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A Mössbauer study of the new phases $Th_4Fe_{13}Sn_5$ and $ThFe_{0.22}Sn_2$

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Abstract

Two new phases $Th_4Fe_{13}Sn_5$ and $ThFe_{0.22}Sn_2$ have been studied by ^{57}Fe and ^{119}Sn Mössbauer spectroscopy. The ^{57}Fe Mössbauer spectra of $Th_4Fe_{13}Sn_5$, measured at room temperature and 4.2 K without and with applied magnetic field up to 5.5 T, exhibit four sextets. Our measurements prove that all four Fe sub-lattices are collinear. The ^{119}Sn Mössbauer spectra of $Th_4Fe_{13}Sn_5$ show two sextets with different B_{eff}, reflecting the influence of ferromagnetic nn iron atoms. The results obtained from full-potential linear augmented plane wave (LAPW) calculations are in agreement with the experimental data and confirm the assignment of Mössbauer spectra. The Mössbauer data for the $ThFe_{0.22}Sn$ compound prove the existence of two different sites both for Fe and Sn, all having icosahedral co-ordination.

Keywords: Intermetallics; Mössbauer spectroscopy; Magnetic properties

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1. Introduction

Recently the synthesis of two new ternary phases of the Th–Fe–Sn system was reported, together with their crystal structures determined by X-ray single crystal diffraction [1]. The first, $Th_4Fe_{13}Sn_5$, has a structure (tetragonal space group *P*4/*mbm*), formed by two different segments alternating along the tetragonal *c*-axis. The structure of the second compound, $ThFe_{0.22}Sn_{2,}$ is similar to $ThSn_2$ ($ZrSi_2$ type) and can also be defined as a defective $CeNiSi_2$ [1]. The first compound is ferromagnetic up to 380 K, where it undergoes a transition to the paramagnetic state, as observed from magnetisation measurements as a function of temperature. The phase transition was confirmed by differential scanning calorimetry (DSC) measurements with an endothermic maximum at 376 K. The $ThFe_{0.22}Sn_2$ compound is paramagnetic down to 4.2 K.

High resolution neutron powder diffraction [2] confirmed the assigned structures: tetragonal for $Th_4Fe_{13}Sn_{5,}$ and orthorhombic for $ThFe_{0.22}Sn_2$. For $Th_4Fe_{13}Sn_5$, the most consistent agreement with the observed low temperature intensities was obtained assuming that the Fe magnetic moments on the four available sites are aligned collinearly, with the easy magnetisation direction along the tetragonal *c*-axis.

The present study uses both ^{57}Fe and ^{119}Sn Mössbauer spectroscopy. The experimental hyperfine parameters were compared with calculations using a full-potential linear-augmented-plane-wave (LAPW) method [3]. Based on the high sensitivity of the experimental method, as well as on the electron density calculated with high accuracy, Fe and Sn local interactions related to their crystalline positions are derived.

2. Experimental details

The alloys were prepared from commercially supplied metals mixed under Ar atmosphere and cold pressed together, as previously reported [1,2]. Then the pellets were repeatedly melted (again in Ar protective atmosphere) in a high frequency induction furnace.

The Mössbauer spectra were acquired by a constant acceleration spectrometer with symmetrical velocity waveform using a ^{57}Co source in a Rh matrix and ^{119}Sn in Ca_2SnO_3. For 'in field' measurements, an Oxford Instruments cryostat with a superconducting coil providing a field up to 7 T, parallel to the γ-direction, was used. A

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current minimisation routine was used to fit the spectra. The isomer shifts are referred to metallic iron and to SnO_2, for Fe and Sn atoms, respectively.

