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# Intrinsic magnetic properties of $(\text{Nd}_{1-x}\text{Sm}_x)\text{Fe}_{11}\text{Ti}$

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## Abstract

A series of  $(\text{Nd}_{1-x}\text{Sm}_x)\text{Fe}_{11}\text{Ti}$  alloys with the  $\text{ThMn}_{12}$  crystal structure have been fabricated and characterized in order to promote a strong uniaxial anisotropy in  $\text{NdFe}_{11}\text{Ti}$  without the need of nitrogenation. The compounds show small changes in the lattice parameters and cell volume, as well as Curie temperature and spontaneous magnetization. The anisotropy field, however, rapidly increases with the incorporation of Sm and overcomes the effect of nitrogenation, reaching values  $> 4$  T for a 30% Sm content. Mössbauer spectroscopy indicates that the quadrupole splitting is correlated with the magnetic anisotropy. These alloys are good candidates for permanent magnets, provided the correct microstructure is developed to increase coercivity.

## Keywords

Rare earth alloys,  $\text{ThMn}_{12}$  structure, magnetic anisotropy, Mössbauer spectroscopy, permanent magnets

## 1. Introduction:

Due to the increasing consumption of permanent magnets (PM) in various applications, and especially in wind turbines and electric vehicles, the need for minimizing the amount of Rare Earth (RE) in the magnets is becoming an urgent task, because RE are critical raw materials with inherent risks for supply and great environmental impact due to their extraction and processing methods [1].

In this respect, a renewed interest in the tetragonal RE(Fe,M)<sub>12</sub> compounds with the tetragonal ThMn<sub>12</sub> structure (1:12 for short) has recently arisen [2-5]. Here M is a transition metal or other element stabilizing the 1:12 structure. These alloys have a reduced RE content (7.7 at.%) as compared with the most efficient and widely used ones, the Nd<sub>2</sub>Fe<sub>14</sub>B (11.8 at.%). As mentioned, the 1:12 structure needs some other element (M) to be stabilized and the amount of M in the compound reduces the magnetization and Curie temperature.

According to the EU classification [1], light RE (Ce, Pr, Nd) are less critical than heavy ones, so they are preferred elements for permanent magnets. Nd is magnetically more convenient because of its intrinsic moment and anisotropy. However, its anisotropy in 1:12 compounds with Fe is usually planar or conical, which precludes their use in PM without further processing.

Overall, regarding the most promising compounds, NdFe<sub>11</sub>Ti is an excellent candidate because of the low content on stabilizing metal (Ti) promotes a large saturation magnetization at room temperature ( $M_s \approx 130 \text{ Am}^2/\text{kg}$ ) and Curie temperature ( $T_C \approx 280^\circ\text{C}$ ). However, at room temperature, this compound exhibits a weak magnetic anisotropy, even though uniaxial, because the anisotropy is dominated by the Fe sublattice. Indeed, the Fe-sublattice anisotropy favors the *c*-axis over all magnetically-ordered temperatures whereas the anisotropy of the Nd-sublattice depends on the combined interaction of the exchange field and the crystalline electric field acting on Nd<sup>3+</sup> ion, which varies with temperature. Thus, a spin reorientation transition at about 185K [6] appears with the change from the uniaxial to conical character of the anisotropy on cooling. However, by introducing interstitial elements (e.g. N, C, H), the crystallographic cell expands and the crystal field coefficient  $A_{20}$  of the Nd changes from negative to positive, inducing a strong uniaxial anisotropy [7].

Another way to turn Nd based 1:12 compounds to strong uniaxial anisotropy could be to mix the Nd with another RE that promotes uniaxial anisotropy. The literature survey revealed that one trial had been performed previously by mixing in equal quantities Nd and Sm resulting in a uniaxial compound [8,9] with large magnetization ( $\mu_0 M_s = 1.21 \text{ T}$ ) Curie temperature (295°C) and anisotropy field ( $\mu_0 H_A = 4.6 \text{ T}$ ). Therefore, it seems worth to explore the progressive substitution of Nd for Sm as to compare with the effect of interstitial elements on the intrinsic magnetic properties. Another advantage of using Sm is its lower price (almost 4 times less [10]) and larger availability [11] as compared with Nd.

