

## The superstructure of stannoidite

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### Auszug

Die Kristallstruktur von Stannoidit  $\text{Cu}_{16}(\text{Fe}, \text{Zn})_6\text{Sn}_4\text{S}_{24}$  wurde mittels partieller Pattersonsynthesen bestimmt und bis  $R = 0,064$  verfeinert. Für einen Kristall von der Konjo Mine in Japan sind die Gitterkonstanten:  $a = 10,767(1) \text{ \AA}$ ,  $b = 5,411(1) \text{ \AA}$ ,  $c = 16,118(2) \text{ \AA}$ ,  $Z = 1$ ; Raumgruppe ist  $I222$ . Die Struktur läßt sich von der Struktur von Zinnkies,  $\text{Cu}_2(\text{Fe}, \text{Zn})\text{SnS}_4$ , ableiten, wenn darin ein Teil des Sn durch Cu ersetzt und außerdem ein Überschuß von Cu in den tetraedrischen Lücken untergebracht wird. Die von S-Atomen gebildeten Tetraeder um die überschüssigen Cu-Atome haben mit benachbarten Tetraedern gemeinsame Kanten. Der kürzeste Abstand zwischen zwei Metallatomen beträgt  $2,70 \text{ \AA}$ . Die Metallatome scheinen im wesentlichen geordnet zu sein. Von drei voneinander unabhängigen S-Atomen sind zwei wie beim Zinnkies an zwei Cu-Atome und je ein Fe(Zn)- und Sn-Atom gebunden; das dritte hat vier Cu-Atome und ein Fe-Atom zu Nachbarn.

### Abstract

The crystal structure of stannoidite,  $\text{Cu}_{16}(\text{Fe}, \text{Zn})_6\text{Sn}_4\text{S}_{24}$ , a derivative of stannite,  $\text{Cu}_4(\text{Fe}, \text{Zn})_2\text{Sn}_2\text{S}_8$ , has been determined from consideration of the partial-Patterson syntheses and refined to  $R = 6.4\%$ , using a crystal from Konjo mine, Japan: Space group is  $I222$ ,  $a = 10.767(1) \text{ \AA}$ ,  $b = 5.411(1) \text{ \AA}$ ,  $c = 16.118(2) \text{ \AA}$ ,  $Z = 1$ . The results revealed that the structure of stannoidite is derivable from the stannite structure by substituting Cu atoms for a set of Sn atoms in stannite and adding excess Cu atoms in a set of tetrahedral vacancies. The tetrahedra formed by sulfur atoms about the excess Cu atoms share edges with neighbouring tetrahedra, the shortest metal-metal distance being  $2.70 \text{ \AA}$ . Metal atoms in the structure seem to be essentially ordered. Of three independent sulfur atoms, two are bonded, like those of stannite, to two Cu, one Fe(Zn), and one Sn, while the third sulfur atom is bonded to five metal atoms: four Cu and one Fe.

### Introduction

Stannoidite (SPRINGER, 1968; PETRUCK, 1973; YAMANAKA and KATO, 1976),  $\text{Cu}_8(\text{Fe}, \text{Zn})_3\text{Sn}_2\text{S}_{12}$ , which was established by KATO (1969) as a new mineral species, is a derivative of sphalerite, the cell

volume of which is six times that of the basic structure. Based upon Mössbauer spectra, YAMANAKA and KATO (1976) proposed the following partitioning of valencies:  $\text{Cu}_8^{1+}\text{Fe}_2^{3+}(\text{Fe}^{2+}, \text{Zn}^{2+})\text{Sn}_2^{4+}\text{S}_{12}^{2-}$ . The crystal structure of this metal-excess derivative of the sphalerite structure has now been worked out with the results as reported in the present paper.

## Experimental

### Unit cell and space group

Crystals used for the present study came from the type locality, Konjo mine, Japan. As shown in Table 1, the chemical composition of the crystals may well be expressed by  $\text{Cu}_{15.94}(\text{Fe}_{4.50}\text{Zn}_{1.80})\text{Sn}_{4.04}\text{S}_{24}$ .

The following cell dimensions were determined with least-squares refinement based on reflections measured on a four-circle automatic diffractometer:  $a = 10.767(1) \text{ \AA}$ ,  $b = 5.411(1) \text{ \AA}$ ,  $c = 16.118(2) \text{ \AA}$ . For this refinement, a program was used written by APPLEMAN (EVANS *et al.*, 1963).

The unit cell contains one formula unit, the calculated density being  $4.655 \text{ g} \cdot \text{cm}^{-3}$ . In Table 2, the cell dimensions are compared with those of related minerals.

X-ray photographs revealed, as reported by KATO (1969), a marked substructure; the axes of the subcell  $a'$ ,  $b'$  and  $c'$  are related to those of the original cell as follows:  $a' = a/2$ ,  $b' = b$ ,  $c' = c/3$ . The extinction rule is consistent with those of the space groups  $Immm$ ,  $Im\bar{m}2$ ,  $I222$  and  $I2_12_12_1$ . Of these, only the last two are consistent with the tetrahedral framework characteristic of the sphalerite structure. Since the possible space group of the substructures was found to be  $A222$ , we assumed, for structure analysis, the space group  $I222$ . In this space

Table 1. *Chemical composition of stannoidite\**

	wt.-%	Number of atoms, based on 12 sulfur atoms
Cu	39.18	7.97
Fe	9.73	2.25
Zn	4.56	0.90
Sn	18.56	2.02
S	29.77	12.00
Total		101.80

\* SPRINGER (1972, private communication).