The LAPW method embodied by Blaha et al., in the WIEN97 code [3] was used to calculate the electronic structure of the $Th_4Fe_{13}Sn_5$ intermetallic phase. Spin-polarised calculations were done in order to obtain the theoretical values of the hyperfine fields at the nucleus. Exchange and correlation effects were treated within density functional theory via the generalised gradient approximation (GGA) [4]. The density of states has been calculated using the modified tetrahedron method of Blöchl et al. [5]. Structural data, previously found by X-ray and high resolution neutron powder diffraction [1,2] were used as starting point for the calculations.

3. Results and discussion

The experimental spectra of the $Th_4Fe_{13}Sn_5$ compound, together with their best fit, are shown in Fig. 1 (Fe, RT and low temperature with and without applied field) and in Fig. 2 (Sn, RT, low temperature). In Fig. 3 the spectra of the $ThFe_{0.22}Sn_2$ compound (Fe and Sn, RT) are presented. Tables 1 and 2 contain the theoretical and experimental hyperfine parameters for the two compounds.

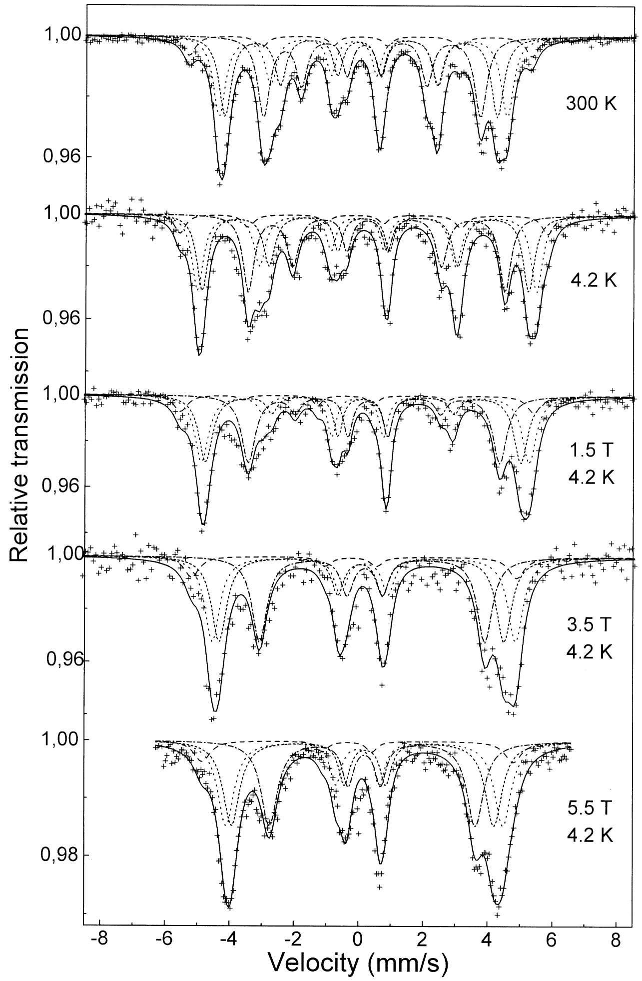

Fig. 1. ^{57}Fe Mössbauer spectra of the $Th_4Fe_{13}Sn_5$ compound at room and 4.2 K temperatures with and without applied field. The computed components are: Fe_4 (dash), Fe_3 (dot), Fe_2 (dash–dot), Fe_1 (short dash).

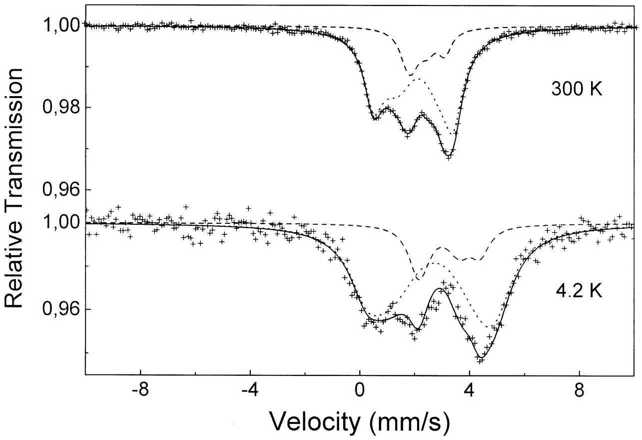

Fig. 2. ^{119}Sn Mössbauer spectra of the $Th_4Fe_{13}Sn_5$ compound at room and 4 K temperatures. The computed components are: Sn_1 (dot), Sn_2 (dash).