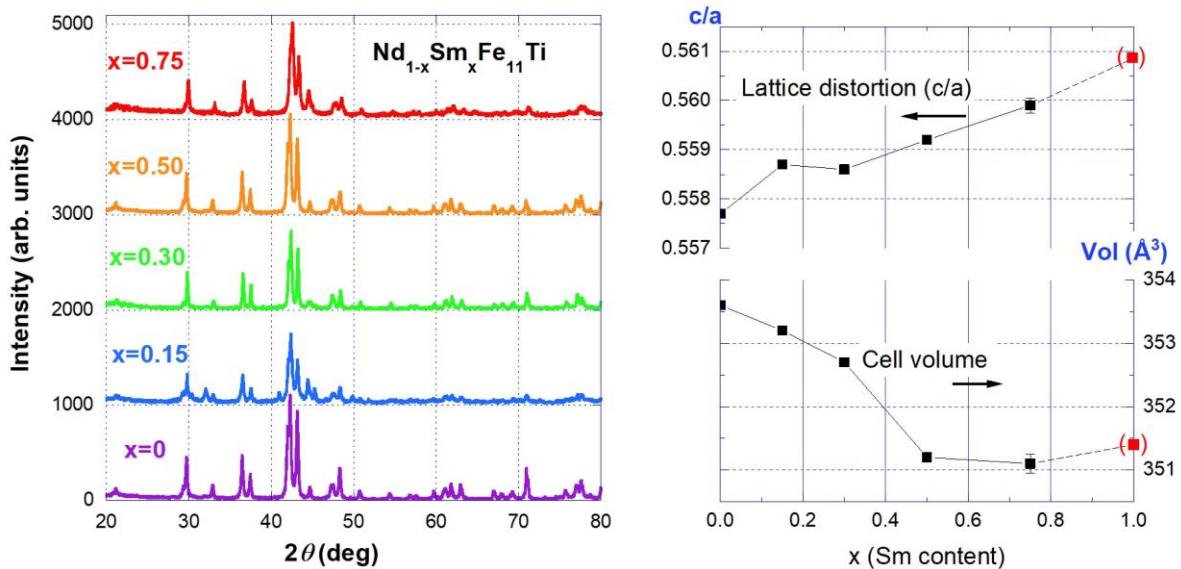
With such a purpose, a series of compounds with general formula: Nd<sub>1-x</sub>Sm<sub>x</sub>Fe<sub>11</sub>Ti have been synthesized and studied systematically as an alternative to nitrogenation of NdFe<sub>11</sub>Ti and possibly to other Nd based 1:12 compounds.

## 2. Materials and method

Alloys were prepared by arc melting of the pure constituents with at least 99.5% purity in Ar. As is well known Sm vapour pressure is very high and dealing with it in melting and alloying, large losses are always produced. In order to avoid Sm evaporation during the alloy production, Sm and Nd were first melted together in the appropriate amounts, and then the full alloy:  $\text{Nd}_{1-x}\text{Sm}_x + 11 \text{ Fe} + \text{Ti}$  was arc-melted at least five times to ensure homogeneity. If necessary, homogenization of the alloys was carried out in quartz tubes sealed under vacuum at 1100°C during long time (1 to 2 days).

The phases of the compounds were characterized by X-Ray diffraction (XRD). Thermogravimetry analysis under magnetic field (MTGA) gave the Curie temperatures. Magnetic measurements in isotropic and oriented powder samples were performed in VSM or SQUID magnetometers to obtain saturation magnetization and magnetic anisotropy, as well as the Spin Reorientation temperatures.

Mössbauer spectra were obtained at room temperature using a constant acceleration spectrometer with a  $^{57}\text{Co}$  source embedded in Pd. The spectrometer was calibrated with a pure bcc-Fe foil. Isomer Shift values are referred to the Fe foil value. Fitting of the spectra was performed using NORMOS program.



