

Supplementary information for

Ferromagnetism of Fe₃Sn and Alloys

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SUPPLEMENTARY INFORMATION Single crystal X-ray diffraction data collection

Single crystal X-ray diffraction measurements were performed on a Bruker SMART APEX CCD-based single crystal X-ray diffractometer with Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Needle crystals of Fe_5Sn_3 were selected under a microscope and cut to a suitable size ($<0.1 \text{ mm}$ on all sides) under Paratone N oil. The crystals were then cooled to $173(2) \text{ K}$ using a cold nitrogen stream and X-ray intensity data were collected at this temperature. The structure solution by direct methods and refinement by full matrix least-squares methods on F^2 were carried out using the SHELXTL software package [1]. SADABS was used to apply absorption correction.

Crystal Structure description and discussion

The Ni_2In structure type (space group $P6_3/mmc$) is derived from the ubiquitous NiAs structure by filling all the trigonal bipyramidal voids. In the Fe-Sn binary system, this filled structure corresponds to a hypothetical Fe_2Sn formula. Among the reported compounds in this binary system, there are two Fe-deficient Fe_{2-x}Sn compositions, namely, Fe_5Sn_3 and Fe_3Sn_2 , which contain partially filled trigonal bipyramidal $2d$ ($1/3$, $2/3$, $3/4$) site. The partially filled structures are more complex than the simple Ni_2In -type, and the challenge of assigning the correct space group and determining the detailed crystal structures of these phases, along with other transition metal based $T_{2-x}\text{Sn}$ (where $T = \text{transition metal}$) compounds, remains to this day [2,3].

The compound Fe_5Sn_3 has been reported to adopt the Ni_2In type structure with the $2d$ site only $2/3$ occupied by Fe, with lattice constant of $a = 4.23 \text{ \AA}$ and $c = 5.208 \text{ \AA}$ [4]. We began with these parameters for the refinement of the single crystal X-ray data; however, such refinements yielded poor fits, elevated reliability factors and unphysical site occupancy factors. The automated pattern indexing procedure by Bruker SMART software suggested a primitive hexagonal cell with $a = 16.82 \text{ \AA}$ and $c = 5.25 \text{ \AA}$. However, our attempts to refine the structure in this 4×1 supercell using various hexagonal space groups were unsuccessful. Consequently, we turned our attention to the related $T_3\text{Sn}_2$ structures as a source for starting models. There have been conflicting reports on structures of $T_3\text{Sn}_2$ [2,3]. Interestingly, for Co_3Sn_2 , X-ray diffraction patterns could be indexed with a hexagonal superstructure (hs) identical to that observed by us with $a_{\text{hs}} = 4a_{\text{h}}$ and $c_{\text{hs}} = c_{\text{h}}$ ($V_{\text{hs}} = 16V_{\text{h}}$) or an orthorhombic (o) superstructure with $a_{\text{o}} = a_{\text{h}} + 2b_{\text{h}} \approx 3^{1/2}a_{\text{h}}$, $b_{\text{o}} = c_{\text{h}}$ and $c_{\text{o}} = 2a_{\text{h}}$ ($V_{\text{o}} = 4V_{\text{h}}$) [2,5]. Due to a lack of single crystals suitable for single crystal X-ray crystallography, however, authors were not able to confirm either cell. Single-domain electron diffraction work and shielded Weissenberg photographs [2] confirmed the orthorhombic structure for Ni_3Sn_2 and Co_3Sn_2 ; however, X-ray diffraction work gave conflicting conclusions with some favoring the hexagonal structure.

After our failed attempts with the hexagonal superstructure (see above), we subsequently used the described orthorhombic supercell [2] for Fe₅Sn₃. An immediate improvement in reliability factors is noticeable, and our work confirms the orthorhombic structure for Fe₅Sn₃. The orthorhombic distortion from hexagonal cell calculated using $[2 \times 3^{-1/2} a_0 / c_0 - 1]$ is ~0.3%. In addition to the presence of Fe vacancies, we also noticed elongations of Sn thermal ellipsoids, and the final refinement included a splitting of Sn2 position. Summary of single crystal X-ray diffraction data and refinement parameters are provided in Table. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2. The structure is shown in Figure S1.

This orthorhombic crystal structure accounts for some of the observed super-lattice reflections observed by powder diffraction, but not others. This suggests that the powder samples may contain multiple crystallographic phases with similar chemical compositions but structures with varying degrees or types of Fe-vacancy order or Sn disorder.