3.1. $Th_4Fe_{13}Sn_5$

3.1.1. ^{57}Fe Mössbauer spectroscopy

The ^{57}Fe Mössbauer spectra of $Th_4Fe_{13}Sn_5$ present magnetic sextets both at room temperature (RT) and 4.2 K (see Fig. 1). The four sextets used to fit the Mössbauer spectra are in agreement with the structural data in Refs. [1,2], where four non-equivalent Fe sites were reported. The relative areas of the Fe_4, Fe_1, Fe_2, Fe_3 components in Table 1 were constrained to the ratio 1:4:4:4, in agreement with the crystallographic site occupations. The ratio A_{21} of second to first lines was assumed to be the same for all sextets, in agreement with the neutron diffraction data,

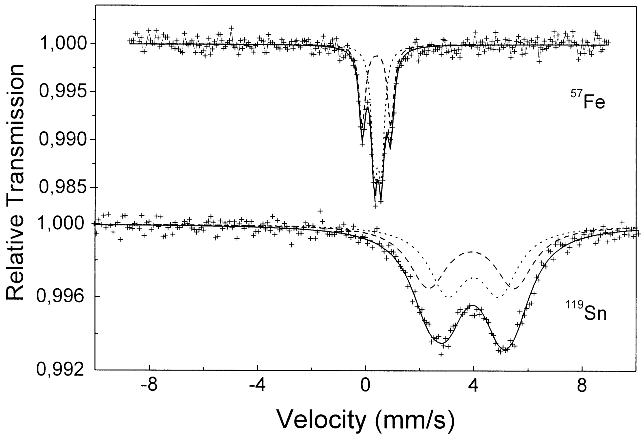

Fig. 3. ^{57}Fe and ^{119}Sn Mössbauer spectra of the $ThFe_{0.22}Sn_2$ compound at room temperature. The computed components are: Sn_1 (dash), Sn_2 (dot) and Fe_1 (dot), Fe_2 (dash).

Table 1
Experimental and theoretical hyperfine parameters of Mössbauer iron sites in $Th_4Fe_{13}Sn_5$ at different temperatures[a]

T (K)	Site	δ^{Th} (mm s^{-1})	δ^{Exp} (mm s^{-1})	Δ^{Th} (mm s^{-1})	B_{hf}^{Th} (T)	B_{hf}^{Exp} (T)	A (%)
RT	Fe_4		−0.01			−33.0	7.6
	Fe_3		−0.06			−27.7	30.8
	Fe_1		−0.01			−26.2	30.8
	Fe_2		0.23			−20.9	30.8
4.2	Fe_4	−0.03[b]	−0.03	−0.28	−36.3	−35.4	7.6
	Fe_3	0.06	0.07	−0.56	−30.9	−32.6	30.8
	Fe_1	0.12	0.14	−0.37	−29.6	−31.4	30.8
	Fe_2	0.30	0.37	0.39	−23.0	−24.7	30.8
RT	Sn_1		2.05			2.1	80.0
	Sn_2		2.27			−0.9	20.0
4.2	Sn_1	2.68[b]	2.68	−1.11	3.8	3.4	80.0
	Sn_2	2.99	3.08	0.81	−2.5	−1.6	20.0

[a] δ, isomer shift; Δ, quadrupole splitting; B_{hf}, internal magnetic field; A, relative area.

