



## Hyperfine Field and Isomer Shift Evolution in Hydrogenated Nd–Fe–B Alloy

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**Abstract.** RE<sub>2</sub>Fe<sub>14</sub>B (RE = rare earth) materials are capable of absorbing hydrogen to form a stable solid solution at room temperature. Hydrogenation produces a number of significant changes in the hyperfine interactions. In this work, <sup>57</sup>Fe Mössbauer effect spectroscopy and X-ray diffraction measurements were performed on Nd<sub>14.01</sub>Hf<sub>0.08</sub>Fe<sub>78.91</sub>B<sub>7.00</sub> alloys submitted to thermal treatment in hydrogen atmosphere. A non-linear increase of the hyperfine fields and isomer shifts with hydrogen concentration was observed. The hyperfine parameters of the 8j<sub>1</sub> site exhibit a rather different evolution than those experienced by the other major sites (8j<sub>2</sub>, 16k<sub>1</sub>, 16k<sub>2</sub>). The origin of the hyperfine field enhancement is analyzed in terms of volume expansion and H nearest neighbors to the Fe sites. A linear expression on these two effects to give account of isomer shift evolution for 8j<sub>1</sub> site is given.

**Key words:** Mössbauer spectroscopy, X-ray diffraction.

### 1. Introduction

Many RE-3d intermetallic compounds are capable of absorbing considerable amounts of hydrogen, and the RE<sub>2</sub>Fe<sub>14</sub>B compounds do so as well. Previous works demonstrated that RE<sub>2</sub>Fe<sub>14</sub>B series form isostructural hydrides and it became clear that hydrogenation produces a number of significant changes in the physical properties [1]. RE<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> (0 ≤ x ≤ 5) are stable at room temperature, and relative to the parent compounds, the following features appear: (i) increased lattice parameters and unit-cell volumes; (ii) enhanced Fe moments and hyperfine fields; (iii) higher Curie temperatures and (iv) markedly lower anisotropy fields. From magnetization measurements and <sup>57</sup>Fe Mössbauer effect spectroscopy (ME) in Y<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub>, Coey [2] concluded that the conversion factor 150 kOe/μ<sub>B</sub>, widely used to relate hyperfine fields to Fe moments in the parent compounds, does not apply to the hydrides. The increase in the magnetic moment certainly indicates that hydrogen exerts an appreciable influence on the electronic structure. Its origin is unclear, then, in absence of any more direct information, the ME spectroscopy appears as a relevant tool for a systematic analysis of the electronic properties evolution with H concentration. In this work, we follow the evolution of hyperfine parameters of major sites by ME and relate it to H content and volume expansion

of the unit-cell. A linear expression for the  $8j_1$  site isomer shift ( $\delta$ ) dependence on these two parameters is proposed.

## 2. Experimental details

Ingot alloy with a nominal composition  $\text{Nd}_{14.01}\text{Hf}_{0.08}\text{Fe}_{78.91}\text{B}_{7.00}$ , crushed into coarse powder (about 1 mm in diameter) was used to perform hydrogenation experiments. Typically, 200 mg of the ingot alloy were used for each experiment.

The samples were evacuated in a quartz tube, at room temperature (RT), to a pressure less than 6 Pa. The tube was sealed and heated in a furnace previously set at the working temperature (240–680°C) during 4 min prior to the admission of pure hydrogen ( $P \approx 120$  kPa). After supplying the gas, the hydrogen bottle was closed. The treatments lasted 30 min at each temperature in the range 240–580°C, or 1, 2, 5, 13 and 16 min at 680°C (see Table I). Then the samples were rapidly cooled to RT. The reactions evolution were microcomputer followed by monitoring simultaneously the hydrogen pressure and the temperature every 1 s. The amount of  $\text{H}_2$  absorbed was determined by means of a procedure described elsewhere [3]. A maximum of 3.4 H per unit formula was achieved.

