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A Fitting Procedure for Magnetic Multiphase Materials Mössbauer Spectra

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Abstract. In this work a practical method of fitting complex multiphase Mössbauer effect spectra is proposed. The task is simplified imposing specific restrictions to the analysing functions, which are appropriate for cases where the component phases spectra do not change substantially during the process under study. The ME spectra can be analysed using the phases subspectra, by defining only a reduced number of parameters. The constraints are equivalent to assume a Doppler velocity transformation $v' = (v - \delta_m)B_{m0}/B_m + \delta_{m0}$ for each phase, where δ_m and B_m are fitting parameters containing information on the phase mean isomer shift and hyperfine field and δ_{m0} and B_{m0} their reference values. In this manner physically meaningful results are easy to obtain. The idea was applied to partially nitrogenated $R_2Fe_{17}N_x$ (R = Sm and Y) and partially hydrogen-decomposed Nd–Fe–B materials.

Key words: multiphase Mössbauer spectra analysis, $R_2Fe_{17}N_x$, Nd–Fe–B hydrogen disproportionated.

1. Introduction

The analysis of ME spectra using the traditional approach of simulating the different sites by their corresponding multiplets, may become impractical when they originate from complex multiphase samples. The principal problem is the existence of too many degrees of freedom, which leads to ambiguous spectra fitting. This, in turn, results in lack of reliability concerning physical interpretation. We faced these problems while analysing spectra of $R_2Fe_{17}N_x$ and partially hydrogen-decomposed Nd–Fe–B materials. In the first case mixtures of $R_2Fe_{17}/R_2Fe_{17}N_x$/Fe occur, while in the second mixtures of $Nd_2Fe_{14}BH_x$/ $NdFe_4B_4$/Fe/Fe_2B/t-Fe_3B appear, with a total of sixteen iron sites. Employing the traditional approach, we would have to use up to ninety-five fitting parameters.

One way of simplifying the task is to impose restrictions to the analysing functions. In the present work, this idea is applied to cases where the spectra of individual phases do not change substantially during the process being studied, i.e., they retain their distinctive form even while undergoing minor changes. The ME

spectra can then be analysed using the phases subspectra, by defining a reduced number of parameters to describe their individual evolution. In the approach we have chosen the magnetic subspectra are described with four parameters: relative area (A), elemental linewidth (Γ). To the other two we shall refer as mean isomer shift (δ_{m}) and mean hyperfine field (B_{m}).

2. Method

Let us consider a system composed of phases $i = \alpha, \beta$, etc., each one containing n_i nonequivalent iron sites. Let $F_i(\{p_i\}, v)$ be the best theoretical function reproducing the experimental spectra i, where v is the Doppler velocity and $\{p_i\}$ is the set of fitting parameters. For each site these parameters are the isomer shift (δ), hyperfine field (B), quadrupole shift or splitting (ε or Δ), relative line intensities (I2/I3 or I1/I2), and linewidth (Γ). The spectra corresponding to the multiphase system can be described by

$$F(v) = \sum_i A_i F_i\big(\{p_i\}, v\big), \quad i = \alpha, \beta, \text{ etc.}, \ \{p_i\} = \big\{\delta_i, B_i, \varepsilon_i, (I2/I3)_i, \Gamma_i\big\},$$

the relative areas being A_i additional fitting parameters. If the component phases remained totally unchanged, the latter would be the only fitting parameters. However, in many cases of interest the hyperfine parameters of each phase undergo slight changes, transforming the subspectra $F_i(v)$ into $F_i'(v)$ by modifying the set $\{p_i\}$ into $\{p_i'\}$. The conventional approach would lead to a theoretical function $F(v)$ involving a large number of fitting parameters, namely, the product $6\sum_i n_i$, when all sites are magnetic. In the model proposed here each multisite phase is described by only the four parameters mentioned in the introduction. The definition of δ_{m} and B_{m} are as follows. We assume that $F_i'(v)$ can be approximated by $F_i(v')$ with $v' = av + b$. This approximation assumes that the most important changes are subspectra expansion/contraction (factor a) and shift (term b). Therefore, $a = B_{\mathrm{m0}}/B_{\mathrm{m}}$, where B_{m0} is the mean hyperfine field of the phase reference state. The following relationships for δ_{m} must hold:

$$\delta_{\mathrm{m0}} = \frac{\int v F(v)\,\mathrm{d}v}{\int F(v)\,\mathrm{d}v} = \frac{\int v' F(v')\,\mathrm{d}v'}{\int F(v')\,\mathrm{d}v'}, \tag{1}$$

$$\delta_{\mathrm{m}} = \frac{\int v F(v')\,\mathrm{d}v}{\int F(v')\,\mathrm{d}v}, \tag{2}$$

where δ_{m0} is the mean isomer shift of the phase reference state. From the equality between the first and third members of (1), using Equation (2) and the variable change $v' = av + b$, the relationship $b = \delta_{\mathrm{m0}} - \delta_{\mathrm{m}} a = \delta_{\mathrm{m0}} - \delta_{\mathrm{m}} B_{\mathrm{m0}}/B_{\mathrm{m}}$ is obtained, therefore, $v' = (v - \delta_{\mathrm{m}})B_{\mathrm{m0}}/B_{\mathrm{m}} + \delta_{\mathrm{m0}}$. In summary, the multiphase spectra can be aproximated by curves

$$F(v) = \sum_i A_i F_i'\big(\{P_i\}, v\big), \quad \{P_i\} = \{\delta_{\mathrm{m}i}, B_{\mathrm{m}i}, \Gamma_i\},$$

finding the best A_i and $\{P_i\}$ values. In practice, each experimental subspectrum of phase reference state i can be approximated by the best sum of Lorentzian functions L, centered at v_{ki}, with depth h_{ki} and width Γ_{mi}, $F_i = \sum_k L(v_{ki}, \Gamma_{mi}, h_{ki})$. Next, δ_{mi0} is calculated, and finally the position of Lorentzian line k is rewritten as $v_{ki} = \delta_{mi} - \delta_{mi0} + (B_{mi}/B_{mi0})v_{k0i}$. In this manner, parameters δ_{mi} and B_{mi} are explicity introduced into F_i.

For the purpose of this work we have measured the different phases in their purest available state: Y_2Fe_{17}, Sm_2Fe_{17}, $Y_2Fe_{17}N_{2.8}$ + Fe, $Sm_2Fe_{17}N_{2.61}$ + Fe, $Nd_2Fe_{14}BH_{0.6}$ + $NdFe_4B_4$, Fe_2B, t-Fe_3B + Fe, which were conventionally fitted in order to obtain the corresponding $F_i(v)$.

3. Application

This approach was applied to partially nitrogenated $R_2Fe_{17}N_x$ (R = Y, Sm) and partially disproportionated $Nd_{14.01}Hf_{0.08}Fe_{78.91}B_{6.99}$. The R_2Fe_{17} ingots were nitrogenated by annealing powders with different particle sizes under high-purity nitrogen gas flow at 430–460°C for up to 17 h. These treatments resulted in N nominal content values of x = 0.6, 1.2, 1.8, 2.44, and 2.8 for Y, and x = 0.28,