[b] The theoretical δ values for Fe_4 and Sn_1 sites have been aligned with experiment.

based on the assumption that the magnetic moments on the four iron sites are aligned collinearly [2].

All iron sites have an icosahedral environment (12 neighbours). Taking into account the number of Fe nearest neighbour atoms (both Th and Sn atoms do not magnetically contribute) it is straightforward to assign the Fe_4 site, which has 12 magnetic exchange integrals, to the highest B_{eff} value. The hyperfine parameters of this spectral component are close to those of α-iron at RT. Previous diffraction data [1,2] indicate the presence of α-iron as an impurity. Its contribution to the Mössbauer spectrum, if any, is negligible and would in any case overlap with the intense subspectrum of the Fe_4 site. The Fe_2 site (with only seven Fe nn) is associated to the smallest B_{eff} value. The assignment of the other two spectral components to Fe_1 and Fe_3 sites is difficult on the basis of distances and number of Fe nn atoms only. In order to improve this situation, the WIEN97 code [3] was used to calculate the electronic structure and Mössbauer parameters on each Fe-site (see below). At 4.2 K all B_{hf} values increase by about 5 T compared with those at RT (Table 1), indicating a rather low T_C, according to Ref. [1]. It is worth mentioning that at RT all sextets, except that attributed to Fe_4, have smaller effective fields than that of α-Fe (33 T). This rather high increase of about 5 T, compared with only 1.3 T for α-Fe [6], is related to the significantly lower T_C, 380 K [1] instead of 1044 K for α-Fe [7]. The higher δ values at low temperature are related to the second order Doppler shift.

Iron spins in the absence of an applied field are assumed to be randomly oriented for a powder sample (Fig. 4). In this case, the ratio A_{21} between the intensities of the second and the first lines should be around $0.\overline{6}$ [7]. Generally, the ratio A_{21} is expressed by:

$$x = \frac{4\sin^2\varphi}{3(1+\cos^2\varphi)} \tag{1}$$

where φ is the angle between the direction of the local spin and that of the γ-ray. According to this equation, a value of 54.7° for φ provides the same ratio A_{21}, namely $0.\overline{6}$, typical of random spin orientation. Therefore, this does not allow to discriminate between randomly oriented powder particles and the situation that all iron spins form an angle of 54.7° with the γ-ray direction.

The x values obtained from Mössbauer spectra at RT and 4.2 K in the absence of an applied field (Table 3) indicate a random orientation of Fe spins. By applying the

Table 2
Room temperature Mössbauer hyperfine parameters of tin sites in $ThFe_{0.22}Sn_2$ sample[a]

Site	δ (mm s^{-1})	Δ (mm s^{-1})	A (%)
Fe_1	0.45	0.25	56.7
Fe_2	0.39	1.05	43.3
Sn_1	3.90	3.17	50.0
Sn_2	3.98	1.92	50.0

[a] δ, isomer shift; Δ, quadrupole splitting; A, relative area.

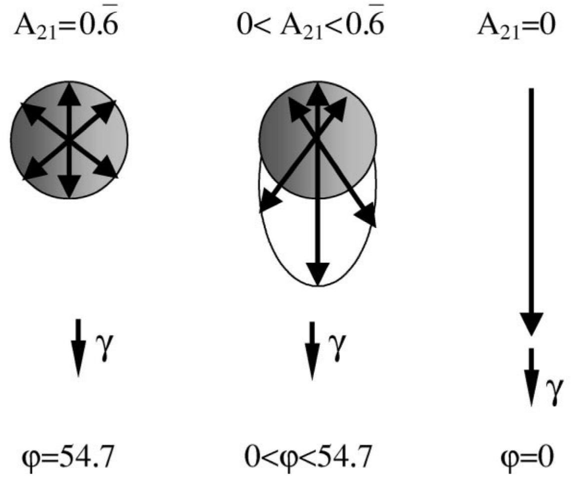

Fig. 4. Iron spin orientations at different formal angle φ (see text).

