ON SPIN HAMILTONIAN FITS TO MÖSSBAUER SPECTRA OF NiFe$_2$O$_4$ NANOPARTICLES SYNTHESIZED BY CO-PRECIPITATION

SOBRE AJUSTES POR HAMILTONIANO DE SPIN DE ESPECTROS MÖSSBAUER DE NANOPARTÍCULAS DE NiFe$_2$O$_4$ SINTETIZADAS POR CO-PRECIPITAÇÃO

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Abstract: Nanocrystalline NiFe$_2$O$_4$ particles prepared by chemical co-precipitation method were studied using magnetic measurements, $^{57}$Fe Mössbauer spectroscopy, X-ray diffraction, and transmission electron microscopy. Fits to Mössbauer spectra, in the range of 4.2 K – 300 K, were done using spin hamiltonian to describe both the electronic and nuclear interactions, a model of superparamagnetic relaxation of two levels (spin $\frac{1}{2}$) and stochastic theory, a log-normal particle size distribution function as well as a dependency of the magnetic transition temperature and the anisotropy constant on particle diameter. We have used evolutionary strategies to fit the more complex Mössbauer spectra line shapes. The nanoparticles have an average size of 7 nm and exhibit superparamagnetism at room temperature. The saturation magnetization (Ms) at 4.2 K was determined from $M$ vs. $1/H$ plots by extrapolating the value of magnetizations to infinite fields, to 24.21 emu/g and coercivity to 3.15 kOe. A magnetic anisotropy energy constant (K) $1.9 \times 10^5$ J/m$^3$, at 4.2 K, were calculated from magnetization measurements. The synthesis characterization, and functionalization of magnetic nanoparticles is a highly active area of current research located at the interface between materials science, biotechnology, and medicine. Superparamagnetic iron oxides nanoparticles have unique physical properties and have emerged as a new class of diagnostic probes for multimodal tracking and as contrast agents for magnetic resonance imaging (MRI).

Keywords: NiFe$_2$O$_4$ nanoparticles. Evolutionary strategies. Fits on Mössbauer spectra.

Resumo: Partículas nanocristalinas de NiFe$_2$O$_4$ preparadas pelo método de co-precipitação química foram estudadas usando-se medidas magnéticas, espectroscopia Mössbauer de $^{57}$Fe, difração de raios-X e microscopia eletrônica de transmissão. Ajustes de espectro Mössbauer, na faixa de 4.2 K – 300 K, foram feitos utilizando-se hamiltonianos de spin para descrever as interações eletrônicas e nucleares, um modelo de relaxação superparamagnética de dois níveis (spin $\frac{1}{2}$) e teoria estocástica, função distribuição de tamanho de partículas log-normal, bem como uma dependência da temperatura de transição magnética e da constante de anisotropia dependendo do diâmetro das partículas. Usamos estratégias evolutivas para ajustar as formas mais complexas das linhas de espectro Mössbauer. As nanopartículas têm um tamanho médio de 7 nm e exibem superparamagnetismo à temperatura ambiente. A magnetização de saturação (Ms) a 4,2 K foi determinada a partir de plotagens de $M$ vs. $1/H$, extrapolando o valor das magnetizações para campos infinitos, para 24,21 emu/g e coercividade para 3,15 kOe. Uma constante de energia de anisotropia magnética (K) $1.9 \times 10^5$ J/m$^3$, a 4,2 K, foi calculada a partir de medidas de magnetização. A síntese, caracterização e funcionalização de nanopartículas magnéticas é uma área altamente ativa de pesquisa atual localizada na interface entre ciência dos materiais, biotecnologia e medicina. Nanopartículas de oxidos de ferro superparamagnéticos têm propriedades físicas únicas e emergiram como uma nova classe de sondas de diagnóstico para rastreamento multimodal e como agentes de contraste para ressonância magnética (RM).

Palavras-chave: Nanopartículas de NiFe$_2$O$_4$. Estratégias Evolucionárias. Ajustes de espectros Mössbauer.