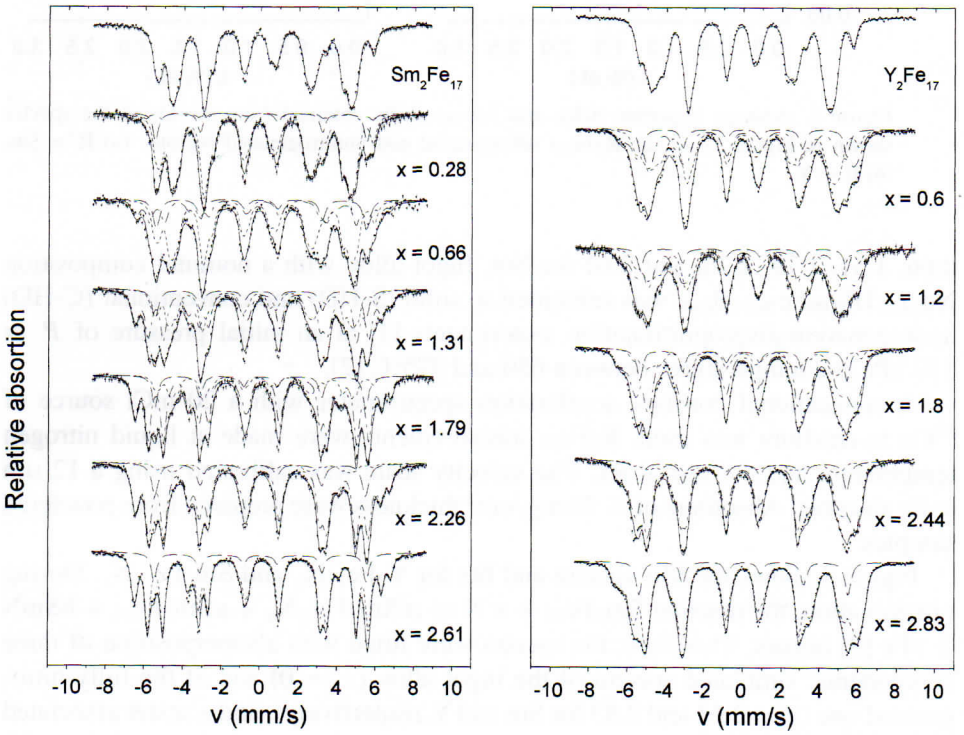

Figure 1. Mössbauer effect spectra of Y_2Fe_{17}, $Y_2Fe_{17}N_x$ (right) and Sm_2Fe_{17}, $Sm_2Fe_{17}N_x$ (left) at 85 K. The three theoretical subspectra correspond to the R_2Fe_{17} nitrogenated and unnitrogenated regions and to α-Fe.

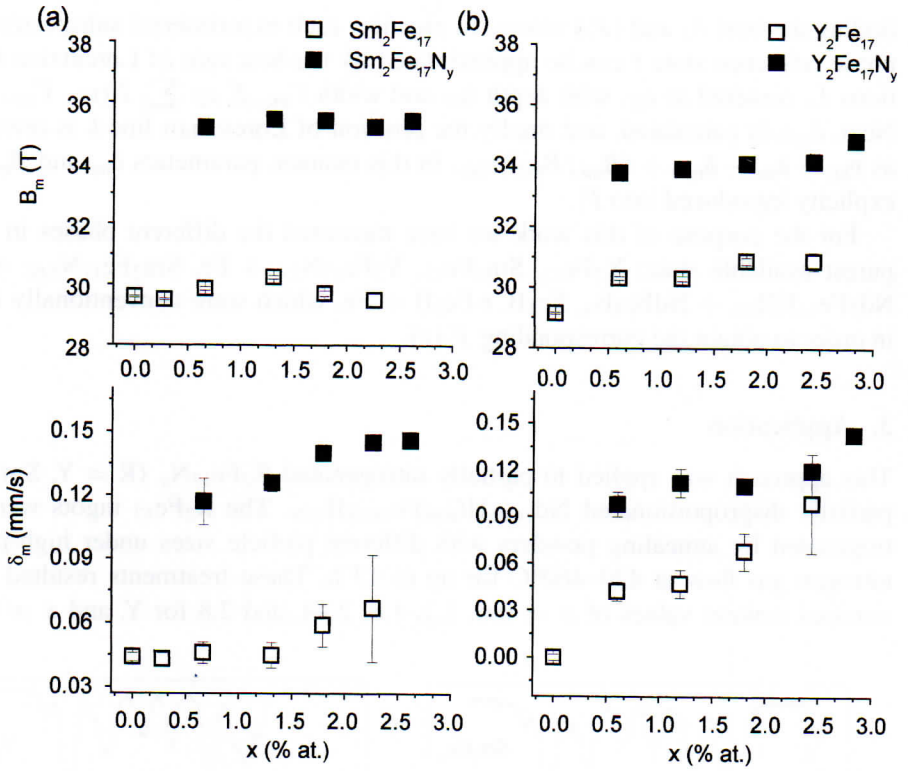

Figure 2. Average hyperfine fields and isomer shifts obtained from the fits of the spectra shown in Figure 1, for the R_2Fe_{17} nitrogenated and unnitrogenated regions. (a) R = Sm, (b) R = Y.