Table 3
A_{21} and φ parameters of Mössbauer spectral components of iron sites in the $Th_4Fe_{13}Sn_5$ sample with and without applied magnetic field B_{ap}

T (K)	B_{ap} (T)	A_{21}	$(\cos\varphi)^2$	$\lvert\cos\varphi\rvert$	φ ($\pm\pi$) (°)
RT	0	0.54	0.42	0.65	50.0
4.2	0	0.67	0.34	0.58	54.5
4.2	1.5	0.19	0.75	0.87	29.0
4.2	3.5	0	1	1	0

external field, the B_{eff} vector rotates towards the direction of γ-rays. Taking into account that the applied magnetic field is parallel to the γ-ray direction, both the mean hyperfine field and the formal direction of the iron spins can be calculated by the vectorial model of Fig. 5. In the presence of an applied field, B_{app}, there is a vectorial relationship between the effective field at the nucleus, B_{eff}, and the hyperfine magnetic field, B_{hf}

$$\vec{B}_{eff} = \vec{B}_{app} + \vec{B}_{hf}, \tag{2}$$

with values derived as

$$B_{hf} = (B_{app}^2 + B_{eff}^2 + 2\,B_{app}B_{eff}\cos\theta)^{1/2}, \tag{3}$$

and the orientation given by

$$\sin\alpha = B_{eff}\sin\theta / B_{hf}, \tag{4}$$

where α (angle between γ-rays and internal magnetic field) corresponds to φ in Eq. (1).

The B_{hf} data in Table 1 show that all B_{eff} of the four Fe sites were oriented in an opposite sense to the applied field and that they rotate towards the direction of γ-rays under its action. We observe from Table 3 that an angle of 29° is obtained for $B_{app} = 1.5$ T between the direction of B_{eff} and γ-rays. The ratio A_{21} is 0 for $B_{app} = 3.5$ T, corresponding to a direction of the effective field B_{eff} parallel to γ-rays. The 'in field' measurements prove that all iron hyperfine fields are aligned collinearly.

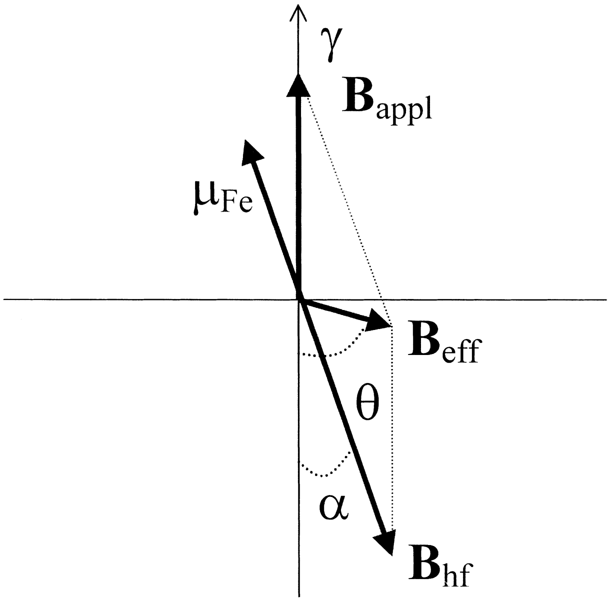

Fig. 5. Vectorial model of the magnetic fields at the iron nucleus.