After each treatment, X-ray diffraction (XRD) and ME characterization were performed. The  $^{57}\text{Fe}$  ME measurements were recorded at RT under transmission geometry with a standard constant acceleration spectrometer having a 5–10 mCi  $^{57}\text{CoRh}$  radioactive source. Quoted isomer shifts ( $\delta$ ) are referred to RT  $\alpha$ -Fe. ME spectra were fitted with Lorentzian curves with respect to the off-resonance background.

*Table I.* Hydrogen content per unit form ( $x$ ), relative volume expansion ( $\Delta V/V$ ) and mean  $B_{\text{HF}}$  and  $\delta$  (relative to  $\alpha$ -Fe at RT) for different hydrogenation temperature ( $T$ ) and treatment length ( $t$ ). Typical errors are lower than: 0.001 for  $\Delta V/V$ , 0.2 T for  $B_{\text{HF}}$  and 0.02 mm/s for  $\delta$

$T_{\text{T}}$ (°C)	$t$ (min)	$x$	$\Delta V/V$	$\delta_{\text{m}}$ (mm/s)	$B_{\text{m}}$ (T)
	Ingot alloy	0	0	−0.047	29.1
680	1	0.33	0.006	−0.049	29.5
680	2	0.48	0.009	−0.040	29.6
680	5	0.73	0.011	−0.047	30.1
680	13	0.77	0.012	−0.046	30.1
680	16	0.80	0.013	−0.035	30.3
580	30	1.9	0.029	0.007	30.8
480	30	2.3	0.039	0.016	30.8
360	30	2.8	0.040	0.012	30.8
240	30	3.4	0.040	0.014	30.9

XRD characterizations were carried out with Cu-K $\alpha$  radiation in a Philips PW1710 diffractometer.

### 3. Results and discussions

ME spectra of the ingot alloy and those treated at 680 and 580°C during 16 and 30 min respectively are shown in Figure 1. They were fitted with six sextets, corresponding to Fe sites in  $\phi$ -phase, an  $\alpha$ -Fe one and a doublet corresponding to NdFe<sub>4</sub>B<sub>4</sub> which is a paramagnetic phase at RT [4].  $\alpha$ -Fe and NdFe<sub>4</sub>B<sub>4</sub> were already present in the ingot alloy and their subspectra relative intensities did not change noticeably as a consequence of the hydrogenation treatments. The relative intensities of the  $\phi$ -phase interactions were constrained to be equal to the relative abundance 16 : 16 : 8 : 8 : 4 : 4 of the crystallographic non-equivalent iron sites in P4<sub>2</sub>/mmn structure. Linewidths were fixed to 0.3 mm/s for  $\phi$ -phase sites, 0.25 mm/s