0.66, 1.31, 1.79, 2.26, and 2.61 for Sm. Ingot alloy with a nominal composition $Nd_{14.01}Hf_{0.08}Fe_{78.91}B_{6.99}$ was submitted to solid (S-HD) and conventional (C-HD) hydrogenation-disproportionation experiments [1] at an initial pressure of $P \approx$ 119 kPa and temperatures between 650 and 975°C [2].

A conventional constant acceleration spectrometer with a 20 mCi source of ^{57}Co in rhodium was used. R_2Fe_{17} measurements were made at liquid nitrogen temperature and the rest at RT. The velocity scale was calibrated using a 12 μm α-Fe absorber. Absorbers of $\cong$ 20 mg/cm^2 thickness were prepared from powdered samples.

Figure 1 shows the ME spectra and fits for $Y_2Fe_{17}N_x$ and $Sm_2Fe_{17}N_x$. During nitrogenation, the reaction $Sm_2Fe_{17} + x\ N \Rightarrow a'Sm_2Fe_{17}N_y + aSm_2Fe_{17} + bSmN + cFe$ [3] occurs. Therefore, the spectra were fitted with a superposition of three components: simulated spectra of the ingot alloy ($x = 0$) and of the fully nitrogenated one ($x = 2.61$ and 2.83 for Sm and Y, respectively), and a sextet associated with α-Fe. Figure 2 displays the evolution of the parameters B_{mi} and δ_{mi} with nitrogen concentration. The evolution of the relative iron fraction in the nitrided (N) and unnitrided (UN) phases, $a'/(a'+a)$, and the nitrogen concentration y in the

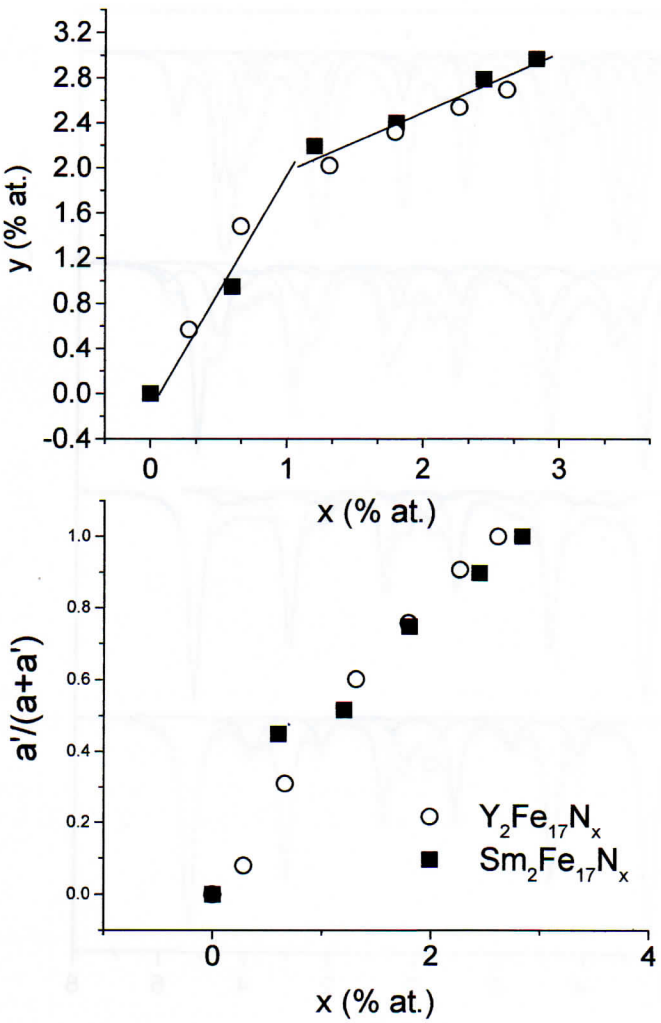

Figure 3. Average nitrogen concentration (y) and relative fraction ($a'/(a + a')$) of the nitrogenated region.