Table 2. Cell dimensions and symmetries of stannoidite and related minerals

Mineral	Cell dimensions			Space group
	<i>a</i>	<i>b</i>	<i>c</i>	
stannite <sup>1</sup> Cu <sub>4</sub> (Fe, Zn) <sub>2</sub> Sn <sub>2</sub> S <sub>8</sub>	5.448 Å	(= <i>a</i> )	5.371 (× 2) Å	<i>I</i> $\bar{4}2m$
stannoidite Cu <sub>16</sub> (Zn, Fe) <sub>2</sub> Fe <sub>4</sub> Sn <sub>4</sub> S <sub>24</sub>	5.384 (× 2)	5.411 Å	5.373 (× 3)	<i>I</i> 222
mawsonite <sup>2</sup> Cu <sub>24</sub> Fe <sub>8</sub> Sn <sub>4</sub> S <sub>32</sub>	5.373 (× 2)	(= <i>a</i> )	5.355 (× 2)	*

\* Probable space group<sup>2</sup>: *I* $\bar{4}2m$ , *I*4mm, *I*422 or *I*4<sub>1</sub>22.

<sup>1</sup> HALL and STEWART (1974, private communication).

<sup>2</sup> YAMANAKA and KATO (1976).

group, which was confirmed through structure analysis, a set of two-fold axes have, like that in *A*222, a point in common.

#### Intensity measurement

The dimensions of the crystal used for intensity measurements were approximately  $0.12 \times 0.16 \times 0.28$  mm<sup>3</sup>. The  $2\theta$ - $\omega$  scan technique was used to measure intensities on a four-circle diffractometer. The number of reflections out to  $2\theta = 65^\circ$  for MoK $\alpha$  was 429. After correcting for Lorentz and polarization factors, the intensities were reduced to structure factors. Corrections for absorption ( $\mu = 159.27$  cm<sup>-1</sup>) were made using the program ACACA written by PREWITT (WUENSH and PREWITT, 1965).

#### Determination and refinement of the structure

The unit cell of stannoidite, whose volume is six times that of sphalerite, contains 24 sulfur atoms and a total of 26 metal atoms, specifically 16 Cu, 6 (Fe, Zn) and 4 Sn. It was thought that this derivative structure is, in principle, characterized by locations of two excess metal atoms and four heavy atoms, Sn. These atoms were readily located in the vector space based on the following consideration.

Let **E** be the set of excess atoms and **B** the set of remaining atoms, the arrangement of which is based on the sphalerite (blende) structure. Then the vector set of the entire structure may be separated into two parts:

$$V = V(\mathbf{B}) + V(\mathbf{EB});$$

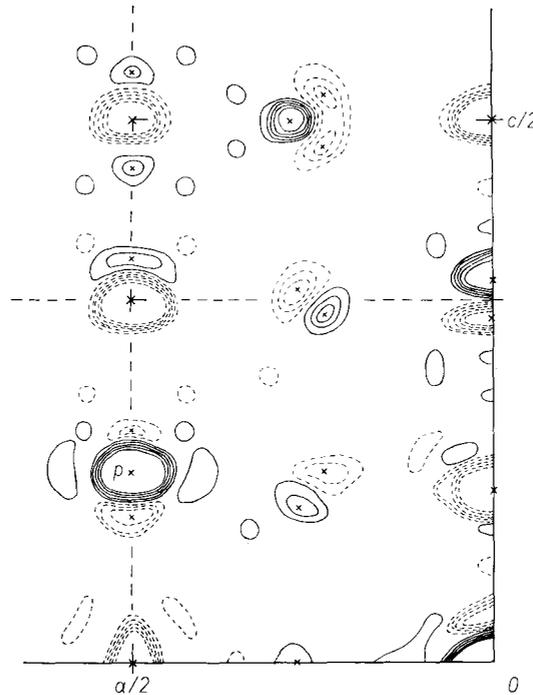


Fig. 1. Portion of the partial-Patterson section,  $y = 0$ , showing the location of Sn, indicated by  $P$ . Contours at equal, but arbitrary, intervals; negative contours dotted. Broken lines indicate the sphalerite superlattice

the first term represents the vector set of  $\mathbf{B}$ , and the second that of  $\mathbf{E}$  plus the set of cross vectors between  $\mathbf{E}$  and  $\mathbf{B}$ . Since the atoms in  $\mathbf{E}$  are presumably located in interstices of a tetrahedral framework of  $\mathbf{B}$  of the sphalerite type, none of the nonorigin vectors of  $V(\mathbf{E}\mathbf{B})$  should coincide with those of  $\mathbf{B}$ . If the two excess atoms of  $\mathbf{E}$  are ordered at a specific set of interstices, the positions should be, according to the space-group requirement, on a set of twofold axes which are separated from each other by translation  $(\mathbf{a} + \mathbf{b} + \mathbf{c})/2$ . This situation secures, in  $V$ , a direct observation of the image of  $\mathbf{B}$  as seen from  $\mathbf{E}$ .

In practice, we calculated the partial-Patterson function (TAKÉUCHI, 1972) based on  $hkl$  reflections other than  $h = 2n$  and  $l = 3n$ , ( $n$  an integer). In this particular case, the peak due to vectors between the excess atoms and Sn should appear in the function as a positive peak having the highest density. In this way, the location of Sn was

directly determined in the  $y = 0$  section of the function (Fig. 1). For the present purpose, the locations of the excess atoms and Sn provide enough knowledge to determine initial phase angles of the superstructure reflections. The initial set of atomic coordinates were then derived by substituting Cu for Zn in the tetrahedral framework of sphalerite and by distributing Sn and the excess atoms according to the above results; all metal atoms other than Sn were tentatively represented by Cu. Structure-factor calculations based on the atomic coordinates gave  $R = 0.168$  for all observed reflections. Full-matrix least-squares refinement with isotropic temperature factors was then carried out using the program ORFLS (BUSING, MARTIN and LEVY, 1962), and applying an equal-weighting scheme. Several cycles of calculations reduced the  $R$  value to 0.085.