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1 INTRODUCTION

Nickel ferrite nanoparticles, NiFe$_2$O$_4$ prepared in different ways, have attracted considerable attention due to both their unusual properties compared to those of the bulk materials and their potential applications (LÓPEZ et al., 2001). Like other iron oxides, e.g., magnetite (Fe$_3$O$_4$), manganese ferrite (MnFe$_2$O$_4$), and cobalt ferrite (CoFe$_2$O$_4$), NiFe$_2$O$_4$ is a soft ferrite and presents easy magnetization and demagnetization. All of them have a spinel structure with octahedral and tetrahedral sites (Fig. 1). Sites A and B are antiferromagnetic and ferromagnetic regions, respectively. The synthesis, characterization, and functionalization of magnetic nanoparticles is a highly active area of current research located at the interface between materials science, biotechnology, and medicine.

![Figure 1: Spinel structure.](source)

Source: Adapted from (MARTINS, 2008).

For many years, it has been known that magnetic particles with a size smaller than few tens of nanometer can be considered as single domains and, hence, display properties markedly different from the bulk (MEDRANO et al., 2018). Another exciting feature of the nanoparticles is due to the surface spin disorder, which is induced by the broken exchange bonds at the surface. This is especially true for the case of ferrites where the (negative) superexchange interaction is mediated by an intervening oxygen ion, and it can be missing at the surface. As a result, the system should be considered a core-shell structure with ferromagnetically aligned core spins and a spin-glass like surface layer. With the reduction of the particle size at the nanoscale, the surface to volume ratio becomes very large, and surface effects may induce a spin-canted structure as well as an enhanced surface anisotropy (KODAMA et al., 1996).
Besides having unique physical properties, nanoparticles are a couple with size range commensurate with biomolecular and cellular systems. These properties make nanoparticles attractive for therapeutic and diagnostic applications (photothermal therapy, imaging, and delivery applications). However, application in biomedicine requires controlled interactions with molecules, like non-cytotoxicity, cellular internalization ability, and carrier ability (SAHA et al., 2011). For the effective utilization of these materials in biomedicine, nanoparticles have been functionalized with a variety of ligands such as surfactants, small molecules, polymers, dendrimers, and biomolecules. Nanoparticles interacting with organic compounds show different effects that depend on how the functionalization is performed (TOURINHO et al., 1989; LÓPEZ et al., 2001). Oleic acid has proved to be useful as a surfactant to magnetic nanoparticles. On the other hand, vegetable oils have in their composition different fatty acids, including oleic acid, palmitic, linolenic, and others.

NiFe$_2$O$_4$ nanoparticles studied in this work were prepared by chemical co-precipitation method using an aqueous solution of Ni(NO$_3$)$_2$·6H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O and the NaOH solution as the precipitating agent. They were studied using magnetic measurements, $^{57}$Fe Mössbauer spectroscopy, X-ray diffraction, and transmission electron microscopy.

Mössbauer spectroscopy (ME) allows displaying the hyperfine structure of an ion in a solid. Due to the interactions of the ion with its environment, the electronic, magnetic moment, and the charge distribution of the ion can fluctuate. The times which characterize these fluctuations depend on the intensity of the interactions. Through the hyperfine coupling, the nucleus feels these effects. By means of ME one can observe fluctuations whose characteristic times are in the interval $10^{-6} - 10^{-11}$ s (CIANCHI et al., 1986).

The paper is organized as follows. In section 2, the basic informations of sample preparation are presented, the basic features of the theoretical model and of the Mössbauer spectroscopy are introduced, and the characteristics of evolutionary algorithms used in the model parameterization are discussed. In section 3, the obtained results are presented and discussed. In section 4, we made conclusions and proposals for future works.
The nanoparticles have an average size of 7 nm (obtained from XRD pattern) and exhibit superparamagnetism at room temperature. The saturation magnetization (Ms) at 4.2 K was determined from $M$ vs $1/H$ plots by extrapolating the value of magnetizations to infinite fields, to 24.21 emu/g and coercivity to 3.15 kOe. A magnetic anisotropy energy constant (K) $1.9 \times 10^5$ J/m$^3$, at 4.2 K, were calculated from magnetization measurements.