N phase are shown in Figure 3. It is remarkable that the same behaviour is observed both for the Y and Sm series. The results obtained from this analysis confirm the model proposed by Zhang *et al.* [3] about the existence of a UN/N configuration for partially nitrogenated states, and suggest a sequence of nitrogen interstitial sites filling. Good fits could be obtained with the UN/N model, even when y actually varies approximately between 0.6 and 2.8. This was interpreted as an indication that lattice volume expansion is the main responsible for δ_m and B_m changes, and that small nitrogen concentrations already produce volume expansions similar to that of the fully nitrogenated state.

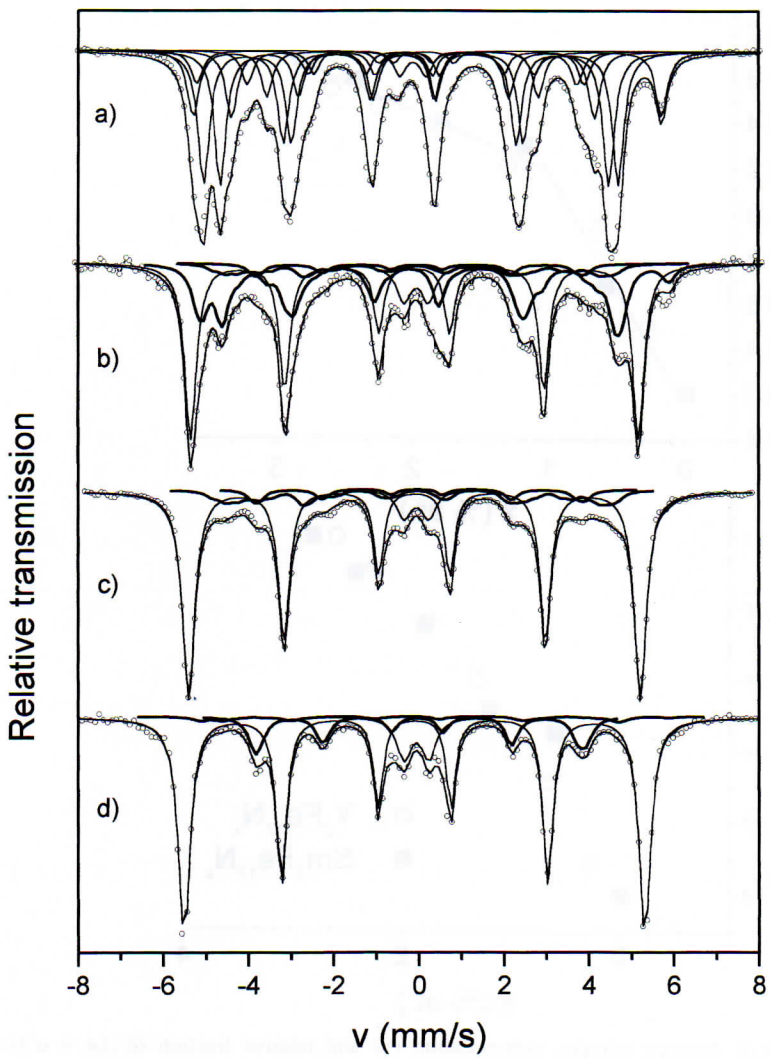

Figure 4. ME spectra corresponding to: (a) Ingot alloy of $Nd_{14.01}Hf_{0.08}Fe_{78.91}B_{6.99}$, (b) partially disproportionated S-HD at 700°C, 30 min, (c) fully disproportionated S-HD at 800°C, 30 min, and (d) almost fully disproportionated C-HD at 800°C, 30 min. Remarked lines correspond to t-Fe_3B (solid), Fe_2B (dashed) and ϕ-phase (dotted). Spectrum (a) was conventionally fitted with six magnetic dipolar interactions (ϕ-phase) and one electric quadrupolar interaction (η-phase).