**Figure 1:** a) Left: XRD of the full series. Only small changes are seen as Sm substitutes Nd b) Tetragonal distortion and cell volume as a function of the Sm content. Values for the pure Sm compound are taken from [12]

## 3. Results and discussion

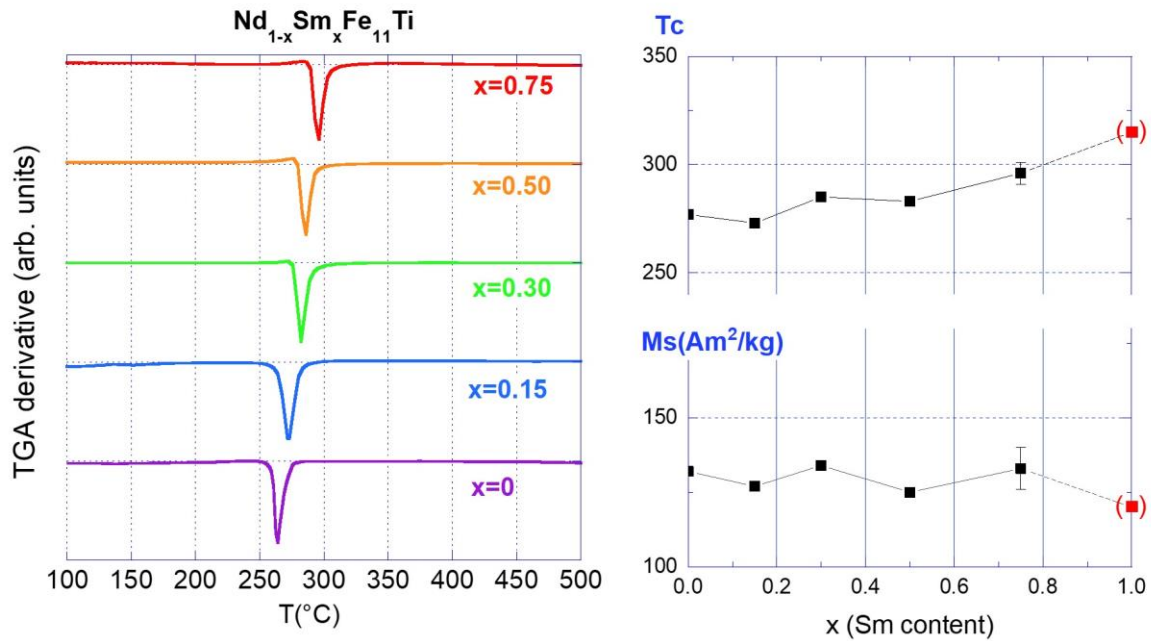
### 3.1 Structural analysis

Pure 1:12 phases ( $\leq 5\%$  bcc-Fe) were usually obtained directly by arc melting, without the need for long annealing at high temperature (Figure 1). Rietveld fitting indicates that the

lattice deforms in a different way along  $a$  and  $c$  axes. Within the experimental uncertainty, parameter  $a$  decreases monotonously as a function of the Sm content, while  $c$  shows a minimum around  $x=0.5$  (Table 1). As a result, the tetragonality ( $c/a$ ) of the compounds increases and the cell volume decreases (Figure 1, right). In any cases, the volume contraction is small ( $\approx 1\%$ ) as the radius of  $\text{Sm}^{3+}$  (180.4 pm) is only slightly smaller (0.94 %) than that of  $\text{Nd}^{3+}$  (182.1 pm). This effect is just opposite to the volume expansion produced by the nitrogen absorption in the interstitial site 2b, which can reach about 4 % [13-15].