Fits to Mössbauer spectra, in the range of 4.2 K – 300 K, were done using spin hamiltonians to describe both the electronic and nuclear interactions, a model of superparamagnetic relaxation of two levels (spin $\frac{1}{2}$) and stochastic theory (CLAUSER; BLUME, 1971; JONES; SRIVASTAVA, 1989), a log-normal particle size distribution function $P(D)$ (Eq. 1) (Fig. 2).

To fits on more complexes Mössbauer spectra lineshapes, it’s necessary to consider a hyperfine magnetic field distribution (which is a purely statistical approach) or, as is done in the Pfannes-Higino model (PFANNES et al., 1998; PFANNES et al., 2001; FILHO, 2001), a dependency of the magnetic transition temperature and the anisotropy constant on particle diameter (Eqs. 2 and 3) (Fig. 3). The magnetic transition temperature dependency on particle diameter leads to a Brillouin function (Eq. 4), a relation between the reduced hyperfine internal field and the reduced temperature (Fig. 4).

\[
P(D) = \frac{1}{\sqrt{2\pi}\sigma D} e^{-\left[\frac{\ln(D/D_0)^2}{2\sigma^2}\right]},
\]  

Figure 2: Log-Normal size distribution, $P(D)$.

Source: The authors.
where $D$ is the particle diameter, $\sigma$ is the standard deviation, $D_0$ is the average size.

$$T_N(D) = -A_1 \times e^{-\frac{D}{\sigma}} + T_{bulk},$$  \hspace{1cm} (2)

where $T_{bulk}$ is the bulk magnetic transition temperature of the sample, and $A_1$ and $A_2$ are parameters to be found.

$$K(D) = AN_{01} + \frac{AN_{02}}{(D \times AN_{03})},$$  \hspace{1cm} (3)

where $AN_{01}$, $AN_{02}$ and $AN_{03}$ are parameters to be found.

$$BR_1\left(\frac{T}{T_N}\right) = BR_{11} \times \left[1.0 - BR_{12} \times \left(\frac{T}{T_N}\right)^{BR_{13}}\right],$$  \hspace{1cm} (4)

where $BR_{11}$, $BR_{12}$ and $BR_{13}$ are parameters to be found.

Figure 3: Transition temperature $T_N$ and anisotropy constant $K$ vs. diameter

Source: (PFANNES et al., 2001).

We have used evolutionary strategies and non-linear to fit the more complex Mössbauer spectra line shapes (RECHENBERG, 1965; SCHWEFEL, 1975; BARBOSA, 2017). The CHI2 parameter is a way of measure the differences between experimental and theoretical spectra, calculated by the theoretical model. CHI2 values in the range [1,6] indicate that experimental and theoretical spectra are in good agreement.

The evolutionary algorithms have been implemented using Python programming.
The parameterization problem is treated as a problem of minimizing the measure of the Root Mean Square Error, RMSE, of the points of the theoretical spectrum obtained by the model, compared to the experimental spectrum.

2.1 Mössbauer Spectroscopy

The Mössbauer effect is the nuclear recoil free emission and absorption of gamma photons (nuclear resonance fluorescence). This effect only occurs when the nucleus is embedded in a solid matrix (GOLDANSKII; HEBER, 1968; YOSHIDA; LANGOUCHE, 2013). The Mössbauer effect was discovered in 1958 by Rudolf L. Mössbauer, who, in order to correctly interpret and explain the effect, developed an experimental technique called Mössbauer spectroscopy (Fig. 5), which is applied in several areas of knowledge, such as the study of magnetism and magnetic materials (GÜTLICH; BILL; TRAUTWEIN, 2011). Mössbauer spectroscopy has high energy resolution that allows the study of electrical and magnetic hyperfine interactions arising from the interaction between electrical and magnetic moments of the nucleus and the fields created by the core electrons. It is widely used, for example, in the characterization of organometallic iron compounds (CHEN; YANG, 2007). Zeeman nuclear splitting for the fundamental and first excited states of the $^{57}$Fe and the respective Mössbauer spectra are shown in Fig. 6 (allowed transitions between nuclear levels are labeled with the magnetic, m, and nuclear spin, I, quantum numbers).