At this stage, an attempt was made to differentiate between the atomic species Cu and Fe(Zn); they might be distributing in an ordered fashion as those in the low-temperature form of chalcopyrite (HALL and STEWART, 1973) and related sulfides. According to the study on Mössbauer spectra and chemical composition (YAMANAKA and KATO, 1976), the iron atoms in stannoidite are mostly in the state of Fe<sup>III</sup>; Fe<sup>II</sup> substitutes for Zn, yielding a cell content which may well be expressed by  $\text{Cu}_{16}(\text{Zn}, \text{Fe})_2\text{Fe}_4\text{Sn}_4\text{S}_{24}$ . Based on multiplicities of metal sites, the problem is then reduced to that of distributing Fe and Cu in the M(1), M(2), ... M(5) sites (Table 3); the eightfold site M(7) should be for Cu, provided that significant disorder is substantially absent. Note that the location of Sn, as determined by the structure analysis, is denoted in Table 3 as M(6). As shown by FRUEH (1953) for chalcopyrite, a Patterson synthesis based on the superstructure reflections only was expected to be helpful to the present purpose. In this case, however, it did not work well because of the presence of heavy atom, Sn, and the distortions of peaks due to atomic displacements.

Table 3. Point symmetries at metal sites, average M—S lengths and temperature factors of metal atoms

Site notation	M(1)	M(2)	M(3)	M(4)	M(5)	M(6)	M(7)
Point symmetry	222	222	222	2	2	2	1
Multiplicity	2	2	2	4	4	4	8
Possible site content	[4Cu, 2(Zn, Fe <sup>II</sup> )]			(4Fe <sup>III</sup> , 4Cu)		Sn	Cu
$\langle \text{M—S} \rangle$	2.35	2.26	2.30	2.33	2.34	2.40	2.32 Å
$B$	1.1	1.6	1.6	1.3	0.9	0.4	1.5 Å <sup>2</sup>

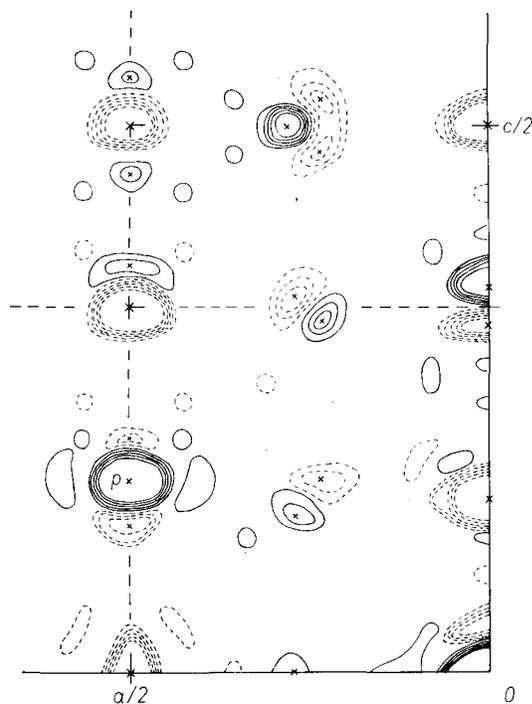


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directly determined in the  $y = 0$  section of the function (Fig. 1). For the present purpose, the locations of the excess atoms and Sn provide enough knowledge to determine initial phase angles of the superstructure reflections. The initial set of atomic coordinates were then derived by substituting Cu for Zn in the tetrahedral framework of sphalerite and by distributing Sn and the excess atoms according to the above results; all metal atoms other than Sn were tentatively represented by Cu. Structure-factor calculations based on the atomic coordinates gave  $R = 0.168$  for all observed reflections. Full-matrix least-squares refinement with isotropic temperature factors was then carried out using the program ORFLS (BUSING, MARTIN and LEVY, 1962), and applying an equal-weighting scheme. Several cycles of calculations reduced the  $R$  value to 0.085.

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$\langle \text{M-S} \rangle$	2.35	2.26	2.30	2.33	2.34	2.40	2.32 Å
$B$	1.1	1.6	1.6	1.3	0.9	0.4	1.5 Å <sup>2</sup>

In dealing with metal ordering in similar structures, HALL and ROWLAND (1973) and HALL and STEWART (1973) suggested that thermal parameters may be useful; the temperature factors of the Cu atoms tend to be significantly higher than those of Fe (SZYMANSKI, 1974; ROWLAND and HALL, 1975). As observed in Table 3, M(7) in which we located Cu, indeed has a high  $B$  value. We find that M(2), M(3) and M(4) likewise have high  $B$  values, suggesting Cu atoms for these sites. M(1) and M(5) are then the sites of Fe(Zn); specifically Zn(Fe) in M(1) and Fe<sup>III</sup> in M(5). This mode of metal ordering is found to be satisfactory on the compositional ground. In this case, as will be discussed later, the four-coordinated S atoms are bonded to two Cu, one

Table 4. *Final atomic parameters and standard deviations* (in parentheses)

Site	Atom	$x$	$y$	$z$
M(1)	Zn(Fe <sup>II</sup> )	0	0	0
M(2)	Cu	$\frac{1}{2}$	0	0
M(3)*	Cu	0	0	$\frac{1}{2}$
M(4)	Cu	0.2511(4)	0	$\frac{1}{2}$
M(5)	Fe <sup>III</sup>	0	0	0.3298(3)
M(6)	Sn	0	$\frac{1}{2}$	0.1693(1)
M(7)	Cu	0.2465( 3)	0.0107(11)	0.1695(2)
S(1)	S	0.1308(13)	0.2443(12)	0.0826(5)
S(2)	S	0.3792(10)	0.7558(13)	0.0801(5)
S(3)	S	0.1294(14)	0.7488(12)	0.2546(5)

Site	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$B$
M(1)	0.0030(4)	0.013(2)	0.0006(2)				1.13 Å <sup>2</sup>
M(2)	47(5)	14(2)	13(2)				1.64
M(3)*	34(8)	19(3)	11(3)				1.57
M(4)	31(3)	12(1)	10(1)			0.0007(12)	1.29
M(5)	27(3)	8(1)	6(1)	-0.001 ( 3)			0.86
M(6)	14(2)	2(1)	4(1)	0.0001(15)			0.44
M(7)	39(2)	12(1)	15(1)	- 7(10)	-0.0002(1)	8( 8)	1.52
S(1)	28(5)	7(2)	8(2)	-21( 9)	2(3)	-14( 4)	0.88
S(2)	24(5)	9(2)	7(2)	27( 7)	1(2)	-15( 4)	0.81
S(3)	21(5)	6(2)	8(1)	-31( 7)	3(2)	- 2( 4)	0.66

The anisotropic temperature factors are expressed in the form  $\exp \{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$ .