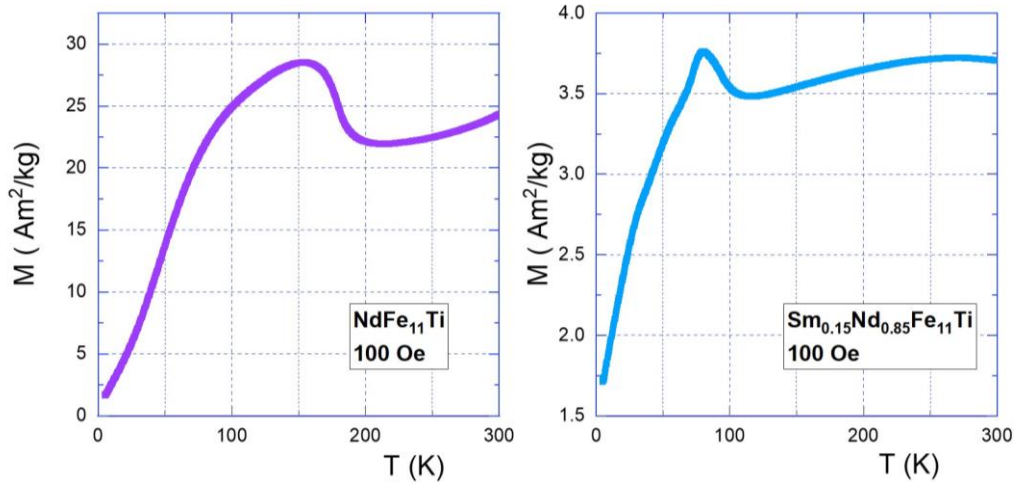
### 3.2 Magnetic properties

The evolution of Curie temperature and saturation magnetization are displayed in Figure 2. There is a steady increase of  $T_C$  with Sm content, while  $M_s$  is almost constant in the full series.



**Fig 2.-** Left: TGA derivative under magnetic field, to determine  $T_C$ . Right: Curie temperature ( $T_C$ ) and Saturation Magnetization ( $M_s$ ) of the  $\text{Nd}_{1-x}\text{Sm}_x\text{Fe}_{11}\text{Ti}$  series as a function of the Sm content. Values for pure Sm are taken from literature [12]

Previous studies in pure  $\text{NdFe}_{11}\text{Ti}$  alloy have shown that the anisotropy is conical at low temperatures and undergoes a spin reorientation (SR) process at around 185K [6]. Here, low field  $M(T)$  measurements show maxima in the susceptibility, which indicates the crossing through zero of the anisotropy constant  $K_1$  at the spin reorientation (SR) temperature. SR takes place at  $T_{\text{SR}} \approx 150$  K in pure Nd alloy and at  $T_{\text{SR}} \approx 75$  K in the  $x=0.15$  alloy (Figure 3). For higher Sm concentrations there is no sign of the SR down to 5 K. This points out that the alloys display uniaxial anisotropy at all temperatures for Sm contents  $x \geq 0.3$ .



