



Fig. 3. Projection de la structure de SnS sur le plan ac mettant en évidence les différentes interactions Sn—S. Les atomes hachurés sont à la cote $y = \frac{1}{4}$, ceux laissés en blanc à la cote $y = \frac{3}{4}$.

tous les atomes de soufre axiaux étant situés du même côté par rapport au plan défini par les atomes de soufre équatoriaux.

— formation du feuillet infini $(\text{SnS})_n$ par les deux couches qui s'emboîtent (Fig. 2*d*).

Dans ces feuillets chaque pyramide SSnS_4 partage donc ses huit arêtes avec huit pyramides voisines.

Entre ces feuillets où se manifestent les paires électroniques non liées (Fig. 3) n'existent que des interactions faibles qui sont de deux types:

— interactions étain—soufre, chaque atome d'étain étant impliqué dans une liaison Sn—S particulièrement longue (3,385 Å).

— interactions étain—étain dont l'existence ne peut être totalement éliminée compte tenu des distances

Sn—Sn entre feuillets de 3,487 Å, qui bien que supérieures sont comparables à celles rencontrées dans βSn qui varie de 3,02 à 3,18 Å (Musgrave, 1963).

La structure de SnS met donc en évidence des liaisons à caractère covalent marqué, dans le cas des liaisons Sn—S les plus courtes, et une activité stéréochimique de la paire électronique non liée de l'étain(II). De telles considérations expliquent la formation de cette structure en feuillet qui se manifeste d'ailleurs par une cristallisation en plaquettes perpendiculaires à la direction [100].

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Structure of the Cubic Iron–Zinc Phase $\text{Fe}_{22}\text{Zn}_{78}$

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Abstract. $\text{Fe}_{22}\text{Zn}_{78}$, cubic, $F\bar{4}3m$, $a = 17.963(10)$ Å, 408 atoms per unit cell, $V = 5796$ Å³; $R = 0.091$ for 211 refined reflections. This complex structure is to some extent related to the γ -brass type. The clusters usually adopted to describe the γ -brass structure can also be discerned in half of the unit cell of the title substance. Between these clusters the packing is different, but still of a related kind.

Introduction. Despite the great technological and scientific importance of the Fe–Zn system, the structures of at least three of the known phases have not been fully established.

The cubic phase $\text{Fe}_3\text{Zn}_{10}$, commonly called Γ , was investigated by Brandon, Brizard, Chieh, McMillan & Pearson (1974), and shown to be of the γ -brass type; weak superstructure reflections, however, indicate that

the structure is more complicated. Bastin, van Loo & Rieck (1974) discovered a cubic phase slightly richer in Zn, which they called I_1 . At room temperature, its homogeneity region extends from 19 to 22 at.% Fe. When the phase contains 19.3 at.% Fe, its formula can be given as $\text{Fe}_3\text{Zn}_{21}$, to emphasize the relation with the γ -brass type. Finally, there exists FeZn_{10} (δ phase) with a very long hexagonal axis ($c = 57.35 \text{ \AA}$), of unknown structure (Bastin, van Loo & Rieck, 1974). Consequently, compositions from 69 to 92 at.% Zn all correspond to very complicated structures. To establish whether these structures have common features the present work on I_1 was undertaken. It is likely that there is indeed a relationship, since a marked alignment occurs when these phases are allowed to be in contact with each other at elevated temperatures (Verplanke, Bastin & van Loo, 1979).

The method of preparing single crystals is described by Verplanke *et al.* (1979). The composition of the crystals is about 22 at.% Fe and, consequently, they are at the Fe-rich side of the homogeneity region. The rarity and smallness of good single crystals was such as to impede accurate determination of the density. Likewise, the alternative way of obtaining the I_1 phase, *i.e.* formation of a layer of it in a solid-state diffusion process, yielded layers too thin to permit a density measurement. A satisfactory crystal was selected by Weissenberg methods; it was a rod 0.4 mm in length with an octagonal cross section with a largest dimension of about 0.1 mm. Data were collected with a Nonius CAD-3 automatic diffractometer and Co $K\alpha$ radiation ($\lambda = 1.79 \text{ \AA}$). Lorentz-polarization and absorption corrections were applied ($\mu = 60.3 \text{ mm}^{-1}$). 955 reflections were obtained. Most unique reflections were measured six times, using different symmetry-related indices; a number were measured three times and a few once, resulting in a set of 211 unique reflections, of which 5 were unobserved below the 3σ level. The cell constant was obtained by least-squares refinement of the angular positions of 40 reflections.

Intensity statistics gave no clear evidence as to the presence or absence of a centre of symmetry. Since the only systematic absence observable is connected with face centring, the possible space groups are $F432$, $F43m$ and $Fm3m$.

The structure was solved by direct methods with *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). An auxiliary program for peak search and interpretation was needed to cope with the high cubic symmetry. First, the centrosymmetric space group $Fm3m$ was tried. Several efforts, however, did not lead to a refineable model. Of the two remaining, noncentrosymmetric, space groups, $F43m$ was considered to be more likely since the related alloy $\text{Fe}_3\text{Zn}_{10}$ has space group $I43m$. All phase sets produced by *MULTAN* were evaluated and one led to a refineable and plausible atomic arrangement, consisting of 14 independent positions, with 19 parameters. Refinement by least squares produced reliable atomic coordinates and an overall temperature factor. Up to this stage, all atoms were assumed to be of one kind (Zn). Three criteria were used to estimate what atomic species may be present at a certain position: (1) the average and minimum distance to neighbouring atoms, (2) the value of the individual isotropic temperature factor after further refinement, (3) the heights of the peaks in a Fourier synthesis. On this basis it was possible to determine with some confidence the nature of 11 atoms. The other three may be either Fe or Zn.

