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Intermetallics 10 (2002) 423–427

Intermetallics

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Defective structure of the $ThFe_{0.2}Sn_2$ and $PrFe_{0.4}Sn_2$ compounds

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Received 11 January 2002; accepted 21 January 2002

Abstract

The defective structure of the $PrFe_{0.4}Sn_2$ and $ThFe_{0.2}Sn_2$ compounds has been studied by ^{57}Fe and ^{119}Sn Mössbauer spectroscopy, first-principle and binomial distribution calculations. It is shown that the iron and tin sites display different local interactions of atoms located in the same structural position of the defective structure. The analysis of the obtained data together with the theoretical calculations show that defect formation in the samples has a thermal origin. The experimental and theoretical data show that the studied defective structure is locally ordered. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: A: Intermetallics, miscellaneous; E. Electronic structure, calculation; F. Spectroscopic methods, various

1. Introduction

The defective structure of numerous ternary compounds RM_yX_2 (R = rare earth, M = transition metal and X = Si, Sn, Ge) have been studied by X-ray and neutron diffraction during the last few years [1–6]. The $CeNiSi_2$-type structure of these compounds has been described as the result of M interlocation in square pyramidal sites of $ZrSi_2$, which is a particular type of the RX_2 framework. The main proposal of these investigations was the evaluation of the y values on the basis of the diffraction data. However, the y values depend not only on the relative size of the host sites and guest M atoms, but also on the interactions between these M atoms and some of their R nearest neighbours [2,3].

As an alternative, the $TbFeSi_2$ structure was proposed for some of these compounds, when the analysis gave for X atoms a concentration coefficient different from 2. The main difference between the two structures resides in the partial replacement of X atoms by M atoms and vice versa [1].

Recently, the synthesis of two new ternary compounds, $ThFe_{0.2}Sn_2$ and $PrFe_{0.4}Sn_2$, with a defective structure of $CeNiSi_2$-type determined by X-ray single crystal diffraction, has been reported [4,5]. The structure of $ThFe_{0.2}Sn_2$ was confirmed by high-resolution neutron powder diffraction at room and low temperature [6]. The ^{57}Fe Mössbauer spectrum of $ThFe_{0.2}Sn_2$ displayed two doublets with rather different quadrupole splitting [7]. Therefore, two different environments for iron atoms are present in the defective structure of the $ThFe_{0.2}Sn_2$ compound, while only one is present in the $CeNiSi_2$-type structure [4,6].

In the present study we report ^{57}Fe and ^{119}Sn Mössbauer spectroscopy data for the mentioned $ThFe_{0.2}Sn_2$ and $PrFe_{0.4}Sn_2$ compounds, compared with first-principle electron structure and binomial distribution calculations, in order to clarify the Fe environments producing the observed spectra.

2. *Experimental*

The alloys were prepared from turnings of commercially supplied pure metals, mixed and cold pressed under an Ar atmosphere as previously reported [4,5]. The pellets were repeatedly melted in the same protective atmosphere in a high frequency induction furnace; the alloys obtained were then wrapped in Ta foils, sealed into quartz ampoules under vacuum and annealed at 1223 K—7 days and 1173 K—14 days, for $ThFe_{0.2}Sn_2$ and $PrFe_{0.4}Sn_2$, respectively. The samples

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PII: S0966-9795(02)00014-6

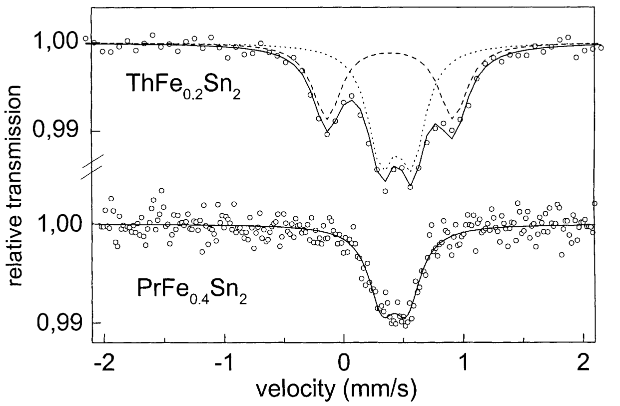

Fig. 1. ^{57}Fe Mössbauer spectra of the $PrFe_{0.4}Sn_2$ and $ThFe_{0.2}Sn_2$ compounds at room temperature. Data points (open circles); best fit (continuous line); Fe_1 (dot), Fe_2 (dash).

