

Compounds with the Marcasite Type Crystal Structure

IV.* The Crystal Structure of FeSb₂

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The crystal structure of FeSb₂ is redetermined at room temperature from three-dimensional single crystal X-ray data, and powder X-ray and neutron diffractometer data, by least squares refinements, and the results obtained by the various techniques are compared. The Hamilton test is applied in deciding between a number of possible structure models, including isotropic as well as anisotropic temperature factors for the atoms. The structure is essentially of the FeS₂-*m* type, but the deduced space group *Pnn2* lacks a mirror plane compared with that currently assumed for the structure of FeS₂-*m*. The best values for the positional parameters are: 2 Fe in position (*a*) with *z*=0 and 4 Sb in position (*c*) with *x*=0.1881(1), *y*=0.3565(1), and *z*=0.0097(5). Both kinds of atoms appear to exhibit anisotropic thermal vibrations at room temperature.

Binary compounds having the FeS₂-*m* (*m*=marcasite) type crystal structure fall into two distinct groups according to the axial proportions of their orthorhombic unit cells. The group specified by axial ratios *c/a* ≈ 0.74 and *c/b* ≈ 0.62 includes FeS₂, FeSe₂, FeTe₂, CoSe₂, CoTe₂, β-NiAs₂, and NiSb₂, whereas that with *c/a* ≈ 0.55 and *c/b* ≈ 0.48 comprises CrSb₂, Mo_{0.6}As₂, FeP₂, FeAs₂, FeSb₂, RuP₂, RuAs₂, RuSb₂, OsP₂, OsAs₂, and OsSb₂. The natural classification of these compounds on the basis of this distinction (while detailed structural data have in general been lacking) has attracted attention since the occurrence of the two groups was first recognized by Buerger¹ in 1937.

The origin of the groupings has been discussed by Buerger,¹ and more recently by Pearson,² on the basis of metal-metal and/or secondary non-metal-non-metal interactions; while Hulliger and Mooser^{3,4} have attributed the distinction to effects described by the Jahn-Teller theorem. The difference in interpretation is clearly reflected in the confusing variety of nomenclature which has arisen, *i.e.* the groups called marcasites and loellingites by Buerger are referred to as normal and compressed marcasites by Pearson, and anomalous and Jahn-Teller marcasites by Hulliger and Mooser. However, the lack

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of understanding of the chemical bonding in the compounds with the FeS_2 - m type structure may (at least partly) be attributed to the incomplete or unreliable information hitherto available on their properties.

The highest symmetric space group $Pn\bar{m}$ (or its equivalent) chosen by Buerger^{1,5} to describe the structure of the prototype FeS_2 - m has been uncritically applied in the later structure determinations of the isostructural compounds, neglecting the fact that essentially the same atomic arrangement is generated by $Pnn2$ which lacks the mirror plane characteristic of the former. Clearly, this ambiguity cannot be eliminated on the basis of systematic extinctions in the X-ray data.

The object of the present paper is to describe a detailed redetermination of the structure of FeSb_2 from three-dimensional single crystal X-ray data, thus forming a continuation of earlier investigations⁶⁻⁸ of the properties of compounds with the FeS_2 - m type structure.

RESULTS AND DISCUSSION

(i) *Unit cell and space group.* FeSb_2 has no appreciable range of homogeneity and its composition is unequivocally confirmed to satisfy the stoichiometric formula.⁶ The following unit cell dimensions:

$$a = 5.8328(5) \text{ \AA}, \quad b = 6.5376(5) \text{ \AA}, \quad c = 3.1973(3) \text{ \AA}$$

have been obtained⁶ as average values for several independent samples, a , b , and c for each sample being deduced from Guinier photographic data by least squares refinements. The standard deviation in the mean value of each parameter is appended in brackets, only the figure corresponding to the final digit being given in each case.

On the basis of the observed density of 8.09 gcm^{-3} , the unit cell contains 2 ($Z_c = 1.99$) FeSb_2 -groups.