The  $B$ 's are equivalent isotropic values (HAMILTON, 1959).

\* Interstitial atom.

Table 5. Comparison of observed and calculated structure factors for stannoidite

h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>					
0	2	0	393	389	3	2	3	94	101	4	0	6	784	787	6	1	9	406	371	6	0	12	89	86	7	1	16	41	37					
4	6	13	616	616	4	8	2	82	85	2	2	2	321	298	3	3	3	330	318	2	2	2	63	64	3	3	3	50	51					
8	240	244	137	144	6	50	60	4	526	501	5	239	227	4	76	74	8	0	16	54	50	8	0	16	54	50	50	55	52					
2	2	0	116	108	5	0	3	122	127	7	0	9	73	76	7	3	12	42	42	0	1	17	67	60	0	1	17	67	60					
4	85	79	4	92	89	6	60	64	6	0	6	73	72	2	2	2	102	94	4	68	64	8	0	12	415	406	3	3	50	51				
6	81	74	6	60	64	6	60	64	4	65	62	6	77	72	6	98	41	8	0	12	150	146	5	5	50	55	50	55						
8	66	59	6	1	3	500	482	6	6	77	72	8	3	9	42	38	8	3	9	42	38	4	313	304	2	1	17	87	84					
3	5	0	51	46	3	3	412	374	7	1	6	41	45	5	42	41	5	42	41	10	0	12	49	52	3	3	74	72						
4	0	0	405	389	5	5	267	275	7	1	6	41	45	5	42	41	9	0	9	79	79	2	2	2	71	73	5	5	59	61				
4	234	226	7	0	3	69	76	8	0	6	234	226	2	2	2	510	485	4	4	73	64	4	48	48	3	4	17	46	42					
6	369	359	2	2	2	78	76	4	4	147	141	6	58	50	12	0	12	110	102	4	1	17	58	56	4	1	17	58	56					
6	0	0	117	106	4	50	60	6	57	55	6	272	267	10	1	9	232	238	14	0	12	73	61	6	1	17	74	71						
2	78	71	9	0	3	96	95	10	0	6	86	85	10	1	9	232	216	14	0	12	73	61	6	1	17	74	71	6	6	66	66			
4	87	87	2	2	2	92	87	4	4	80	75	6	52	46	11	0	9	45	40	0	3	13	43	43	5	5	48	42	50					
6	61	57	4	4	4	69	72	6	60	57	12	0	6	363	328	2	2	2	121	116	4	1	13	42	41	7	2	17	42	42				
7	3	0	46	49	6	60	57	14	0	6	47	41	14	1	9	168	152	0	2	14	70	59	10	1	17	55	57	5	5	57	57			
8	0	0	610	590	10	1	3	334	292	2	2	2	121	116	4	4	4	54	54	0	2	14	70	59	10	1	17	55	57					
2	234	224	3	3	3	261	261	14	0	6	47	41	14	1	9	168	152	1	1	14	69	62	10	1	17	55	57	5	5	57	57			
4	419	408	5	5	5	201	190	15	0	9	45	39	15	0	9	45	39	3	3	3	60	61	0	0	18	137	155	2	2	365	363			
6	96	97	11	0	3	62	54	0	1	7	83	67	0	2	10	67	72	5	5	5	44	41	0	0	18	137	155	4	4	99	108			
10	0	0	54	55	2	49	47	0	1	7	83	67	0	2	10	67	72	3	3	3	114	67	66	4	4	99	108	4	4	99	108			
2	88	85	4	4	4	50	49	0	1	7	83	67	0	2	10	67	72	3	3	3	114	67	66	4	4	99	108	4	4	99	108			
4	44	49	13	0	3	75	65	3	3	75	65	5	46	52	1	1	10	62	62	3	3	52	58	2	0	18	68	74	2	2	67	67		
6	64	68	2	2	2	61	63	2	1	7	42	22	3	3	3	45	53	5	46	48	4	0	14	68	57	2	2	67	67	4	4	64	65	
12	0	0	148	140	4	63	54	2	1	7	42	22	3	3	3	45	53	5	46	48	4	0	14	68	57	2	2	67	67	4	4	64	65	
2	349	329	14	1	3	181	183	4	1	7	61	52	3	3	3	60	61	5	43	36	5	1	14	54	58	2	2	120	127	4	4	286	273	
4	106	96	3	3	3	168	154	5	5	5	46	48	4	0	10	63	73	5	45	53	7	1	14	63	63	6	0	18	54	59				
14	0	0	72	72	15	2	3	55	38	8	1	7	54	48	5	43	36	5	1	14	54	58	2	2	120	127	4	4	286	273				
2	46	40	1	1	1	4	85	85	12	3	7	46	34	4	4	4	43	39	7	1	14	63	63	6	0	18	54	59	6	6	68	69		
4	69	64	3	3	3	65	69	0	0	8	56	40	5	1	10	46	51	3	61	52	4	4	4	64	64	4	4	64	64	4	4	64	64	
15	3	0	42	39	3	4	44	49	0	0	8	56	40	5	1	10	46	51	3	61	52	4	4	4	64	64	4	4	64	64	4	4	64	64
16	0	0	229	203	3	1	4	91	92	4	4	52	36	3	3	3	45	42	5	56	46	8	0	18	115	107	2	2	267	263				
0	1	1	66	75	5	56	60	1	1	8	87	80	7	1	10	55	60	7	1	10	55	60	8	2	14	46	46	8	8	115	107			
3	81	76	5	5	5	56	60	1	1	8	87	80	7	1	10	55	60	7	1	10	55	60	8	2	14	46	46	8	8	115	107			
2	1	1	93	71	5	1	4	55	61	3	3	23	65	5	5	5	44	43	9	1	14	42	42	10	0	18	65	63	2	2	47	48		
3	65	54	7	1	4	75	70	3	3	3	55	37	7	48	37	8	2	10	45	42	3	3	45	50	2	2	47	48	2	2	47	48		
4	1	1	94	77	3	3	70	70	3	1	8	89	85	3	3	3	67	68	9	3	10	45	36	11	1	14	52	51	0	0	20	59	65	
3	63	48	11	1	4	55	60	3	3	3	67	68	9	3	10	45	36	11	1	14	52	51	0	0	20	59	65	4	4	43	58			
5	61	58	3	3	3	48	41	4	2	8	53	36	5	1	10	42	47	11	3	10	42	47	1	0	15	64	70	3	3	46	41			
6	1	1	64	53	5	51	49	4	2	8	53	36	5	1	10	42	47	11	3	10	42	47	1	0	15	64	70	3	3	46	41			
3	54	43	15	1	4	44	36	5	1	8	60	61	5	3	3	62	62	0	1	11	83	65	4	6	55	56	3	1	20	50	52			
8	1	1	63	55	0	1	5	109	85	5	5	42	41	3	3	3	77	68	0	1	11	83	65	4	6	55	56	3	1	20	50	52		
3	60	55	3	3	3	69	54	5	5	5	57	56	7	7	7	51	54	2	1	15	339	311	4	2	20	51	59	4	4	64	64			
10	1	1	46	37	5	63	65	7	1	8	79	74	3	3	3	72	67	2	1	11	116	97	5	5	211	201	5	5	211	201				
12	1	1	44	45	2	1	5	121	101	3	3	72	67	2	1	11	116	97	5	5	5	91	83	3	0	15	72	75	7	7	47	49		
3	42	40	3	3	3	94	78	5	5	5	57	57	8	0	8	44	30	5	62	62	3	0	15	72	75	7	7	47	49	7	7	47	49	
1	1	2	93	92	4	1	5	87	68	9	1	8	47	50	4	1	11	80	66	4	4	4	70	64	6	0	20	47	52	6	6	47	52	
3	5	52	56	7	7	47	52	3	3	3	41	39	5	50	50	5	5	5	66	58	5	0	15	74	74	1	0	21	55	57	5	5	48	45
3	1	2	99	97	6	1	5	92	77	11	1	8	61	60	6	1	11	92	82	6	1	11	92	82	4	4	65	63	4	4	48	51		
3	83	81	3	3	3	76	65	3	3	3	56	48	3	3	3	75	68	6	1	11	92	82	4	4	65	63	4	4	48	51	4	4	48	51
5	43	51	5	5	5	49	49	5	5	5	48	47	5	55	57	5	55	57	6	1	15	262	269	2	2	121	181	207	3	3	175	173		
5	1	2	70	71	7	0	5	50	34	13	1	8	47	33	8	1	11	58	55	3	3	3	233	225	3	3	175	173	3	3	175	173		
5	49	54	2	2	2	45	28	15	1	8	51	43	10	1	11	63	58	10	1	11	63	58	4	4	44	38	5	2	21	46	40			
7	1	2	89	83	8	1	5	71	60	1	0	9	108	115	3	3	3	57	55	9	0	15	56	61	1	0	21	46	40	2	2	53	53	
3	70	63	5	5	5	51	49	1	0	9	108	115	3	3	3	57	55	9	0	15	56	61	1	0	21	46	40	2	2	53	53			
5	60	58	5	5																														