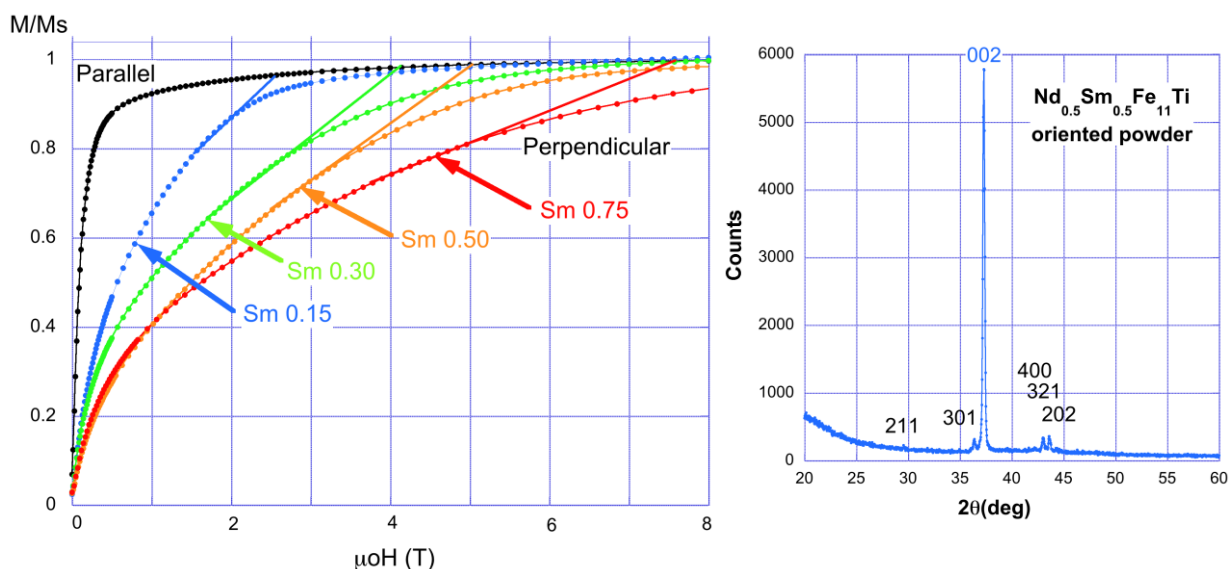
**Figure 3:** Spin reorientation temperature determined by low field magnetization in  $Nd_{0.85}Sm_{0.15}Fe_{11}Ti$  (left) and  $NdFe_{11}Ti$  (right).

Magnetic anisotropy at room temperature was determined by magnetization measurements in oriented powder samples. The magnetization curves are shown in Figure 4. Because the samples have not been annealed at high temperature, the crystal grain size is around a few microns and is lower than the powder grain size, which is about 30  $\mu m$ . Therefore, there exist some dispersion in the oriented grains (Fig. 4 right), and long tails appear in the perpendicular magnetization curves, extending to very high fields. The anisotropy field has been estimated by extrapolating the linear part of the perpendicular magnetization to reach the parallel curve and must be taken as a first approximation to its actual value. As a result, anisotropy field reaches 2.5 T at very low Sm concentration ( $x=0.15$ ) and becomes similar to the nitrogenated pure Nd phase at  $x=0.3$  ( $\mu_0H_A = 4.1$  T). Coercivity of the powder samples (crystal size of several  $\mu m$ ) is very low, about 5-10 mT (50-100 Oe) because the microstructure is not favourable to develop any coercivity at this stage. All the characteristics of the compounds are summarized in Table 1.

**Table 1.-** Structural and magnetic characteristics of  $Nd_{1-x}Sm_xFe_{11}Ti$  compounds. Values for pure Sm are from [12], also some literature values for  $x=0$  are given for comparison