Single crystals of approximately spherical shape were prepared by chemical transport reactions, using traces of iodine as the transport agent. A good yield of crystals was obtained by applying a temperature gradient of $\sim 1^\circ\text{C}/\text{mm}$ along a $\sim 200 \text{ mm}$ long (evacuated and sealed) silica capsule, with the hot end, containing the polycrystalline FeSb_2 sample, at $\sim 800^\circ\text{C}$. Under these conditions the majority of crystals grew in a narrow region at the cold end of the capsule. Oscillation, Weissenberg, and Guinier photographs confirm the identity of the crystals as being of the FeSb_2 phase.

The systematic extinctions in the diffraction data are of the type $0kl$ absent when $k+l=2n+1$ and $h0l$ absent when $h+l=2n+1$ and the possible space groups are accordingly limited to $Pn\bar{m}$ and $Pnn2$.

(ii) *Refinements of the structure.* Single crystal X-ray photographs were taken in an integrating Weissenberg camera of 57.3 mm diameter with $\text{MoK}\alpha$ -radiation using the multiple-film technique. Three-dimensional data consisting of 757 independent reflections (of which 129 had zero intensity) were collected and their intensities were measured microphotometrically except for the weakest reflections which were estimated visually. The intensities were

corrected for the combined Lorentz and polarization factors, and for absorption ($\mu R=1.4$) and secondary extinction.⁹

The atomic scattering factors for the calculations of F_c -values were taken from Hanson *et al.*,¹⁰ and the least squares refinements were carried out according to a programme by Dahl *et al.*¹¹ The extent of the agreement between the observed and calculated structure factor data is judged from the average and weighted reliability factors:

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$R^* = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{\frac{1}{2}}$$

where w denotes the weight factor. The unobserved reflections are not included in the calculations of R and R^* , and are omitted from the least squares refinements. (The observed and calculated structure factor data are available from the authors upon request.)

The overall correctness of the FeS_2 - m type structure for FeSb_2 has recently been confirmed⁷ on the basis of powder diffraction data (see also section iii), and least squares refinements could accordingly be started at once. In order to promote a test of the presence or absence of the mirror plane characterizing the space group of higher symmetry, a description based on $Pnn2$ was chosen for these calculations. In terms of space group $Pnn2$ the FeS_2 - m type structure places 2 Fe atoms in position (a) $0,0,z; \frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z$ with $z \approx 0$ and 4 Sb atoms in position (c) $x,y,z; \bar{x}, \bar{y}, z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ with $x = 0.188 \pm 0.001$, $y = 0.357 \pm 0.001$, and $z \approx 0$. One of the z -parameters can obviously have ascribed to it an arbitrary fixed value, without introducing any reduction in the generality of the final solution. In order to facilitate comparison of the two space groups it is convenient therefore to keep the z -parameter of Fe fixed at zero throughout the present calculations.

Taking into account a possible anisotropic thermal motion of the atoms, there readily arise seven distinct models to describe the complete FeS_2 - m type structure of FeSb_2 . In connection with the use of the six-term, tensor expressions for description of the thermal anisotropy, it is clear that considerations of symmetry imply limitations in the choice of value for some of the parameters β_{ij} . Since two-fold axes pass through the Fe atoms parallel to [001] it follows that $\beta_{13} = \beta_{23} = 0$ for these atoms. In addition, fixing $z = 0$ for Sb, which is equivalent to the imposition of mirror planes of symmetry perpendicular to [001] at $z = 0$ and $z = \frac{1}{2}$, leads to the identical relationship $\beta_{13} = \beta_{23} = 0$ for the Sb atoms.

Executing the least squares refinements of the structure factor data (subject to the above limitations) until negligible shifts were obtained for all variables, produced the results listed in Table 1. Application of the significance test due to Hamilton¹² in assessing the validity of the various models, requires determination of the R^* -factor ratio $\mathcal{R} = R_r^*/R_u^*$ (where R_r^* and R_u^* correspond to the weighted reliability factors for restrained and unrestrained models, respectively). According to this scheme, the relative probability of the correctness of the different models is judged by comparison of \mathcal{R} with $\mathcal{R}_{b,n-m,\alpha}$ (*cf.* Table 1), b being the dimension of the assumed hypothesis, $n-m$ the degrees of freedom of the data, and α the significance level.