Zn(Fe), and one Sn. This is essentially the same coordination as that in stannite; the proposed model therefore appears to be acceptable. Assuming various ordering in models other than this, we carried out cycles of refinements, but we did not obtain any results which rule out this ordering model.

Based on this model, therefore, we carried out least-squares refinement with anisotropic temperature factors which converged to give  $R = 0.064$ ; the weighting used was of the form (CRUICKSHANK *et al.*, 1961):

$$w = 1/(a + F_o + cF_o^2), \quad a = 2F_{\min} = 10.0, \quad c = 2/F_{\max} = 0.004.$$

Finally, corrections for anomalous dispersion were applied using  $\Delta f'$ ,  $\Delta f''$  values given by CROMER (1965). Excluding  $hk0$ ,  $0kl$  and  $h0l$  reflections, least-squares refinements were carried out for the working model of structure and its centric equivalent, giving  $R = 0.066$  and  $0.064$  respectively. According to the significance test (HAMILTON, 1965), the difference in  $R$  was found to be significant. The atomic coordinates given in Table 4 are those obtained by the refinement of the latter model. Observed and calculated structure amplitudes are compared in Table 5.

### Discussion

Compared to stannite (Table 2), stannoidite is deficient in Sn but has an excess of Cu; it has in total of two excess metal atoms. The stannoidite structure that bears a superstructure relation to stannite is, in principle, characterized by the distribution of Sn in its structure (Fig. 2). The relationship may best be explained in the following way. In the body-centered lattice of stannite, with Sn at each lattice point (Fig. 3), if the sublattice defined by translation vectors  $\mathbf{t}$  and  $\mathbf{t}'$  is suppressed, the remaining array of Sn atoms define another sublattice that corresponds to the stannoidite lattice. The structure of stannoidite is then derived by locating Cu atoms in the set of tetrahedral positions from which Sn atoms were removed, and by filling the tetrahedral vacancies adjacent to the tetrahedra of new Cu atoms with excess metal atoms (Fig. 4). In the result, the stannoidite structure has as whole a remarkable similarity to the stannite structure.

