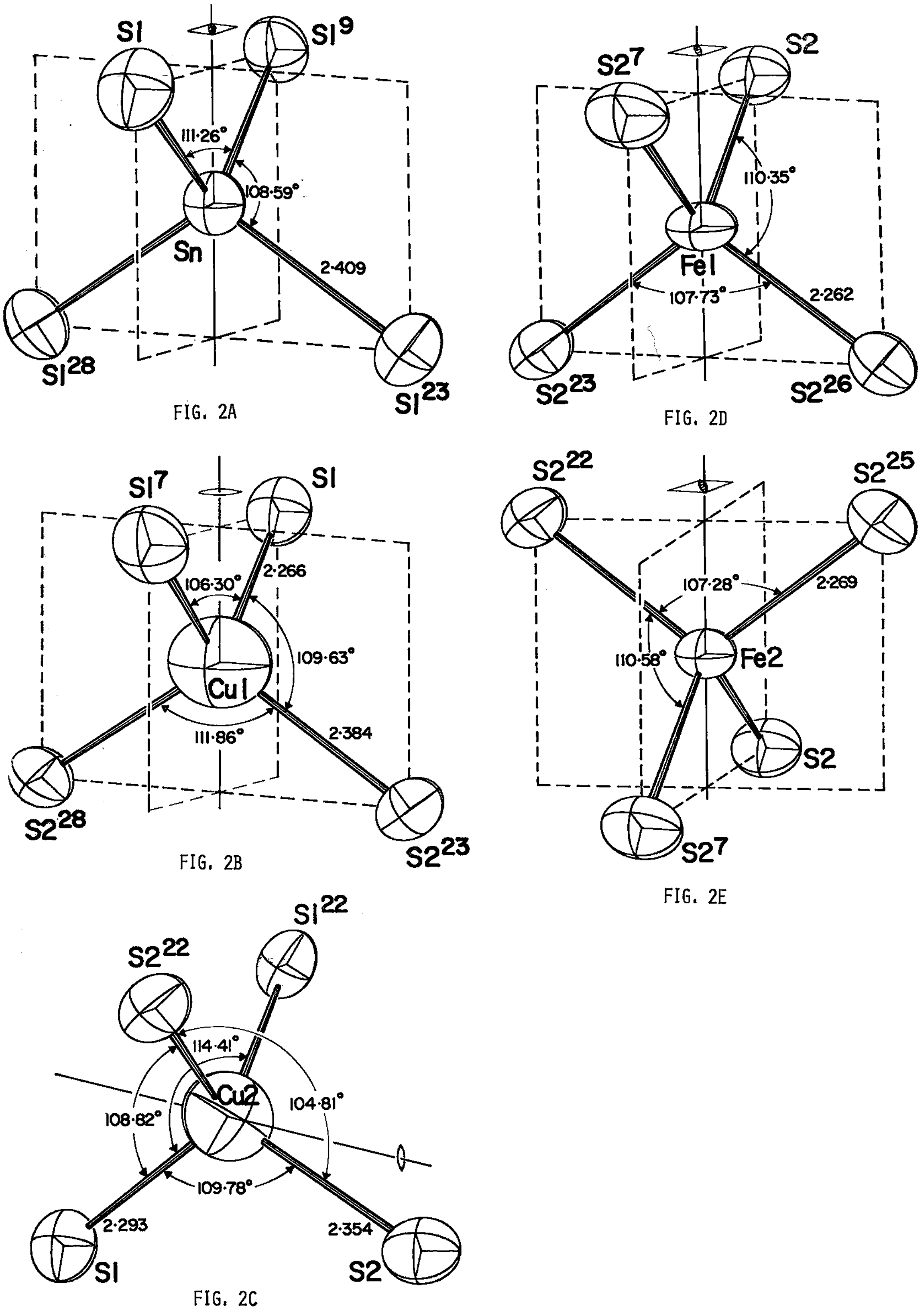
FIG. 2A

FIG. 2D

FIG. 2B

FIG. 2E

FIG. 2C

FIG. 2. Metal-sulfur coordination tetrahedra: (A) around Sn; (B) around Cu1; (C) around Cu2; (D) around Fe1; (E) around Fe2; (on page opposite): sulfur-metal coordination polyhedra; (F) around S1; (G) around S2.