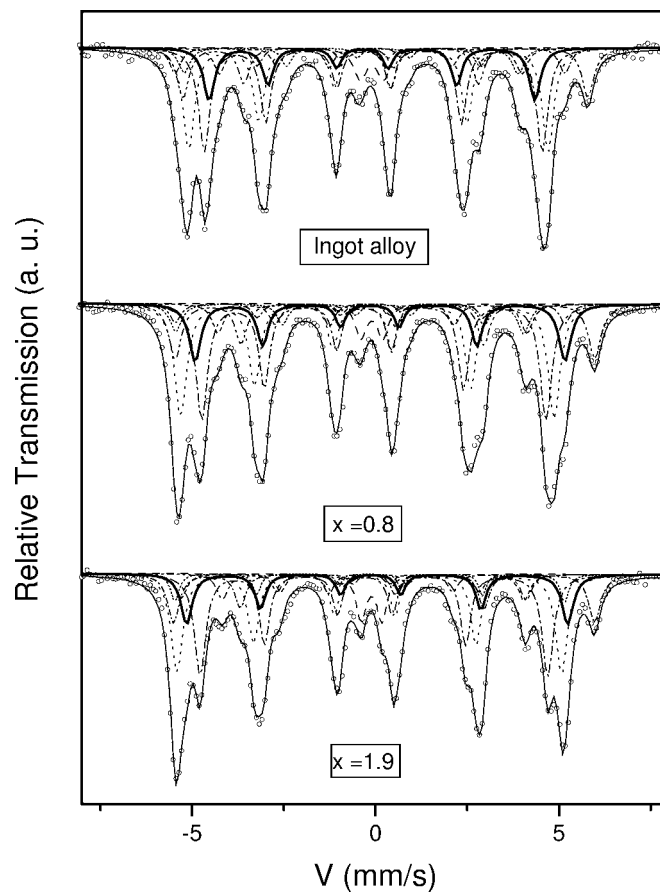


Figure 1. ME spectra of ingot alloy Nd<sub>14.01</sub>Hf<sub>0.08</sub>Fe<sub>78.91</sub>B<sub>7.00</sub> and hydrogenated at 680°C, 16 min ( $x = 0.8$ ) and at 580°C, 30 min ( $x = 1.9$ ). Bold line for 8j<sub>1</sub> subspectra.

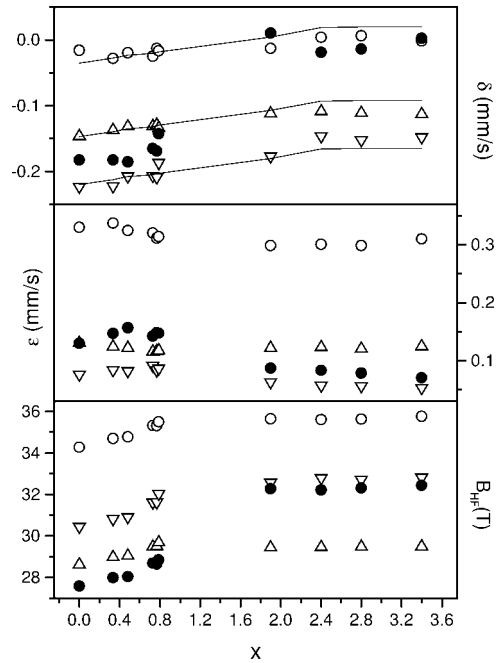


Figure 2. Hyperfine parameters evolution of  $16k_1$  ( $\Delta$ ),  $16k_2$  ( $\nabla$ ),  $8j_1$  ( $\bullet$ ), and  $8j_2$  ( $\circ$ ) sites. On top, solid lines correspond to isomer shifts calculated with Ingalls formula.

for Fe in  $\alpha$ -Fe and 0.4 mm/s for the quadrupolar interaction. Although, it is well known that there is no unique decomposition [5] into individual subspectra, we followed here Long *et al.*'s [6] assignment which is the most frequently accepted. This assignment is based on a chemical and structural analysis of probe environments. Mean values of relevant fitted parameters are shown in Table I. Hydrogen absorption modifies the spectra shape in a complex way rather than a simple shift or an increase of mean hyperfine field ( $B_{\text{HF}}$ ). This is evidence that not all Fe sites are equally modified under hydrogenation. For instance, the  $8j_1$   $B_{\text{hf}}$  field has a relative larger increase than the other sites, as can be observed in Figures 1 and 2.

The evolution of 16k and 8j sites hyperfine parameters plotted as a function of H per unit form are shown in Figure 2. It can be observed that  $B_{\text{HF}}$  and  $\delta$  exhibit a smooth behavior for the  $8j_2$  and  $16k_1$  sites. According to neutron diffraction results, these sites have no hydrogen nearest neighbor [7]. A step increases are observed between  $0.7 < x < 2$  for the  $16k_2$  and especially for  $8j_1$  sites (3.2 and 12%, respectively). The  $16k_2$  and  $8j_1$  sites have two and three hydrogen nearest neighbor for  $x = 4$ . Higher H concentration does not notoriously modify any of the hyperfine parameters. The  $8j_1$  site exhibits an anomalous behavior as compared to the other major sites. The parameters corresponding to 4c and 4e subspectra, which have the lower intensities, are not shown in Figure 2 and will not be included in our analysis because they are not so reliable.