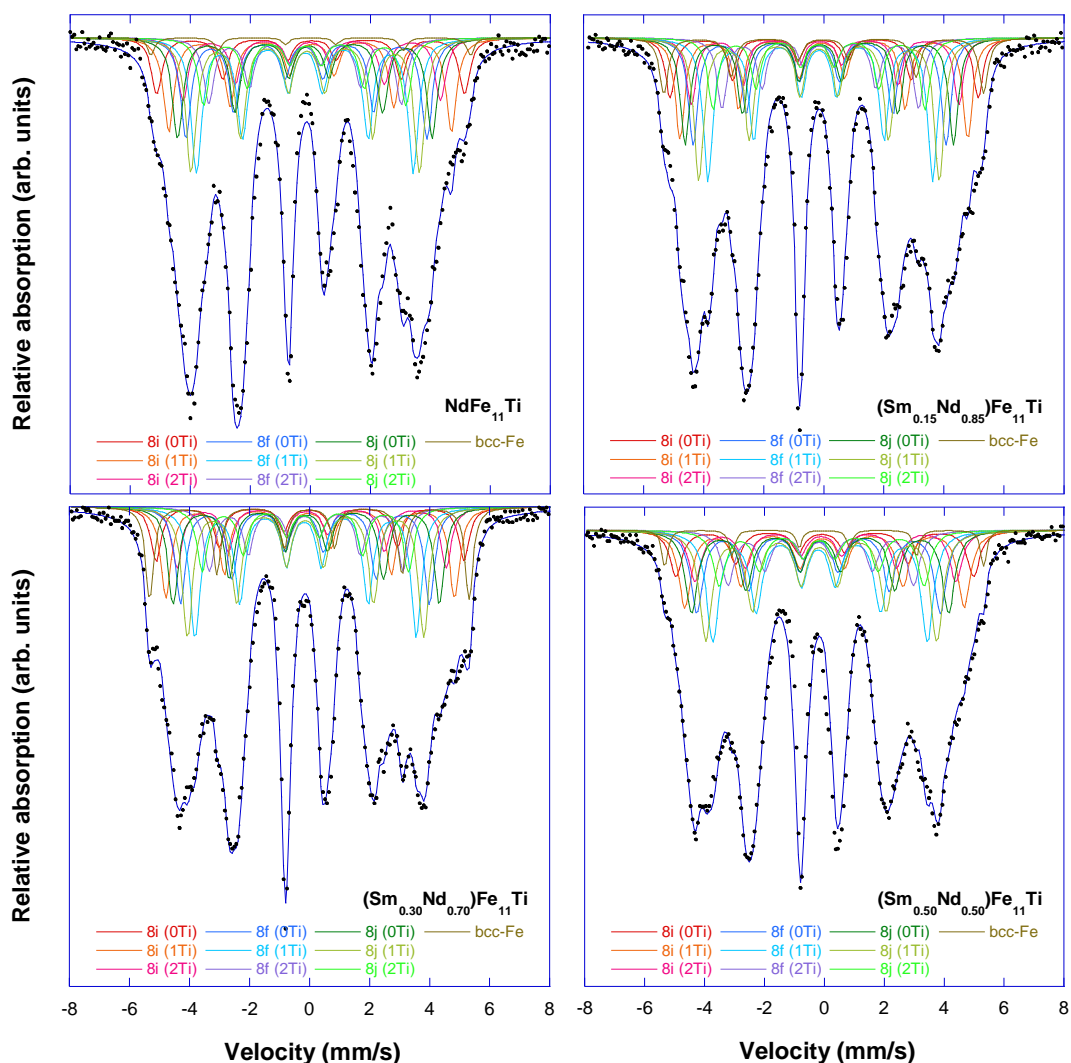
Sample	$a$ (Å)	$c$ (Å)	$c/a$	$V$ (Å <sup>3</sup> )	$T_C$ (K)	$M_s$ (Am <sup>2</sup> /kg)	$\mu_0H_A$ (T)	EMD @300K	$T_{SRT}$ (K)
$NdFe_{11}Ti^a$	8.5740	4.794	0.5591	352.4	-	-	-	Uniaxial	185
$NdFe_{11}Ti$	8.591	4.791	0.5577	353.6	537	132	0.6	Uniaxial	150
$Sm_{0.15}Nd_{0.85}Fe_{11}Ti$	8.5810	4.7951	0.5587	353.2	546	127	2.5	Uniaxial	75
$Sm_{0.3}Nd_{0.7}Fe_{11}Ti$	8.5785	4.7918	0.5586	352.7	558	128	4.1	Uniaxial	-
$Sm_{0.5}Nd_{0.5}Fe_{11}Ti$	8.5639	4.7886	0.5592	351.2	556	125	5.0	Uniaxial	-
$Sm_{0.75}Nd_{0.25}Fe_{11}Ti$	8.5593	4.7929	0.5599	351.1	569	124	7.6	Uniaxial	-
$SmFe_{11}Ti^b$	8.5572	4.7994	0.5609	351.4	588	120	10	Uniaxial	-

$a$ : ref [6];  $b$ : ref [12];  $c$ : corrected for the bcc-Fe content determined by Mössbauer



**Figure 4:** Left: Parallel and perpendicular magnetization curves of field aligned powders of  $Nd_{1-x}Sm_xFe_{11}Ti$ . To obtain the anisotropy field the linear part of the perpendicular curves has been extrapolated as shown. Right: XRD of the oriented powder indicating some dispersion in the crystal axes orientation, as reflections other than the 002 are still present.