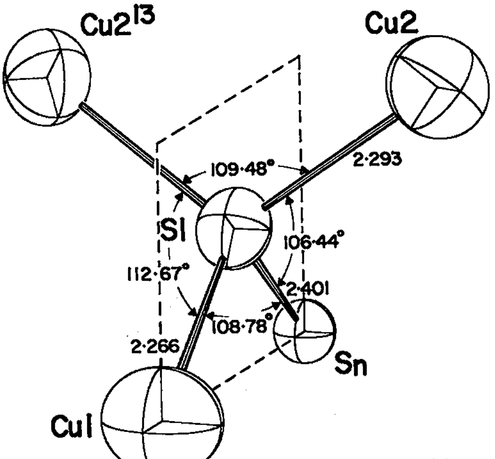

FIG. 2F

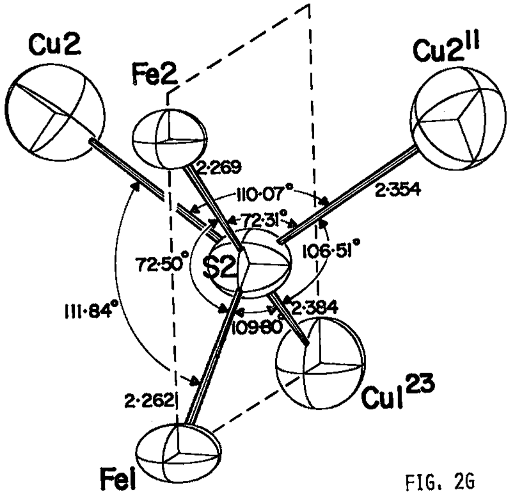

FIG. 2G

interaction in the z-direction to occur, probably via the nearest sulfur atoms (S2). However, such a -Fe-S-Fe-S- interaction can only be one-dimensional in the case of mawsonite as the distance between the iron "chains" is too large (7.603Å). Similar one-dimensional systems are known, e.g., $CsCoCl_3 \cdot 2H_2O$ and $RbFeSl_3$; the latter has inter- and intra-chain distances very close to those found in mawsonite, and both $CsCoCl_3 \cdot 2H_2O$ and $RbFeCl_3$ have very low Néel temperatures.

The deviations of the coordination tetrahedra from ideal geometry can be accounted for in terms of two factors: (1) the additional iron metal at the (½,½,½) position results in some degree of "crowding" around the five-coordinate S2 atom, with consequent distortions of all angles involving S2; (2) the larger tin atom at the origin gives rise to a displacement of the coordinating sulfurs away from this position. The Sn-S bond length (2.409Å) is very close to those found in stannite (2.411Å) and kesterite (2.408Å) (Hall *et al.* 1975) and is much larger than any of the other metal-sulfur distances in the structure. The sulfur atoms are moved away from tin much more in the x-y plane than in the z-direction, and this results in a "flattened" tetrahedron, with the S1-S1-S1^{9} angle opened up to 111.26°, and the S1-Sn-S1^{23} angle compressed to 108.59° from the ideal value of 109.47°.

The thermal parameters for all the atoms are in close agreement with those found in stannite and kesterite, and follow the general pattern observed in the chalcopyrite series [$\bar{B}$(Cu)>$\bar{B}$(Fe)], except that the magnitudes of $\bar{B}$(Fe) observed here are less than in the chalcopyrite series. This is probably due to the "crowding" occurring around the centre of the mawsonite cell. This factor also explains why $\bar{B}$(Fe2) and $\bar{B}$(Cu2) are less than $\bar{B}$(Fe1) and $\bar{B}$(Cu1) respectively.

The cell parameters obtained in this work [a 7.603(2), c 5.358(1)Å] are slightly, but not significantly larger than the reduced cell of Yamanaka & Kato (1976); a 7.598(1), c 5.355 (3)Å. It is probable that the selenium replacement of some sulfur in the present mawsonite specimen results in the fractionally larger cell parameters.

POWDER DIFFRACTION PATTERN

Long-exposure Gandolfi single-crystal powder photographs were obtained for the crystal used in the structure determination. After the structure was solved and refined, the computer program POWGEN (Hall & Szymański 1975) was run. This program calculates the X-ray powder pattern using either the observed or the calculated single-crystal intensities, for either a specific wavelength or combination of wavelengths. The Gandolfi pattern was compared to the calculated pattern, and excellent agreement was found.

However, serious discrepancies were observed between these two patterns and the recently published mawsonite powder pattern of Yamanaka & Kato (1976). Their lines observed at d=7.60 (hkl=100), 2.461(102) and 1.319(104) have such weak calculated and observed single-crystal intensities that they should not have been observable. Their line at d=1.302(512) is too strong to be due to mawsonite alone, and also, their line at d=3.388, which was not observed on the Gandolfi films, cannot be indexed using the true mawsonite cell. It seems that despite their careful purification procedures, their mawsonite specimen may have contained extraneous material.

Table 6 gives the X-ray powder pattern for mawsonite obtained from the single-crystal observed intensities.

TABLE 6. X-RAY POWDER PATTERN OF MAWSONITE CALCULATED FOR Co$K\alpha$ RADIATION FROM OBSERVED SINGLE-CRYSTAL DIFFRACTOMETER INTENSITIES

d(Å)	I_{calc}	hkl	d(Å)	I_{calc}	hkl
5.37	11	110,001	1.619	43	421,203
4.38	14	101	1.581	2	213
3.800	6	200,111	1.550	6	402
3.100	100	201	1.462	3	431,303
2.871	13	211	1.365	3	521,323
2.683	26	220,002	1.341	13	440,004
2.401	6	310,112	1.303	1	512
2.291	4	301	1.232	20	601,423
2.190	2	202	1.201	9b	620,442,224
1.962	3	321	1.096	34	622,404
1.899	70	400,222	1.033	22	641,603,205
1.790	3	330,312	0.949	25	800,444
1.742	3	411,103			

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