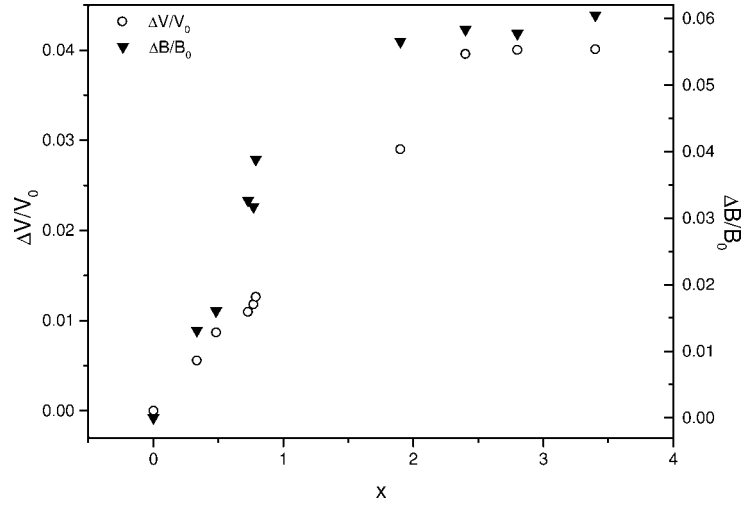


Figure 3. Relative volume expansion of the  $\phi$ -phase (○) and relative increase of the mean  $B_{\text{HF}}$  (▼) as a function of H content per unit form ( $x$ ).

$B_{\text{HF}}$  enhancement can be attributed to the following possible mechanisms: (i) narrowing of the 3d bands by the lattice expansion producing greater 3d electron localization and leading to concomitant moment enhancement as well as to modification of the exchange energy, highly sensitive to interatomic distances [8], (ii) localized low-lying states created by hydrogen that are filled from the 3d bands, leading to a lower Fermi energy, increased exchange splitting, and larger Fe moments [9], (iii) the overlap of Fe 3d and Nd (5d, 6s) wave function might be screened by hydrogen and thus increase the localization and magnitude of the Fe moments [10].

Figure 3 shows the relative volume expansion of the  $\phi$ -phase, as determined from XRD reflection line shift to lower angles [3], together with the relative increase of the mean  $B_{\text{HF}}$ , as a function of H content per unit form. Similar dependencies are observed for both  $B_{\text{HF}}$  and  $V$  parameters. In particular, we point out the fact that  $\Delta B_{\text{HF}}(x)/B_{\text{HF}}(0)$  saturates when  $\Delta V(x)/V(0)$  does, indicating that the main cause of hyperfine field enhancement is not just the hydrogen addition, but the volume expansion induced by it, i.e., mechanism (i).

For H contents higher than  $x = 1.9$  a volume expansion of approximately 4% is obtained. It should be pointed out that other authors [7, 11] have reported higher H concentrations for this volume expansions in samples treated at  $2 \times 10^6$  Pa.

Isomer shifts of  $16k_1$ ,  $16k_2$  and  $8j_2$  sites approximately follow the relation between the  $\delta$  increase and relative volume expansion determined by Ingalls [12]:

$$\Delta\delta \cong 1.37 \frac{\Delta V}{V} \text{ mm/s.} \quad (1)$$

The agreement between measured and calculated values is shown in Figure 2. In this expression it is assumed that relative expansion of Wigner–Seitz cell is approx-