The improvement of the magnetic anisotropy as Sm is introduced has its origin in the Sm interaction with the crystal field and subsequent exchange coupling that transmits the Sm anisotropy to the Nd and Fe atoms. As a consequence, we observe a slight increase of  $T_C$  but  $M_s$  stays nearly constant. This mechanism is completely different to that of the hydrogenation or nitrogenation. The latter proceeds via the geometrical distortion of the lattice and the increase of volume, favouring the anisotropy and increasing the exchange between Fe atoms. The increase of exchange constants gives rise to an increase of the Curie temperature and in consequence to an increase of  $M_s$  at room temperature [16].



**Figure 5.-** Room temperature Mössbauer spectra of some selected compounds. Some bcc-Fe appears in the compounds with  $x=0.15$  and  $0.50$  deforming the right side of the spectra.

### 3.3 Hyperfine interactions

Mössbauer spectra were obtained at room temperature for  $x=0, 0.15, 0.30$  and  $0.5$  compositions. The spectra are displayed in Figure 5. They show a monotonous distortion as Sm enters in the structure. The fitting was performed using various subspectra for each Fe position (8i, 8j and 8f), which take into account the different probabilities of having  $n$  Ti atoms surrounding a given Fe atom. The relative resonant areas of each contribution have been calculated by a binomial distribution taking into account that Ti atoms are located exclusively in the 8i site and were fixed in the fitting. Only those contributions with a resonant area over 2.5% have been considered, resulting in three subspectra per Fe site, corresponding to 0, 1 or 2 Ti atoms surrounding the resonant Fe atom. A linear relationship