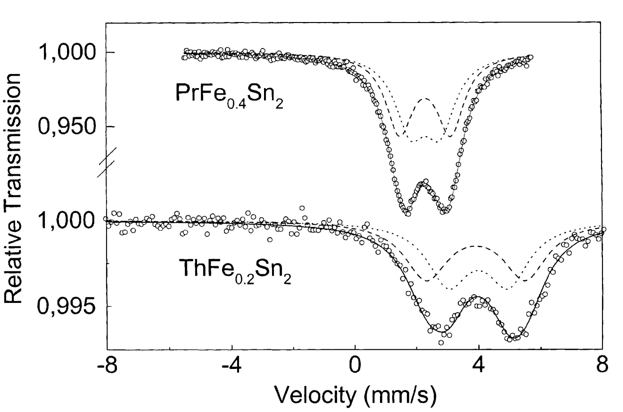

Fig. 2. ^{119}Sn Mössbauer spectra of the $PrFe_{0.4}Sn_2$ and $ThFe_{0.2}Sn_2$ compounds at room temperature. Data points (open circles); best fit (continuous line); Sn_1 (dash), Sn_2 (dot).

Table 1
Room temperature Mössbauer hyperfine parameters of Fe and Sn sites in $PrFe_{0.4}Sn_2$ and $ThFe_{0.2}Sn_2$ samples: δ, isomer shift; Δ, quadrupole splitting; Γ, linewidth; A, relative area

Compd	Site	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	A (%)
$PrFe_{0.4}Sn_2$	Fe	0.42	0.21	0.27	100
	Sn_1	2.30	1.65	1.07	50.0
	Sn_2	2.31	0.95	1.21	50.0
$ThFe_{0.2}Sn_2$	Fe_1	0.45	0.25	0.27	56.7
	Fe_2	0.39	1.05	0.28	43.3
	Sn_1	3.90	3.17	1.73	50.0
	Sn_2	3.98	1.92	1.64	50.0

Constrained values are underlined.

were checked by X-ray powder diffraction using a Guinier camera.

The room-temperature Mössbauer spectra were acquired by a constant acceleration spectrometer with symmetrical velocity waveform using ^{57}Co:Rh and ^{119}Sn:Ca_2SnO_3 sources. The spectra have been fitted by a current minimisation routine.

The LAPW (linear augmented plane wave) method embodied by Blaha et al. in the WIEN97 code [8] was used to calculate the electronic structure of the Th–Fe–Sn compound. Four different model structures are investigated and discussed below. The calculations employ the generalized gradient approximation (GGA) within density functional theory (DFT). Since specific Fe positions could lead to large structural relaxations, we relaxed all internal parameters until the resulting forces on the atoms were negligible.

3. Results and discussion

The ^{57}Fe and ^{119}Sn Mössbauer spectra of the $ThFe_{0.2}Sn_2$ and $PrFe_{0.4}Sn_2$ compounds are shown in Figs. 1 and 2, respectively, and appear as combinations of paramagnetic doublets. The hyperfine parameters isomer shift δ, quadrupole splitting Δ, and linewidth Γ resulted from the best fit are reported in Table 1.

We discuss first the ^{57}Fe Mössbauer spectra, whose components are characterised by a rather narrow linewidth. In the case of $PrFe_{0.4}Sn_2$ there is only one doublet, while in the case of $ThFe_{0.2}$ Sn_2 there is evidence of two doublets Fe_1 and Fe_2. One of them has parameters very close to the doublet in $PrFe_{0.4}Sn_2$, while the second has a quadrupole splitting $\Delta = 1.05$ mm/s, a rather high value for an intermetallic compound.