Figure 4(a) shows the spectrum of the ingot alloy $Nd_{14.01}Hf_{0.08}Fe_{78.91}B_{6.99}$ composed of the six $Nd_2Fe_{14}B$ ϕ-phase sextets and the $NdFe_4B_4$ η-phase doublet. Figures 4(b) and (c) show representative ME spectra obtained after S-HD treatments at 700 and 800°C. The S-HD reactions can be described as $Nd_2Fe_{14}B + (2 + x)H_2 \Rightarrow 2NdH_{2+x} + 11Fe + Fe_3B \Rightarrow 2NdH_{2+x} + 12Fe + Fe_2B$. Then, the ME spectra were fitted as a superposition of five components: the simulated

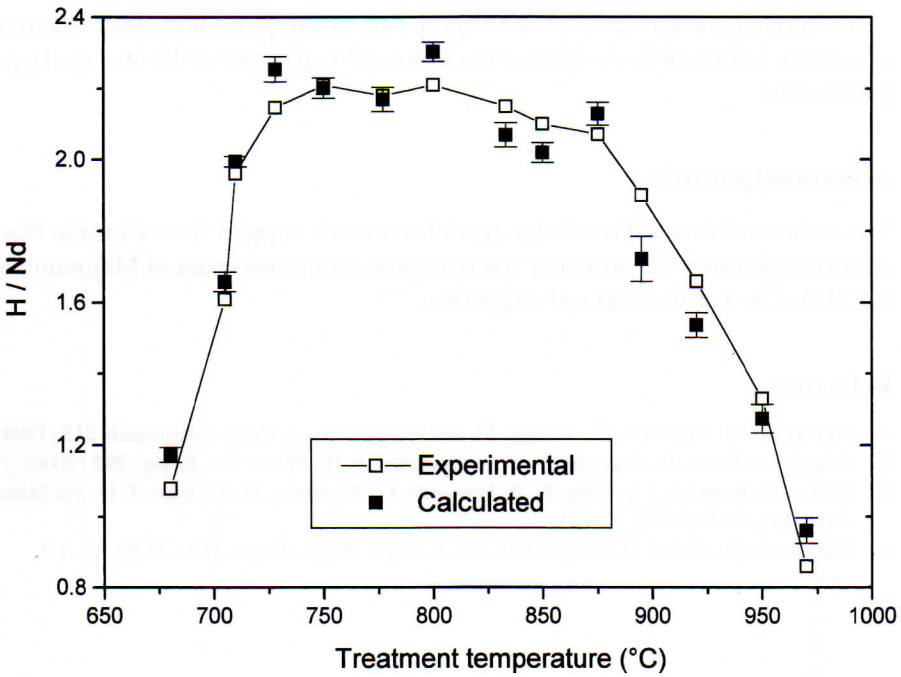

Figure 5. Plot of experimentally obtained from ME spectra, and calculated H/Nd ratios as a function of temperature is shown.

spectra of ϕ-phase with 0.6 hydrogen atom per unit formula, Fe_2B and t-Fe_3B, one sextet corresponding to α-Fe and a doublet corresponding to the η-phase. In all the experiments the average hyperfine field and isomer shift of all phases remained approximately constant. Figure 5 shows values of the experimental and calculated H/Nd ratio. The second was obtained by fitting the values u and v of H/Nd in the Nd hydride and the hydrogenated ϕ-phase, respectively, with the expression $fu+(1-f)v = (\mathrm{H/Nd})_{\mathrm{exp}}$, where f is the Nd at. fraction in the disproportionated mixture and $1-f$ its fraction in the ϕ-phase (calculated from the ME analyses), and $(\mathrm{H/Nd})_{\mathrm{exp}}$ is the ratio obtained from the absorption curves. The best fit was obtained with $u = 2.6$ and $v = 0.6$, values consistent with the accepted Nd hydride stoichiometry and with the observed shift of the XRD ϕ-phase lines. These results confirm the reliability of the analysis method and are discussed elsewhere [2]. Similar analyses of S-HD and C-HD samples (Figures 4(c) and (d)) clearly indicate the formation of t-Fe_3B exclusively in the first case, in agreement with reported XRD and HRSEM experiments [4].

Although the imposed constraints do reduce the fitting results ambiguity, interference among the subspectra may still occur. In our case it takes place between the ϕ-phase and t-Fe_3B subspectra due to their similar Doppler velocity ranges, increasing the Fe fractions uncertainties to about 3–4%.

In summary, it was shown that the proposed fitting procedure allows the retrieval of reliable information on relative fractions and variations of the average hyperfine parameters.

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