The Mössbauer theoretical lineshape used in the model is a complicated expression that calculates the Laplace transform of the correlation function for the nuclear transition operator. A detailed deduction of this expression can be found in (CIANCHI et al., 1986).
3 RESULTS AND DISCUSSION

With the aim to evaluate the algorithm’s parameterization performance, we applied the Differential Evolution (DE) and Evolution Strategies (ES) algorithms (BARBOSA, 2017) in the fitting procedure of nickel ferrite powder Mössbauer spectra in several temperatures. All experiments involved in this work were carried out in the Physics Department, Federal University of Minas Gerais.
Experimental and theoretical Mössbauer spectra of the powder sample at temperatures in the range of 4.2 K – 300 K are shown in Figs. 7 to 10. The spectra collapse rapidly in the range of 140 K – 300 K without showing a pronounced central peak (characteristic of superparamagnetic relaxation) initially. There should be another cause of internal field reduction besides increasing relaxation frequency. We adopted a dependence of $T_N$ and the anisotropy on the particle diameter (Fig. 3). For each diameter D, we obtain $T_N$, and from this and the actual temperature T, we get an internal magnetic field value corresponding to the variation of the internal field dependence shown in Fig. 4. A lot of parameters must be found during the fit process. Table 1 shows these parameters founded for the spectrum at 140 K. For comparison, the two algorithms obey the termination criterion of 6,000 evaluations of the objective function. Each algorithm has been executed 30 times.

Table 1: Parameters founded during the fit on the spectrum at 140 K.

| Parameters | Values found   |
|------------|----------------|
| $AN_{01}$  | 4641.009       |
| $AN_{02}$  | 279736378.496  |
| $AN_{03}$  | 20.000         |
| $BR_{12}$  | 4.500          |
| $BR_{13}$  | 5.600          |
| $BR_{21}$  | -0.200         |
| $BR_{22}$  | 5.499          |
| $BR_{23}$  | 2.224          |

Source: The authors.

Figure 7: Nickel ferrite Mössbauer spectrum at 4 K (CHI2 = 5.77).

Source: The authors.
The values of CHI2 in the range [1.81 - 5.77] show that the model can reproduce the main features of the Mössbauer spectra, even in the situations when the thermally activated phenomena produce complex lineshapes. A good agreement between the experimental and theoretical spectra occurs in all temperatures in the range 4.2 K to 300 K, and the model describes the collapse of the hyperfine field at high temperatures due to superparamagnetic relaxation or magnetic transition temperature dependency on the particle diameter.
4 CONCLUSIONS

Nickel ferrite nanoparticles were successfully synthesized by the co-precipitation method, and their magnetizations are affected by the thermally activated phenomena predicted in the Pfannes-Higino model.

Effects like particle size distribution as well as a dependency of the magnetic transition temperature on particle diameter are very important to the analysis of the Mössbauer spectra of nanoparticles, and these effects can substitute the hyperfine field distributions, a statistical
Evolutionary algorithms and a theoretical model based on superparamagnetic relaxation phenomena and particle size distribution, as well as a dependency of the magnetic transition temperature on particle diameter, can be successfully used on Mössbauer spectra fits. The values of CHI2 are in the range [1.81 – 5.77]. Future works include modifications in the theoretical model and application of evolutionary algorithms on the fits of more complex Mössbauer spectra, taking into account other physical phenomena, e.g., interparticle interactions and surface effects.

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