In contrast to the present Mössbauer spectroscopy results, previous X-ray and neutron diffraction data [4,6] give only one iron site in the $ThFe_{0.2}Sn_2$ compound. The difference between the quadrupole splittings of the two iron doublets in the Mössbauer spectrum can have several origins. From previous structural studies [5] one knows that the Fe atoms are inside a pyramid with a square basis formed by Sn atoms. Since the iron site is only partially occupied, the neighbouring Sn-pyramids may or may not contain a Fe atom, leading to 0–4 nearest Fe neighbours. This will influence the ^{57}Fe Mössbauer spectrum. The RM_yX_2 ternary compounds can crystallise into the two similar structures, $CeNiSi_2$ and $TbFeSi_2$ [1]. A possible interchange between Fe and Si atoms in the $TbFeSi_2$-isotype structure can lead to Fe atoms in two crystallographic sites with different hyperfine parameters [7]. The relaxation of the atomic positions, due to the possible different environments of Fe atoms, can also influence the hyperfine parameters.

In order to check the influence of the mentioned factors on the Mössbauer parameters of iron atoms, the WIEN97 code [8] has been used to calculate the electronic structure and the Mössbauer parameters for some different arrangements of iron atoms in the Th–Fe–Sn compound. For these calculations we had to use a virtual composition of $ThFe_{0.25}Sn_2$, which is close to the real one, but can be approximated by some simple unit cells and still allows geometry optimisation (moving all atoms until the residual forces are close to zero):

(i) an unit cell of 13 atoms and 3 Fe vacancies (Th_4FeSn_8) [4–6]. The Fe atoms form a single layer with no Fe-vacancies in this layer, while there are three more "empty" Fe-layers in this structure, and no Fe atoms are at Sn sites (Fig. 3a);

(ii) a 2×2 supercell along the *a* and *c* axes with 52 atoms and 12 Fe vacancies ($Th_{16}Fe_4Sn_{32}$), where all Fe atoms within the plane are separated from each other, but Fe is now present in all four layers of the unit cell (Fig. 3b);

(iii) a supercell of two unit cells along the *a* axis, containing 26 atoms and 6 Fe vacancies ($Th_8Fe_2Sn_{16}$), with Fe chains along the c axis (Fig. 3c);

(iv) a supercell of two cells along *c* axis, with 26 atoms plus 6 Fe vacancies, in which the Fe atom substitutes a Sn atom within the basal plane of the pyramids and one Sn atom occupies the Fe position inside the pyramid (Fig. 3d).