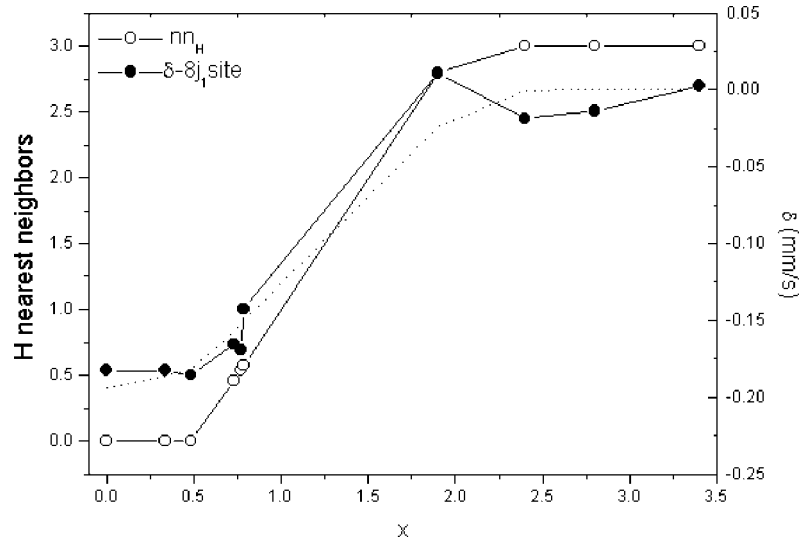


Figure 4. Proposed model for H nearest neighbor number (○) and  $8j_1$  site isomer shift (●) evolution as a function of H content per unit form ( $x$ ). Dotted line represents a fit using Equation (2).

imately equal to the observed structure volume expansion. Ingalls expression is not enough to reproduce the  $8j_1$  site  $\delta$  evolution.

Assuming the H filling scheme proposed in [7] for  $x = 1, 2, 3$  and 4, an interpolation of these data with our  $\Delta V/V$  values was performed for  $1 < x < 2$ ,  $2 < x < 3$  and  $3 < x < 4$ . This interpolation and the assumption that the  $8j_1$  site has no hydrogen nearest neighbor for  $x \leq 0.5$  (see Figure 4) allowed us to propose the following formula

$$\delta(8j_1\text{-site}) = 1.37 \cdot \frac{\Delta V}{V} + \alpha \cdot nn_H + \beta, \quad (2)$$

for the  $8j_1$   $\delta$  behavior, where  $nn_H$  represents the number of H nearest neighbors to the Fe probe,  $\alpha$  and  $\beta$  are fitting parameters. Obtained values (in mm/s) for fitting parameters, are:

$$\begin{aligned} \alpha &= 0.046 \pm 0.004, \\ \beta &= -0.194 \pm 0.008. \end{aligned}$$

The obtained  $\alpha$  value is lower than increase of +0.1 mm/s per hydrogen nearest neighbor [13], and  $\beta$  is nearly equal to the measured  $\delta$  in starting alloy as expected.

In Figure 4 the fitted curve is shown, which has a good agreement with experimental results.

#### 4. Conclusions

Hydrides  $\text{Nd}_2\text{Fe}_{14}\text{BH}_x$  ( $0 < x < 3.4$ ) formed from  $\text{Nd}_{14.01}\text{Hf}_{0.08}\text{Fe}_{78.91}\text{B}_{7.00}$  alloy were characterized by ME spectroscopy.

A rather differentiated evolution of hyperfine parameters of the  $8j_1$  site compared with the other major sites was observed. It was attributed to a severe modification of its environment due to H presence, which induces changes in electronic band structure of the Fe probe.

A description which successfully reproduces the  $8j_1$  site isomer shift in terms of the number of H nearest neighbors and relative volume expansion for the Fe site is provided.

In order to estimate volume expansion and H insertion contributions to hyperfine field and isomer shift, calculations of electronic structure in Nd–Fe–H systems are in progress.

#### Acknowledgements

The authors are grateful to ANPCyT, CONICET and FOMEC of Argentina for partial support of this work.

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