Table 1. Positional parameters and temperature factors for seven possible refinement models of FeSb₂ according to space group $P4m2$. (The standard deviations are given in parentheses behind the corresponding parameter values. In presenting these figures the decimal points and all zeros have been omitted in order to save space.)

Refined parameters	Restrained models							Unrestrained model	
	$z=0$, B_{Fe} and B_{Sb} isotropic	$z=0$, $\beta_{13}=\beta_{23}=0$ for Sb	B_{Fe} and B_{Sb} isotropic	B_{Sb} isotropic	B_{Fe} isotropic, $\beta_{13}=\beta_{23}=0$ for Sb	$\beta_{13}=\beta_{23}=0$ for Sb	No. 6		No. 7
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7		
Fe	B 0.15(2) β_{11} 0.0011(1) β_{22} 0.0009(1) β_{33} 0.0037(5) $2\beta_{12}$ —	— 0.0016(3) 0.0008(2) —0.0018(22) —0.0001(4)	0.19(2) 0.0014(1) 0.0011(1) 0.0046(5) —	— 0.0018(3) 0.0008(2) 0.0060(27) —0.0002(4)	0.20(2) 0.0015(1) 0.0012(1) 0.0049(5) —	— 0.0018(3) 0.0008(2) 0.0050(26) —0.0003(4)	— 0.0018(3) 0.0008(2) 0.0052(26) —0.0003(4)	— 0.0018(3) 0.0008(2) 0.0052(26) —0.0003(4)	
Sb	x 0.1883(1) y 0.3564(1) z 0 B 0.29(1) β_{11} 0.0021(1) β_{22} 0.0017(1) β_{33} 0.0071(2) $2\beta_{12}$ — $2\beta_{13}$ — $2\beta_{23}$ —	0.1883(1) 0.3565(1) 0 — 0.0020(3) 0.0018(1) 0.0063(9) —0.0002(1) 0 0	0.1881(1) 0.3565(1) 0.0095(6) 0.28(1) 0.0021(1) 0.0016(1) 0.0068(2) — — —	0.1881(1) 0.3565(1) 0.0095(6) 0.28(1) 0.0021(1) 0.0016(1) 0.0068(2) — — —	0.1881(1) 0.3565(1) 0.0097(5) — 0.0020(1) 0.0018(1) 0.0049(8) —0.0003(1) 0 0	0.1881(1) 0.3565(1) 0.0097(5) — 0.0020(1) 0.0018(1) 0.0049(8) —0.0003(1) 0 0	0.1881(1) 0.3565(1) 0.0097(5) — 0.0020(1) 0.0018(1) 0.0049(8) —0.0003(1) 0 0	0.1881(1) 0.3565(1) 0.0097(5) — 0.0020(1) 0.0018(1) 0.0049(8) —0.0003(1) 0 0	0.1881(1) 0.3565(1) 0.0097(5) — 0.0020(1) 0.0018(1) 0.0049(8) —0.0003(1) 0 0
R	0.0941	0.0933	0.0886	0.0885	0.0877	0.0875	0.0875	0.0875	
R^*	0.1361	0.1345	0.1207	0.1203	0.1190	0.1190	0.1185	0.1185	
\mathcal{R}	1.149	1.135	1.019	1.015	1.004	—	—	—	
$\mathcal{R}_{b,n-max}$	1.017	1.007	1.015	1.011	1.003	—	—	—	
b	7	1	6	3	3	—	—	—	

No. of observations, $n=628$; No. of parameters in model No. 6, $m=11$; significance level, $\alpha=0.005$, except for model No. 5 where $\alpha=0.25$.

Comparison of the unrestrained model No. 7 with No. 6 (defined by $\beta_{13} = \beta_{23} = 0$ for Sb) shows that identical values of R and R^* are obtained for both models. The fact that no improvement in R and R^* is achieved by allowing freedom to β_{13} and β_{23} for Sb, demonstrates that these parameters are unnecessary (*cf.* Hamilton¹²) in the analysis of the present structure factor data. (This conclusion is evidently consistent with the values and standard deviations derived for β_{13} and β_{23} for Sb according to model No. 7.) Being the simpler of the two models No. 6 is therefore preferable and may be used as the relevant unrestricted case in the following considerations. It should be emphasized, however, that the limitation $\beta_{13} = \beta_{23} = 0$ for Sb may prove to be an inadequate approximation in dealing with improved data.