The quadrupole interaction is treated in magnetically ordered compounds as a perturbation of the main magnetic interaction, which produces a much larger line splitting. The absorption lines are shifted by an amount, which strongly depends on Euler angle transformations, obtained from mixing quadrupole and magnetic interactions. Consequently, the line-shifts are smaller than the quadrupole splitting, Δ, evidenced in a pure paramagnetic state, except the case when both the magnetic field and quadrupole axis directions are parallel. One should compare the calculated Δ values with the ones obtained above the Curie temperature. The Mössbauer spectrum recorded at 400 K could be fitted with two doublets showing similar Δ values (0.53–0.59 mm s^{-1}). The two values of isomer shift, δ, are -0.10 and -0.22 mm s^{-1}, respectively. Comparing these values with those of components obtained at a temperature lower than T_C, we assign the doublet with less negative δ to the Fe_2 site. The relative area of this doublet corresponds to that of the Fe_2 site subspectrum in the spectra at lower temperatures. The second doublet has a relative area corresponding to the sum of populations of the three sites Fe_1, Fe_3 and Fe_4.

It was suggested in Ref. [1] that a structural similarity of $Th_4Fe_{13}Sn_5$ exists with the structure of $Nd_5Fe_{13}Si$ type (space group $I4/mmm$) [8], i.e. $Nd_6Fe_{13}Sn$ [9]. The B_{hf} values observed in Refs. [8,9] without an applied field are very similar to our data of $Th_4Fe_{13}Sn_5$, but the magnetic structure is different. Indeed, there are four non-equivalent Fe positions, in the same (1:4:4:4) ratio, but $Nd_6Fe_{13}Sn$ shows a ferrimagnetic spin arrangement, proved by in field measurements [8]. This latter compound, in which Nd moments also contribute, showed a meta-magnetic transition in applied fields up to 14 T, with a critical field of 7.1 T. Compounds of $R_5Fe_{13}M$ type, with various R and M, mostly show ferrimagnetic or spin canting magnetic structures [8–11]. The studied magnetic structure of $Th_4Fe_{13}Sn_5$, with four ferromagnetic collinear iron atoms, rarely appears in intermetallics.

3.1.2. ^{119}Sn Mössbauer spectroscopy

As reported in previous papers [1,2], the Sn atoms are located in two very different environments. There is an icosahedral site for Sn_2 (12 nearest neighbours) similarly to all Fe-sites. The Sn_1 site surprisingly exhibits an octahedral co-ordination, which appears very seldom in metals or intermetallic compounds. It should be mentioned that, while Sn_1 has only Th and Sn as nn atoms, Sn_1 has four iron atoms (three Fe_2 and one Fe_1) in the first shell of 12 nn. The influence of an existing magnetic field on the ^{119}Sn nucleus will display a splitting larger than the ^{57}Fe one, since the nuclear magnetic moment of Sn is about eight times that of Fe both in the excited and ground state

[7]. Moreover, according to electronic structure calculations (see below), there is a low but not negligible magnetic splitting of the nuclear levels due to the influence of iron atoms on both Sn sites. As a consequence, one should expect two sextets for Sn_1 and Sn_2 subspectra.

The marked difference in the local structure between the two Sn sites allows to assign the Mössbauer components as follows. The spectral profiles measured at both temperatures appear in a first approximation as the sum of two doublets, with an area ratio of about 4:1. It is straightforward to assign the less intense doublet to the Sn_2 site, according to structural data in Refs. [1,2]. The apparent doublets have very large linewidths. Moreover, the increase of line splitting at low temperature for both components is very high, indicating that we are dealing effectively with two unresolved sextets, in agreement with the above-mentioned influence of the Fe atoms nn on Sn sites. From these unresolved sextet components it is impossible to derive uniquely the values of the quadrupole interactions, which is supposed to be of the same order of the magnetic interaction, and then the directions of EFG and magnetic axis.

We can observe in Table 1 that the increase at low temperature of B_{eff} for Sn sites agrees with a corresponding increase of B_{eff} for all Fe sites. The values of isomer shifts (see Table 1) are in agreement with those for intermetallics containing Sn atoms [7].