The number of atoms thus found in the unit cell is 408, whereas this number should be 416 if 16 $\text{Fe}_3\text{Zn}_{21}$ formula units were present. There is no indication of fourfold positions such as 0,0,0 being occupied, either from a Fourier synthesis or from structure factor calculations. The number of Fe atoms is about 90, given the composition of the crystal.

The final refinement produced the set of coordinates listed in Table 1. Occupation numbers were not refineable. To account for the number of Fe atoms, the occupation of the atomic sites 9, 10 and 11 was

Table 1. Atomic coordinates ($\times 10^4$) and temperature factors

Atom	Atomic species	Site geometry	Position	x	y	z	B (\AA^2)
1	Zn	CO	48(h)	944 (5)	944 (5)	2285 (6)	0.8 (1)
2	Zn		48(h)	578 (4)	578 (4)	7268 (6)	0.7 (1)
3	Zn	CO	48(h)	1495 (4)	1495 (4)	9643 (7)	0.8 (1)
4	Zn		48(h)	1425 (4)	1425 (4)	4669 (7)	0.6 (1)
5	Zn		48(h)	2001 (4)	2001 (4)	5880 (6)	1.0 (1)
6	Fe	OH	24(f)	1615 (14)	0	0	0.9 (1)
7	Zn		24(f)	3940 (10)	0	0	0.7 (1)
8	Zn	OH	24(g)	649 (10)	2500	2500	0.5 (1)
9	Fe,Zn	OT	16(e)	845 (7)	845 (7)	845 (7)	0.6 (1)
10	Fe,Zn	IT	16(e)	1986 (10)	1986 (10)	1986 (10)	1.0 (1)
11	Fe,Zn	OT	16(e)	3317 (11)	3317 (11)	3317 (11)	1.2 (1)
12	Fe		16(e)	6014 (10)	6014 (10)	6014 (10)	1.0 (1)
13	Zn		16(e)	8097 (9)	8097 (9)	8097 (9)	1.2 (1)
14	Fe	IT	16(e)	9527 (10)	9527 (10)	9527 (10)	1.6 (2)

assumed to be about $\frac{2}{3}\text{Fe} + \frac{1}{3}\text{Zn}$, but, in fact, any Zn atom at a 24-fold or 16-fold position may be partly substituted by Fe.

The value of R was 0.091 ($R = \sum |\Delta F| / \sum |F_o|$ based on all measured reflections).^{*} The atoms are generally 12-coordinated with neighbouring atoms at $< 3 \text{ \AA}$. The Zn atoms 5 and 13 are nine-coordinated. Zn-Zn contacts range from 2.60 to 2.90 \AA , Fe-Zn contacts from 2.49–2.76 \AA and Fe-Fe contacts from 2.38–2.60 \AA .

The minimum values of the interatomic distances are slightly smaller than the sums of the commonly accepted metallic radii (Zn $\simeq 1.38 \text{ \AA}$, Fe $\simeq 1.26 \text{ \AA}$) but are not abnormal. For instance, in the related compound FeZn₁₃ there occur Zn-Zn distances of 2.58 and 2.60 \AA (Brown, 1962; Koster, 1980).

Discussion. Comparison with the structure of the Γ phase, Fe₃Zn₁₀, shows that the lattice constant of Γ_1 is almost exactly twice the lattice constant $a = 8.982 \text{ \AA}$ of the Γ phase. As was demonstrated by Brandon *et al.* (1974) this packing is of the γ -brass type, with space group $I\bar{4}3m$, if we neglect superstructure. If we stack eight cells of the Γ phase together, doubling the cell in the x , y and z directions, a large cell with space group $F\bar{4}3m$ is formed. When we compare the list of coordinates of the atoms in this supercell, using the structure determination by Brandon *et al.* (1974), it is evident that the Γ and Γ_1 structures have much in common. The atoms 1, 3, 4, 6, 8, 9, 10, 11, 12 and 14 have almost the same positions. Customarily the γ -brass structure is regarded as an array of clusters, consisting of four atoms forming an inner tetrahedron (*IT*), four outer-tetrahedron atoms (*OT*), six octahedron atoms (*OH*) and twelve atoms forming a cubo-octahedron (*CO*). On inspection of the list of

coordinates of all 408 atoms, it is readily seen that these clusters are also found in the Γ_1 phase; there are eight in the unit cell. One cluster consists of atoms 1, 8, 10 and 11 and the other of atoms 3, 6, 9 and 14. Both clusters occur four times due to the face-centred lattice; half the atoms in the unit cell are involved in these clusters. The type of coordination is indicated in Table 1. The clusters have the same orientation with respect to the cubic axes as those in the Γ phase and so the easy alignment of the Γ and Γ_1 phases is understandable.

The nature of the atoms at a given position within the cluster does not seem to be constant; for instance, bond lengths suggest that the octahedron atoms (*OH*) in one cluster are Fe, in the other Zn.

Between the clusters, an intricate network exists, in which certain features of the γ -brass structure are preserved. For instance, atom 12 is coordinated in almost the same way as atom 10 or 14. A complete γ -brass-type cluster is, however, not formed. Atom 13 is remarkable since its coordination involves only the atoms 3 and 5.

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^{*} A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36122 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.