Of three independent sulfur atoms, S(1) and S(3), which are unaffected by the presence of interstitial atoms, have essentially the same coordination as that in stannite; each of these are bonded to two Cu, one Zn(Fe) and one Sn (Fig. 5). Bond lengths in these coor-

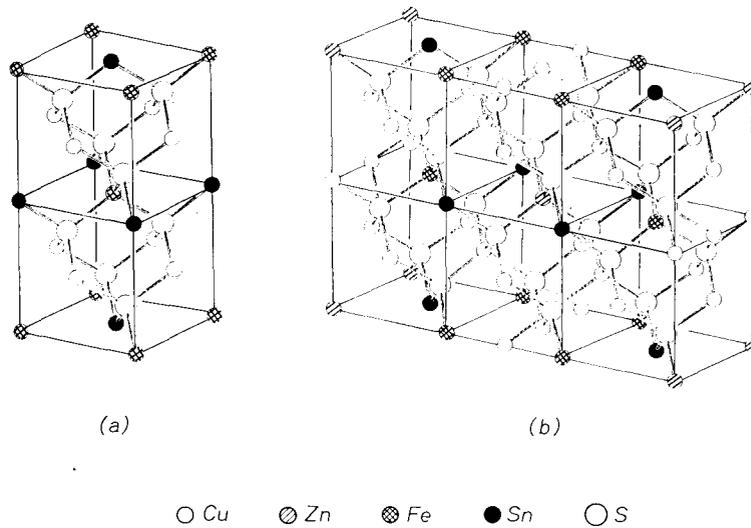


Fig. 2. Comparison of the crystal structures of (a) stannite,  $\text{Cu}_4(\text{Fe}, \text{Zn})_2\text{Sn}_2\text{S}_8$ , and (b) stannoidite,  $\text{Cu}_{16}(\text{Fe}, \text{Zn})_6\text{Sn}_4\text{S}_{24}$

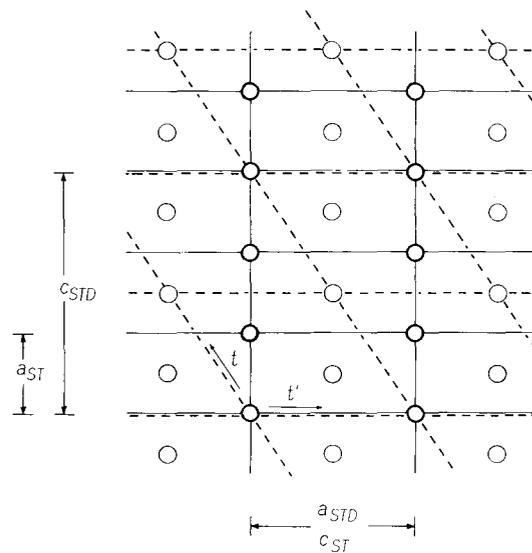


Fig. 3. The body-centered lattice of stannite (ST), showing, by circles, locations of Sn at lattice points (heavy and light circles are respectively at  $y = 0$  and  $y = \frac{1}{2}$ ). If the sublattice indicated by broken lines is removed, the remaining set of lattice points defines another sublattice corresponding to that of stannoidite (STD)

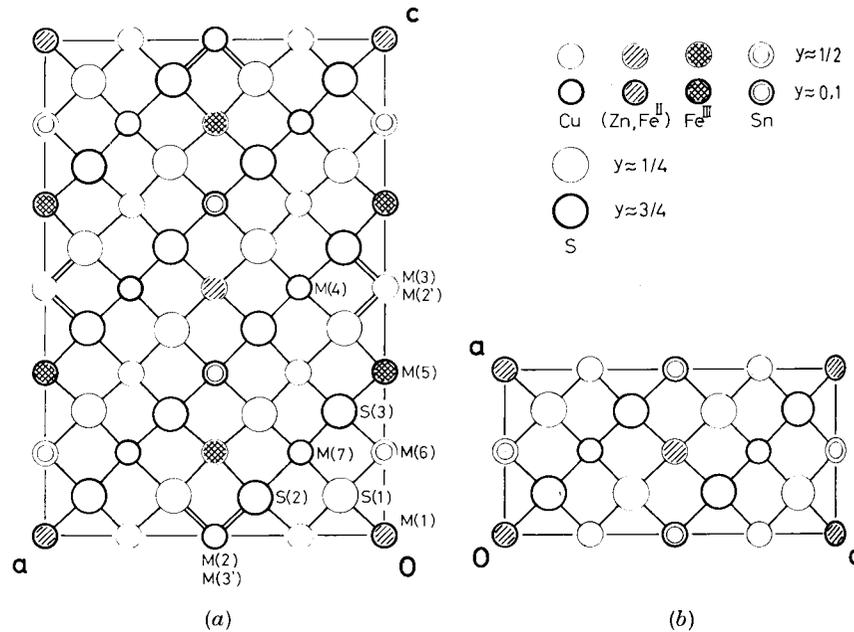


Fig. 4. Comparison of the structures of stannoidite and stannite: (a) The *b*-axis projection of the stannoidite structure. (b) The stannite structure (HALL and STEWART, 1974, private communication), as viewed along the *b* axis

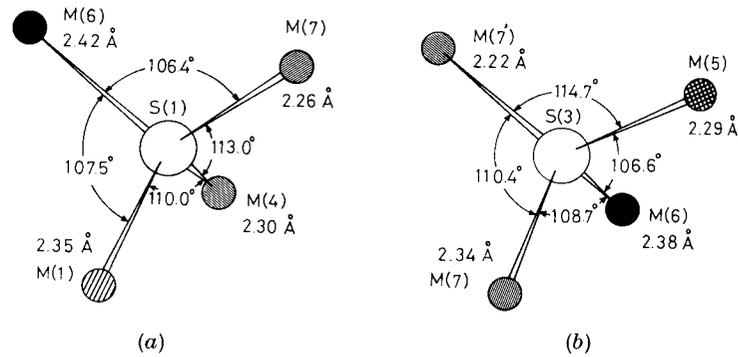


Fig. 5. Coordinations of S(1) and S(3)

dination about the sulfur atoms agree closely with the corresponding lengths of stannite (Fig. 6). The result may in turn suggest that the proposed ordering model may well be correct. Although some disorder would probably be expected for this sort of structures, it would not be a predominant feature for stannoidite.