Independent of the degree of anisotropy assumed, the models Nos. 1 and 2, where $z = 0$, are rejected in favour of No. 6 at a significance level < 0.005 . Models Nos. 3 and 4 are similarly rejected at the same level of significance. The rejection of model No. 5 in which the Fe atoms are regarded as moving isotropically and $\beta_{13} = \beta_{23} = 0$ for Sb must be made at the much higher significance level $\alpha = 0.25$ owing to the low \mathcal{R} value. Although a high significance level is used for rejection of model No. 5, the description based on No. 6 is preferred owing to a conformity with the results derived for the isostructural compounds FeS_2 -*m*, FeTe_2 , and CoTe_2 .¹³

Further examination of the results obtained for model No. 6 shows that the parameters β_{12} for atoms of both kinds, are very small and uncertain (*cf.* their standard deviations) which implies a virtual coincidence of the principle axes of the vibration ellipsoids of the atoms with the crystallographic axes.

The above analysis definitely shows that the mirror plane which is characteristic of the higher symmetric space group $Pn\bar{m}$ is absent in the structure of FeSb_2 as is seen from the departure of z_{Sb} from 0 by 0.0097, which is approximately 20 times as great as the corresponding standard deviation. It should be noted, however, that this conclusion refers to room temperature conditions, and the value of z may be expected to depend on the amplitudes of thermal vibration, and in particular is likely to increase on reducing the temperature.

(iii) *Comparison of various techniques.* The single crystal results referred to in the preceding section may be compared with those obtained from powder samples by means of X-ray and neutron diffractometer techniques.^{7,14} In so doing, the paucity of reflections accessible through the use of powder samples, necessitates the simplifying assumption of isotropic temperature factors in the least squares refinements, where descriptions based on both of the possible space groups were applied. The positional parameters and B -values derived according to the various methods are compared in Table 2. Despite the suitability of model No. 6 (see section ii and Table 1) the single crystal data quoted in Table 2 refer to the rejected models Nos. 1 and 3 where only isotropic temperature factors are used.

The B -values derived by the various methods are seen to differ considerably as is to be expected when different methods (and corrections) are employed. In connection with the values for the positional parameters x and y good

Table 2. Positional parameters and isotropic temperature factors (with standard deviations) for FeSb_2 , deduced according to the method of least squares from data collected by different experimental techniques.

Type of data	Space group	x	y	z	B_{Fe} (\AA^2)	B_{Sb} (\AA^2)	R
Powder X-ray diffractometer data recorded on strip-charts	$Pnmm$	0.188(1)	0.357(1)	—	3.2(4)	2.7(3)	0.082
	$Pnn2$	0.1875(5)	0.3579(6)	0.027(9)	3.2(3)	2.6(3)	0.078
Powder X-ray diffractometer data counted by step-scanning	$Pnmm$	0.1882(6)	0.3552(7)	—	3.4(6)	2.9(4)	0.052
	$Pnn2$	0.1879(6)	0.3550(7)	0.038(7)	3.3(6)	2.8(4)	0.045
Powder neutron diffractometer data counted by step-scanning	$Pnmm$	0.1885(2)	0.3561(4)	—	0.1(2)	0.1(2)	0.026
	$Pnn2$	—	—	No convergence obtained	—	—	—
Single crystal X-ray data from integrated Weissenberg films	$Pnmm$	0.1883(1)	0.3564(1)	—	0.15(2)	0.29(1)	0.0941
	$Pnn2$	0.1881(1)	0.3565(1)	0.0095(6)	0.19(2)	0.28(1)	0.0886

conformity is obtained for the results, which agree within two standard deviations.

Determinations of the z parameter from powder data are limited by the small number of reflections available with $l \neq 0$. As a particular consequence of this no convergence was obtained in the refinement of the neutron diffraction data in terms of the description based on space group $Pnn2$, and the values of z deduced by the X-ray powder methods are seen to differ substantially from that derived from the definitive single crystal data (*cf.* Table 2).