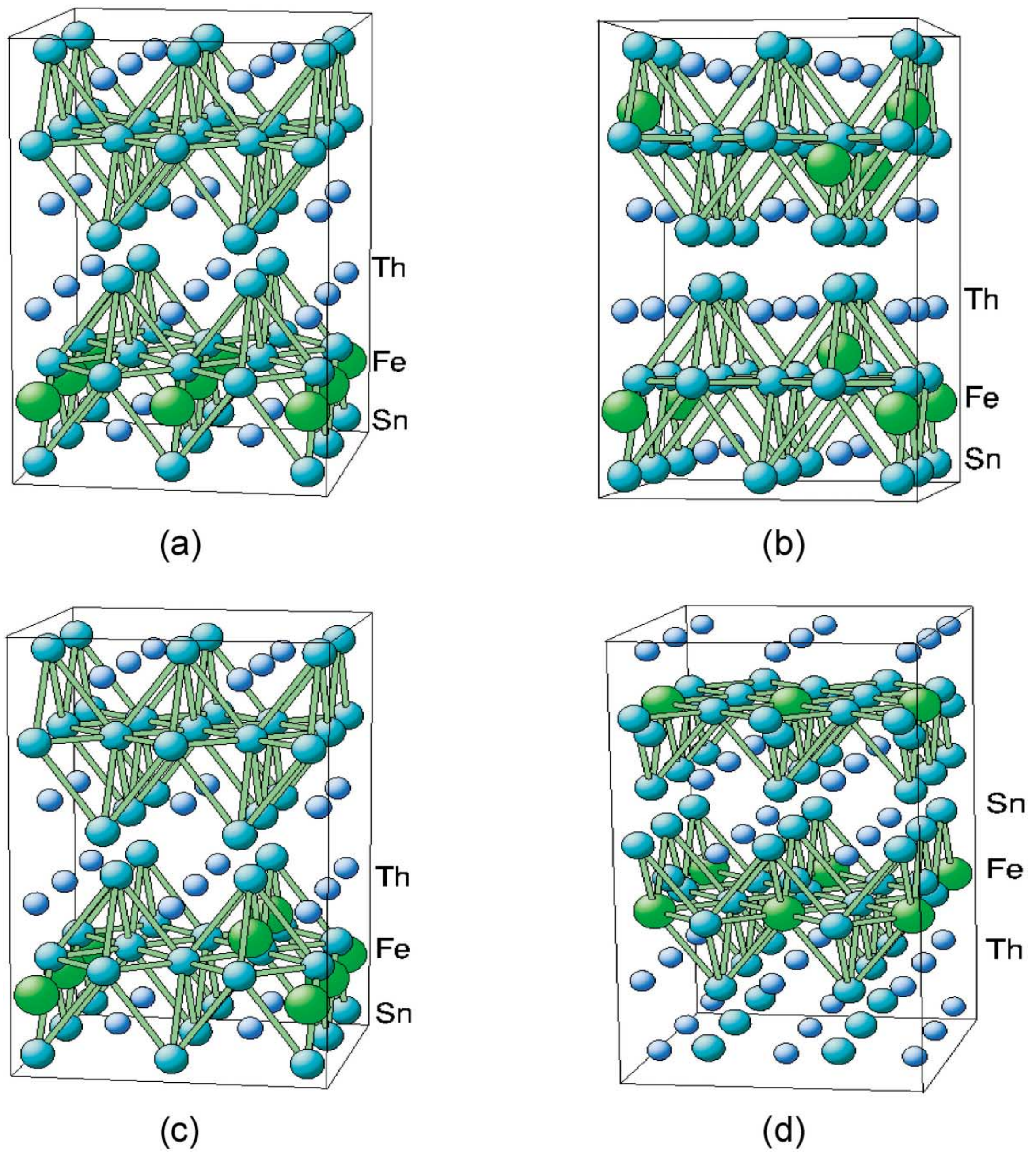

Fig. 3. Atomic arrangement in the structures corresponding to the discussed models (i), (ii), (iii) and (iv) (see text).

Table 2
Calculated hyperfine parameters of Fe atoms in the $ThFe_{0.2}Sn_2$ compound (see text). ρ is the electron density at the iron nucleus and Δ the quadrupole splitting (using $Q = 0.16$ b). Underlined values are given after geometry optimisation

Model	Atom	Crystallographic position	Number of Fe neighbours	ρ	Δ (mm/s)	ρ	Δ (mm/s)
(i)	Fe	Fe	0	15309.2	0.24	15308.2	0.19
(ii)	Fe	Fe	1	15308.9	0.40	15308.3	0.25
(iii)	Fe	Fe	2	15309.1	0.59	15308.5	0.68
(iv)	Fe	Sn_1	0	15308.4	0.66	15308.3	0.64

From the calculations, whose results are reported in Table 2, we observe that the Δ values of iron crystallographic sites in $ThFe_{0.2}Sn_2$ are strongly influenced by the number of neighbouring iron atoms, while the electron densities at the iron nucleus, related to δ values, are quite similar. For Fe atoms substituting Sn the Δ values are very close to that of Fe with 2 Fe neighbours.

Due to the high sensitivity of Δ value to every change in the neighbourhood of iron atoms, a definitive assignment of both doublets to iron sites in the $ThFe_{0.2}Sn_2$ compound requires the calculation of a larger number of various models with the exact experimental composition. Nevertheless, the low occupancy of iron sites in the $ThFe_{0.2}Sn_2$ compound and the quite good consistency of experimental and theoretical Δ values (Fe_1 data and model *i)* in Tables 1 and 2, respectively) allow us to suppose that the experimental Fe_1 site in $ThFe_{0.2}Sn_2$ corresponds to iron atoms without neighbour iron atoms in the second basis of the pyramid. The same assignment can be made for the Fe site in $PrFe_{0.4}Sn_2$, due to the similarity in the environment. The site interchange of Sn by Fe atoms (model iv), and therefore the formation of a $TbFeSi_2$-isotype structure instead of $CeNiSi_2$ [7] can be excluded for the following reasons. The calculation gives similar Δ values for Fe atoms substituting Sn and for Fe atoms sitting in the Ni crystallographic site of $CeNiSi_2$ [see Table 2, models (iv) and (iii), respectively], so that no conclusion can be drawn from that, but the atomic interchange between Sn and Fe would lead to large displacements of the atoms, in contrast to the experiment in [4,6]. As a conclusion, we suggest to assign the second doublet Fe_2 to the same crystallographic Fe site as Fe_1 but with a different number of Fe neighbours, in agreement with the X-ray and neutron diffraction data [4,6].