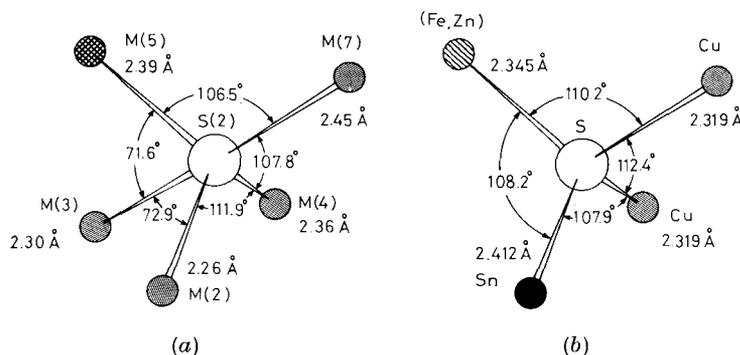


Fig. 6. Comparison of neighbours of S(2) in stannoidite, (a), and those of S in stannite, (b), (HALL and STEWART, 1974, private communication)

Bond lengths and angles in the stannoidite structure are given in Table 6a, b, in which we find that the M(2)—S(2) lengths have an unusually small value, 2.26 Å; in tetrahedral structures, Cu—S lengths are, without exception, around 2.31 Å (TAKÉUCHI and OZAWA, 1975). Sulfur atom S(2) is bonded, unlike S(1) and S(3), to five metal atoms which include the interstitial atom M(3). This short bond length is then thought to be related to possible distortions of coordination polyhedra caused by the presence of Cu in M(3).

Table 6a. *Interatomic distances*

	<sup>iv</sup> M(1)	<sup>iv</sup> M(2)	<sup>iv</sup> M(3)	<sup>iv</sup> M(4)	<sup>iv</sup> M(5)	<sup>iv</sup> M(6)	<sup>iv</sup> M(7)	$\bar{L}_S$
<sup>iv</sup> S(1)	2.35 Å (1,4)			2.30 Å (1,2)		2.42 Å (1,2)	2.26 Å (1,1)	2.33 Å
<sup>v</sup> S(2)		2.26 Å (1,4)	2.30 Å (1,4)	2.36 (1,2)	2.39 Å (1,2)		2.45 (1,1)	2.35
<sup>iv</sup> S(3)					2.29 (1,2)	2.38 (1,2)	2.34 (1,1) 2.22 (1,1)	2.31
$\bar{L}_M$	2.35	2.26	2.30	2.33	2.34	2.40	2.32	

Estimated errors for each bond length are  $\pm 0.01$  Å. Numbers in parentheses indicate the number of bonds reaching the sulfur (left) and the number of bonds reaching the metal (right). The Roman numeral denotes the coordination number.  $\bar{L}_S$  and  $\bar{L}_M$  represent the average distances around sulfur and metal, respectively.

Table 6b. *Edge lengths of polyhedra and bond angles*

Coordination group		Neighbours		Edge length ( $\sigma = 0.02 \text{ \AA}$ )	Angle ( $\sigma = 0.5^\circ$ )
Tetrahedron	about M(1)	S(1)	S(1) <sub>op</sub>	2.75 $\text{\AA}$ ( $\times 2$ )	106.2 $^\circ$ ( $\times 2$ )
			S(1) <sub>p</sub>	3.86 ( $\times 2$ )	110.8 ( $\times 2$ )
		S(1) <sub>op</sub>	S(1) <sub>p</sub>	3.88 ( $\times 2$ )	111.4 ( $\times 2$ )
		average		3.50	
	M(2)	S(2) <sub>w</sub>	S(2) <sub>s</sub>	3.71 ( $\times 2$ )	110.3 ( $\times 2$ )
			S(2) <sub>q</sub>	3.69 ( $\times 2$ )	109.7 ( $\times 2$ )
		S(2) <sub>s</sub>	S(2) <sub>q</sub>	3.66 ( $\times 2$ )	108.4 ( $\times 2$ )
		average		3.69	
	M(3)	S(2)	S(2) <sub>s</sub>	3.80 ( $\times 2$ )	111.6 ( $\times 2$ )
			S(2) <sub>q</sub>	3.79 ( $\times 2$ )	111.0 ( $\times 2$ )
		S(2) <sub>s</sub>	S(2) <sub>q</sub>	3.66 ( $\times 2$ )	105.8 ( $\times 2$ )
		average		3.75	
	M(4)	S(1) <sub>s</sub>	S(1) <sub>r</sub>	3.84	113.0
			S(2) <sub>s</sub>	3.85 ( $\times 2$ )	111.4 ( $\times 2$ )
			S(2) <sub>s</sub>	3.75 ( $\times 2$ )	107.0 ( $\times 2$ )
		S(2) <sub>s</sub>	S(2) <sub>r</sub>	3.79	106.9
		average		3.81	
	M(5)	S(2) <sub>tp</sub>	S(2) <sub>t</sub>	3.80	105.2
			S(3) <sub>w</sub>	3.83 ( $\times 2$ )	109.5 ( $\times 2$ )
			S(3) <sub>wp</sub>	3.79 ( $\times 2$ )	108.0 ( $\times 2$ )
		S(3) <sub>w</sub>	S(3) <sub>wp</sub>	3.89	116.1
average			3.82		
M(6)	S(1)	S(1) <sub>wp</sub>	3.95	109.4	
		S(3)	3.89 ( $\times 2$ )	108.5 ( $\times 2$ )	
		S(3) <sub>wp</sub>	3.94 ( $\times 2$ )	110.6 ( $\times 2$ )	
	S(3)	S(3) <sub>wp</sub>	3.87	109.3	
	average		3.91		
M(7)	S(1)	S(2) <sub>w</sub>	3.76	105.7	
		S(3) <sub>w</sub>	3.86	113.9	
		S(3) <sub>tp</sub>	3.68	110.4	
	S(2) <sub>w</sub>	S(3) <sub>w</sub>	3.89	108.5	
		S(3) <sub>tp</sub>	3.77	107.4	
	S(3) <sub>w</sub>	S(3) <sub>tp</sub>	3.75	110.6	
	average		3.79		