It may therefore be concluded that any one of the methods used provides satisfactorily accurate values for the parameters x and y , and thus an adequate overall description of the structure, and good average values for the interatomic distances. Information on those details of the structure which are associated with the z -parameter and the degree of thermal anisotropy, requires, however, the performance of three dimensional single crystal measurements.

The results of the powder X-ray and neutron diffraction measurements at the temperatures 4 and 80°K show that there is no change in the crystal symmetry from that at room temperature, and that the structure remains essentially of the FeS_2 - m type. The values of x and y derived from these data agree, within standard deviations, with those given in Table 2. These findings are of particular interest in relation to the anomalous temperature variation of the quadrupole splitting observed for FeSb_2 by Temperley and Lefevre¹⁵

Table 3. Some important interatomic distances and angles (with standard deviations) in the crystal structure of FeSb_2 .

Interatomic distances (Å)		Interatomic angles (°)	
Fe—Sb(2) ^a	2.5762(6)	Sb—Fe—Sb(2)	75.97(4)
Fe—Sb(2) ^a	2.5782(11)	Sb—Fe—Sb(2)	87.95(3)
Fe—Sb(2) ^a	2.6164(11)	Sb—Fe—Sb(2)	88.78(3)
		Sb—Fe—Sb(2)	91.19(3)
		Sb—Fe—Sb(2)	92.06(3)
		Sb—Fe—Sb(1)	102.95(4)
		Sb—Fe—Sb(1)	105.11(4)
Sb—Fe(1) ^a	2.5762(6)	Fe—Sb—Fe(1)	75.97(4)
Sb—Fe(1) ^a	2.5782(11)	Fe—Sb—Fe(1)	127.81(5)
Sb—Fe(1) ^a	2.6164(11)	Fe—Sb—Fe(1)	129.57(5)
Sb—Sb(1) ^a	2.8871(12)	Sb—Sb—Fe(1)	105.32(2)
		Sb—Sb—Fe(1)	107.18(4)
		Sb—Sb—Fe(1)	107.45(4)
Sb—Sb ^b	3.1973(3)		
Fe—Sb ^c	4.0818(12)		
Sb—Sb ^c	3.6056(13)		
Fe—Fe ^c	3.1973(3)		

^a Bonding interatomic distances.

^b Possible bonding interatomic distances.

^c Shortest interatomic distances neglected as bonding.

by means of Mössbauer effect spectroscopy. Thus if this anomaly is associated with a structural variation, as suggested by Temperley and Lefevre, the implication is that there is a dependence upon z (see section ii).

(iv) *Interatomic distances and angles.* Interatomic distances and angles calculated from the unit cell dimensions and the positional parameters for model No. 6 in Table 1 are listed in Table 3. Each Fe atom in the structure is octahedrally coordinated to six near Sb atoms and each Sb atom is surrounded by three near Fe and one near Sb in a tetrahedral configuration. The reduction in the symmetry of the coordination octahedra of the Fe atoms introduced by the present data constitutes a small, but not insignificant, increase in the irregularity of these polyhedra. The lack of the mirror plane in space group $Pnn2$ leads to three non-equivalent bonding Fe—Sb distances, each occurring twice per Fe—Sb octahedron (Table 3). Application of Cruickshanks^{16,17} significance test to these distances (a) 2.5762(6), (b) 2.5782(11), and (c) 2.6164(11) Å places the differences between (c) and either (a) or (b) in the highly significant category, while that between (a) and (b) is insignificant.

The more detailed description of the crystal structure of FeSb_2 suggests that the actual bonding schemes for the compounds with the FeS_2 - m type structure are more complex than those discussed by Pearson,² and Hulliger and Mooser.^{3,4} In particular, it is to be noted that the shifting of the Fe atoms away from the centres of the Sb_6 octahedra, consequent on the change to space group $Pnn2$, may be of comparable importance to the deviation of the octahedral angles from 90° , in judging the applicability of the Jahn-Teller effect as an explanation of the degree of irregularity of the immediate coordination around the Fe atoms (*cf.* Hulliger and Mooser^{3,4}). A further discussion of the compounds with the FeS_2 - m type structure in relation to the Jahn-Teller effect will be presented in a forthcoming paper.¹³

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