Table 1. Crystal data and structure refinement for Fe₅Sn₃.

Empirical formula	Fe _{1.65} Sn _{1.01}	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P n m a	
Unit cell dimensions	a = 7.2997(10) Å	α = 90°.
	b = 5.2473(7) Å	β = 90°.
	c = 8.4026(11) Å	γ = 90°.
Volume	321.85(7) Å ³	
Z	8	
Density (calculated)	8.757 Mg/m ³	
Theta range for data collection	3.70 to 26.37°.	
Index ranges	-9 ≤ h ≤ 9, -6 ≤ k ≤ 6, -10 ≤ l ≤ 10	
Reflections collected	3519	
Independent reflections	365 [R(int) = 0.0211]	
Completeness to theta = 26.37°	99.7 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	365 / 0 / 43	
Goodness-of-fit on F ²	1.237	
Final R indices [I > 2σ(I)]	R1 = 0.0721, wR2 = 0.1936	
R indices (all data)	R1 = 0.0733, wR2 = 0.1942	

Largest diff. peak and hole

6.245 and -3.334 e / Å³

Table 2. Atomic coordinates, site occupancy, and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Fe_5Sn_3 . $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	occupancy	$U(\text{eq})$
Sn(1)	0.0989(4)	0.2500	0.6386(3)	1	20(1)
Sn(2A)	0.0569(12)	0.2500	1.0898(17)	0.67(6)	7(2)
Sn(2B)	0.094(5)	0.2500	1.135(3)	0.34(5)	35(5)
Fe(1)	0.2653(4)	-0.0043(6)	0.8738(4)	1	12(1)
Fe(2)	0.0866(8)	-0.2500	0.6273(6)	1	20(1)
Fe(3)	-0.072(3)	0.2500	0.8778(19)	0.31(3)	21(6)

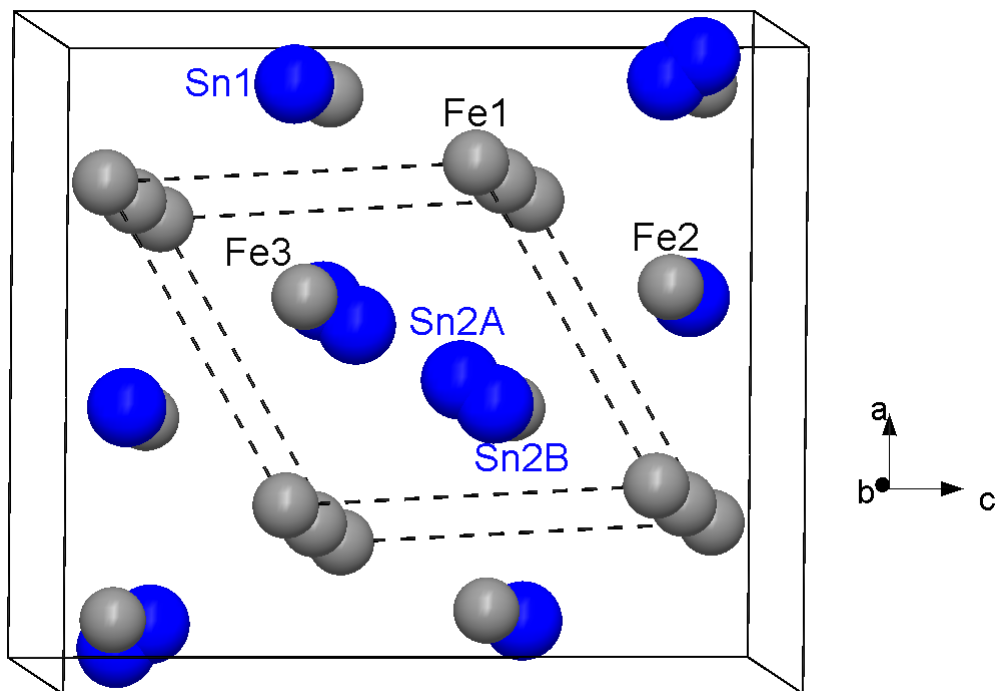


Figure S1. Orthorhombic crystal structure of Fe₅Sn₃. The solid lines outline the unit cell. The dashed lines outline the Ni₂In-type hexagonal sub-cell.

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