Table 6b. (Continued)

Coordination group		Neighbours		Edge length ( $\sigma = 0.005 \text{ \AA}$ )	Angle ( $\sigma = 0.5^\circ$ )
Tetrahedron	about S(1)	M(1)	M(4) <sub>u</sub>	3.808 $\text{\AA}$	110.0°
			M(6)	3.843	107.5
			M(7)	3.810	111.6
		M(4) <sub>u</sub>	M(6)	3.825	108.2
			M(7)	3.805	113.0
		M(6)	M(7)	3.749	106.4
		average		3.807	
Trigonal bipyramid	about S(2)	M(2) <sub>v</sub>	M(3) <sub>ur</sub>	2.705	72.9
			M(4) <sub>u</sub>	3.825	111.9
			M(5) <sub>us</sub>	3.853	111.9
			M(7) <sub>v</sub>	3.863	110.0
		M(3) <sub>ur</sub>	M(4) <sub>u</sub>	2.703	71.0
			M(5) <sub>us</sub>	2.743	71.6
			M(7) <sub>v</sub>	4.749	177.1
		M(4) <sub>u</sub>	M(5) <sub>us</sub>	3.851	108.4
			M(7) <sub>v</sub>	3.886	107.8
		M(5) <sub>us</sub>	M(7) <sub>v</sub>	3.884	106.5
		average		3.606	
		Tetrahedron	about S(3)	M(5) <sub>v</sub>	M(6)
M(7) <sub>u</sub>	3.802				114.5
M(7) <sub>v</sub>	3.704				106.1
M(6)	M(7) <sub>u</sub>			3.768	110.0
	M(7) <sub>v</sub>			3.832	108.7
M(7) <sub>u</sub>	M(7) <sub>v</sub>			3.748	110.4
average				3.766	

[o] to [w] are code indicators showing coordinates of atoms equivalent by space group operation to the atoms at  $xyz$ . Corresponding operations are:

[o] twofold rotation at $0, y, 0$	[t] twofold screw at $x, \frac{1}{4}, \frac{1}{4}$
[p] twofold rotation at $0, 0, z$	[u] twofold screw at $\frac{1}{4}, y, \frac{1}{4}$
[q] twofold rotation at $x, \frac{1}{2}, 0$	[v] translation $b$
[r] twofold rotation at $\frac{1}{2}, y, 0$	[w] translation $-b$ .
[s] twofold rotation at $\frac{1}{2}, \frac{1}{2}, z$	

Two code indicators in sequence imply an atom related to the one at  $xyz$  by successive application of the two symbolized operations.

The location of each tetrahedral interstice in which M(3) occurs is such that it is surrounded by six metal atoms, M(2) [ $\times 2$ ], M(4) [ $\times 2$ ] and M(5) [ $\times 2$ ], each having tetrahedral coordination (Fig.4). An

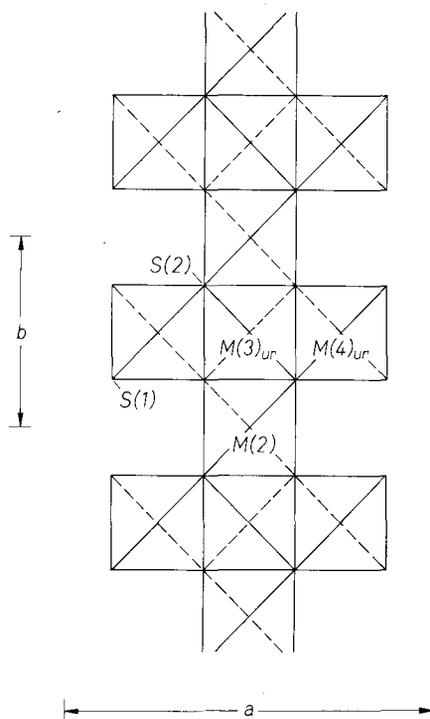


Fig. 7. Showing that by sharing edges, tetrahedra M(2)-S and M(3)-S form an infinite chain parallel to the  $b$  axis. The subscripts,  $u, r$ , refer to Table 6

opposite pair of edges of the M(3) tetrahedron are shared by M(2) tetrahedra to form an infinite chain parallel to the  $b$  axis (Fig. 7). The remaining four edges of M(3) tetrahedron are shared with M(4) and M(5) tetrahedra; the metal atoms, M(5), M(4) and M(3) are in a plane perpendicular to the chain axis. The atoms, M(4) and M(5), are displaced from the ideal metal positions of the respective pseudocubic subcell, giving rise to lengthenings of the M(4)-S(2) and M(5)-S(2) distances. As shown in Fig. 6, the M(7)-S(2) distance is even longer; presumably M(7) is more strongly bonded to S(1) and S(3) as seen in Table 6*a*. It follows that bonding to S(2) depends, to a great extent, on M(3) and M(2); the M(2)-S(2) and M(3)-S(2) bonds tend to be short.

The M(2) corresponds to the Sn position in the stannite structure from which the Sn atom was removed, as mentioned earlier, to derive the stannoidite structure. Therefore, suppose that M(2) in Fig. 6 is

replaced by Sn and M(3), the extra atom is removed; we then find that the resulting coordination about S(2) is essentially the same to that of the corresponding sulfur atom in stannite. This would mean that the effect on bonding caused by removing Sn<sup>IV</sup> from the stannite to derive stannoidite is supplemented by adding two Cu<sup>I</sup> atoms. The structure of mawsonite (Table 2), the other mineral which is closely related to stannite, would probably be based on the same principle.

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