3.1.3. Electronic structure and Mössbauer parameters

The hyperfine parameters at the Fe nuclei in the $Th_4Fe_{13}Sn_5$ compound were obtained theoretically by spin-polarised electronic structure calculations. The isomer shift (IS) can be calculated from the total electron density at the nuclear site using $IS=\alpha(\rho_a(0)-\rho_s(0))$, where we take α as -0.24 mm s^{-1} for Fe [12] and 0.092 mm s^{-1} for Sn [13]. The contact term of the hyperfine field is just equal to the spin-density (difference of spin-up and spin-down density) averaged over the Thomson radius [12]. Finally, the electric field gradient (EFG) can be calculated from the total charge density using $V_{zz}=\int \rho(r)\, Y_{20}/r^3\, dr$. Thus, the EFG is proportional to the non-spherical components in the charge density and it can be converted to experimental quadrupole splittings using $Q=0.16$b [14] for Fe and $Q=0.128$b for Sn [13].

Our results are also shown in Table 1. For the four Fe sites, both the hyperfine fields as well as the IS agree perfectly well between theory and experiment. Since we did not perform IS calculations for the experimental reference systems, the theoretical IS were shifted to match the smallest experimental IS. All spectra components could be definitively assigned to the crystallographic iron sites, because significant differences were found also for the hyperfine parameters of Fe_1 and Fe_3 sites, whose assignment was uncertain due to similar crystallographic environments.

Table 4
Transferred field parameters on Th and Sn sites in the $Th_4Fe_{13}Sn_5$ sample[a]

Atom	D (Å)	μ (μ_B)	B_{eff} (T)
Th_2	3.2	0.24	−53.1
Th_1	3.8	−0.01	8.2
Sn_1	2.6	−0.04	3.8
Sn_2	5.0	0.03	−2.5

[a] D, distance from Fe nn; B_{eff}, effective magnetic field; μ, magnetic moment.

The agreement of the experimental and theoretical data for the two Sn sites is again very good. The stronger magnetic character of Sn_1 as compared to Sn_2 depends on the different influence of Fe sites. The Fe 3d electrons polarise by hybridisation the 4s electrons which, being very diffuse, produce a long ranging polarisation of the nn atoms, correlated roughly to the distance from Fe atoms. Consequently, the nuclear levels of nn atoms are magnetically split. These ‘transferred’ fields regard also Th atoms. Table 4 reports the results of calculations on the particular magnetic structure of the studied compound.

3.2. $ThFe_{0.22}Sn_2$

The ^{57}Fe Mössbauer spectrum of the $ThFe_{0.22}Sn_2$ compound cannot be described with only one component: two doublets are necessary to fit satisfactorily the experimental profile (Fig. 3). This result is rather surprising, taking into account that the X-ray single crystal and neutron powder diffraction investigations on $ThFe_{0.22}Sn_2$ indicated a $CeNiSi_2$ structure with only one iron site [1,2]. A first explanation of the present results could be that there is partial ordering of the disordered structure and there are at least two preferred Fe environments in this $CeNiSi_2$ structure with different nn vacancy and atom neighbourhoods. Alternatively, we suggest the possibility of an interchange between Fe and Sn sites in the $BaAl_4$ slabs of the very similar $TbFeSi_2$-type structure, as was stressed in Ref. [15].

The ^{119}Sn room temperature Mössbauer spectrum is de-convoluted in two doublets with almost the same isomer shift (Fig. 3). The different quadrupole splitting reflect that Sn atoms sit in two different distorted sites having the same icosahedral environment.

4. Conclusions

Mössbauer spectroscopy of $Th_4Fe_{13}Sn_5$ confirms the ferromagnetic character and site occupancy of all four sites of iron atoms, according to previous data deduced from neutron diffraction and magnetic measurements. Moreover, it has been evidenced that the two Sn sites are influenced by nn iron atoms and exhibit a weak magnetic structure.

The structure of the $ThFe_{0.22}Sn_2$ phase has not been definitely established. The existence of two tin structural sites in an icosahedral environment has been confirmed, but there is clear evidence of two sites for iron atoms, which contradicts previously found structural data.

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