The ^{119}Sn Mössbauer spectra of the $ThFe_{0.2}Sn_2$ and $PrFe_{0.4}Sn_2$ compounds have been fitted with two doublets, in agreement with the X-ray single crystal diffraction data which give the presence of two sites for tin. The differences in the hyperfine parameters are due to the different surroundings of Sn atoms in the two compounds. In particular, the linewidths for $PrFe_{0.4}Sn_2$ are lower that for $ThFe_{0.2}Sn_2$, reflecting a less disordered distribution of Fe atoms and defects, in agreement with the above findings by ^{57}Fe Mössbauer spectroscopy. The theoretic values fluctuate randomly within the range of the experimental values, depending on the number of neighbours. The calculations prove also that δ fluctuates in a short range of about 0.5 mm/s for both Sn sites, in agreement with the experimental data.

Table 3
Arrangement of randomly distributed iron atoms as neighbours to iron atoms in the RFe_ySn_2 ternary compounds

Iron neighbours	Probability	
	$y = 0.2$	$y = 0.4$
0	0.41	0.13
1	0.41	0.35
2	0.15	0.35
3	0.02	0.15
4	–	0.02

The previous attempts to study the defective structure of these compounds have shown that the vacancies have a disordered distribution at the transition element site, in agreement with the absence of any superstructure in the X-ray diffraction data [1–6]. This disordered distribution is expected to influence the hyperfine parameters for every site of the structure in which Fe and Sn atoms are located. In Table 3 we report the number of neighbouring atoms in the environment of the iron site in the case of random distribution, for the studied structure with two different values of y. This gives three or four different electronic shells, while our experimental evidence gives only one or two preferred sites for iron. Moreover, experiment and electron structure calculations indicate that the number of Fe neighbours to Fe atoms in the $PrFe_{0.4}Sn_2$ sample is lower than in the $ThFe_{0.2}Sn_2$ sample, which is a reversed situation to that corresponding to the random distribution of Table 3. So, there is no correspondence between iron concentration, y value, and the distribution of vacancies in the studied compounds. Therefore, the formation of $CeNiSi_2$-type compounds is governed by the thermal conditions of their synthesis and not by the structural origin of the vacancies. Our experimental data give two Fe sites in $ThFe_{0.2}Sn_2$ and only one in $PrFe_{0.4}Sn_2$, proving that the studied compounds are locally ordered, in disagreement with previous literature reports [1–6].

4. Conclusions

^{57}Fe and ^{119}Sn Mössbauer spectroscopy measurements have shown, in agreement with previous X-ray single crystal and neutron powder diffraction data, that the structure of the $ThFe_{0.2}Sn_2$ and $PrFe_{0.4}Sn_2$ compounds (of $CeNiSi_2$ type) is defective. Experiments and electronic structure calculations prove that the local interactions of Sn and Fe atoms are different in the $ThFe_{0.2}Sn_2$ and $PrFe_{0.4}Sn_2$ compounds, due to the different distribution of Fe atoms. Mössbauer spectroscopy also displays a local ordering in a structure otherwise seen as disordered on average by XRD. Moreover, the defective structure in the studied compounds is found to be of thermal origin.

Acknowledgements

Planning and development of the studies presented here form a part of an Italian National Research Project entitled *Leghe e composti intermetallici: stabilità termodinamica, proprietà fisiche e reattività.* The authors would like to thank the Italian Ministero della Ricerca Scientifica e Tecnologica (*Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale*) for financial support.

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