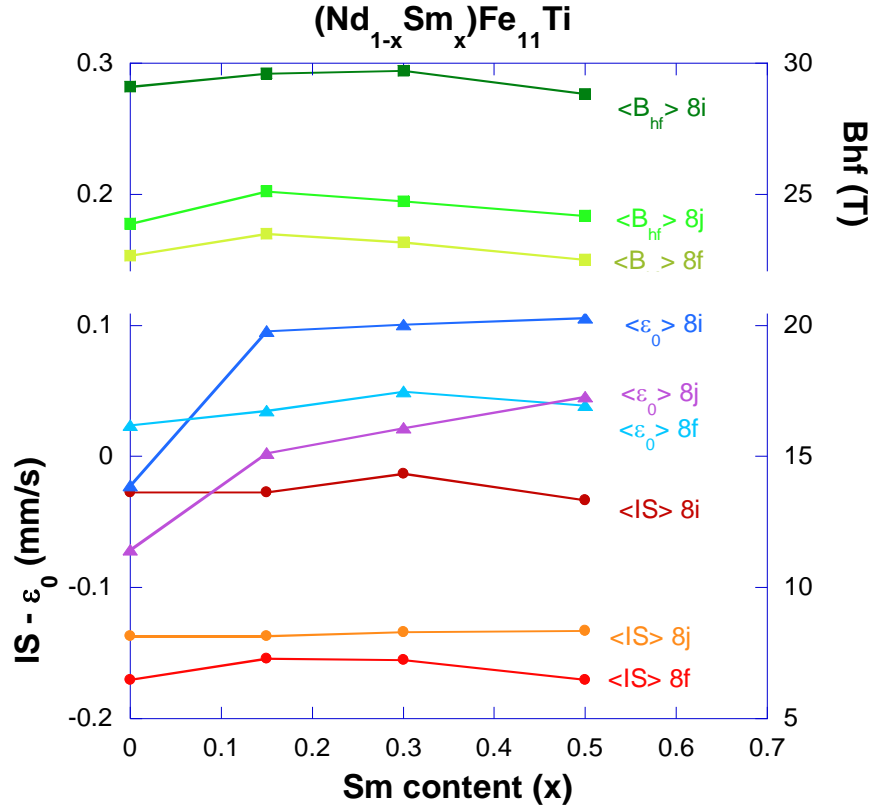


between hyperfine parameters and Ti content in the neighbourhood has been assumed. The Mossbauer parameters obtained in this way are very appropriate for comparing a series of compounds, as they involve a reduced set of parameters and avoid the dispersion that could arise when using of a full set of independent free parameters. This procedure has been successfully used on many occasions for ThMn<sub>12</sub> alloys [6,17-19]. Table 2 and Figure 6 show their variation as function of the Sm content. For the sake of clarity, only average values for each Fe site in the 1:12 structure are listed here. The complete set of fitting parameters for all subspectra is available in the Supplementary Information file.

**Table 2.-** Average Mossbauer parameters for each Fe site as a function of the Sm content. The free Fe content is also indicated in % of Fe atoms.

Sm content (x)	Fe site	IS (mm/s)	$\epsilon_0$ (mm/s)	$B_{hf}$ (T)	bcc-Fe (at.% Fe)
0	8i	-0.03	-0.02	29.1	< 2.0
	8f	-0.17	0.02	22.7	
	8j	-0.14	-0.07	23.9	
0.15	8i	-0.03	0.10	29.6	5.5
	8f	-0.14	0.04	23.5	
	8j	-0.15	0.01	25.1	
0.30	8i	-0.01	0.10	29.7	8.3
	8f	-0.16	0.05	23.2	
	8j	-0.13	0.02	24.7	
0.50	8i	-0.03	0.11	28.8	2.6
	8f	-0.17	0.04	22.5	
	8j	-0.13	0.05	24.2	

The contribution of Sm is not very large for the Isomer Shift (IS) or for the Hyperfine field ( $B_{hf}$ ), which is in agreement with the same number of valence electrons for Nd and Sm and similar magnetic moment, as macroscopic measurements disclose. The most prominent change occurs in the Quadrupolar Splitting ( $\epsilon_0$ ), as corresponds to the competing contributions of Nd and Sm to the magnetic anisotropy. It can be seen that Sm rapidly changes the  $\epsilon_0$  of the 8i and 8j sites and change its sign from negative to positive. The largest and most rapid change occurs for the 8i site, which lies the closest to the rare earth position. As it has been observed, a quantity of 0.15 of Sm content substituting Nd atoms is enough to reinforce and thrive the uniaxial anisotropy, changing at the same time the profile of the electric gradients around the Fe nuclei. Further increase of Sm atoms would not alter that profile and the changes in the QS would be only relative. In addition, the most significant relative change in  $c/a$  lattice parameters ratio takes also place at  $x=0.15$  when Nd is firstly substituted by Sm (as it can be consulted in Table 1). Above this concentration, the  $c/a$  ratio hardly varies up to  $x \geq 0.5$ . Thus, the gradient of electric field on the Fe nuclei is not considerably altered which is reflected in the slight evolution of the QS values.



**Figure 6.-** Mössbauer parameters as a function of the Sm content. Changes in  $\langle \epsilon_0 \rangle$  are correlated with the macroscopic magnetic anisotropy (see the text). Other parameters do not change appreciably.

#### 4. Conclusions:

A series of  $(\text{Nd}_{1-x}\text{Sm}_x)\text{Fe}_{11}\text{Ti}$  alloys with the  $\text{ThMn}_{12}$  crystal structure have been fabricated and characterized structurally and magnetically. By substituting the Nd with inexpensive Sm, we observe almost no changes in lattice parameters and cell volume, as well as in Curie temperature and spontaneous magnetization. On the other hand, we are able to tune the magnetic anisotropy and an anisotropy field of 4.1 T can be reached for a low content of Sm (30%). Mössbauer spectroscopy shows that the quadrupole splitting is correlated with the magnetic anisotropy. These results highlight the possibility to tune the magnetic anisotropy of the NdFeTi-alloy for permanent magnet applications without the use of nitrogenation.

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