ON SPIN HAMILTONIAN FITS TO MÖSSBAUER SPECTRA OF $NiFe_2O_4$ NANOPARTICLES SYNTHESIZED BY CO-PRECIPITATION

SOBRE AJUSTES POR HAMILTONIANO DE SPIN DE ESPECTROS MÖSSBAUER DE NANOPARTÍCULAS DE $NiFe_2O_4$ SINTETIZADAS POR CO-PRECIPITAÇÃO

Jose Higino Dias Filho[1] iD

Jorge Luis Lopez Aguilar[2] iD

Adriana Silva de Albuquerque[3] iD

Renato Dourado Maia[4] iD

Wesley de Oliveira Barbosa[5] iD

Ernando Campos Ferreira[6] iD

Fellipe Silva Pereira[7] iD

Kátia Guimarães Benfica[8] iD

[1]Doutor em Física, Universidade Estadual de Montes Claros, higino.filho@unimontes.br

[2]Doutor em Física, Universidade Federal do Acre, jorge0503@gmail.com

[3]Doutora em Engenharia Química, Serviço de Nanomateriais do CDTN /CNEN, asa@cdtn.br

[4]Doutor em Engenharia Elétrica, Universidade Estadual de Montes Claros, renato.dourado@unimontes.br.

[5]Mestre em Modelagem Computacional e Sistemas, Instituto Federal do Norte de Minas Gerais, wesley.oliveira@live.com

[6]Mestre em Modelagem Computacional e Sistemas, Escola Estadual Irmã Beata, hermesso@bol.com.br.

[7]Mestre em Modelagem Computacional e Sistemas, Escola Estadual Zinha Meira, fipsax@gmail.com

[8]Mestre em Modelagem Computacional e Sistemas, Escola Estadual Gilberto Caldeira Brant, katiafgp2015@gmail.com

Abstract: Nanocrystalline $NiFe_2O_4$ 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 hamiltonians 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) 1.9×10^5 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: $NiFe_2O_4$ nanoparticles. Evolutionary strategies. Fits on Mössbauer spectra.

Resumo: Partículas nanocristalinas de $NiFe_2O_4$ 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 óxidos 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 $NiFe_2O_4$. Estratégias Evolucionárias. Ajustes de espectros Mössbauer.

1 INTRODUCTION

Nickel ferrite nanoparticles, $NiFe_2O_4$ 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_3O_4), manganese ferrite ($MnFe_2O_4$), and cobalt ferrite ($CoFe_2O_4$), $NiFe_2O_4$ 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.
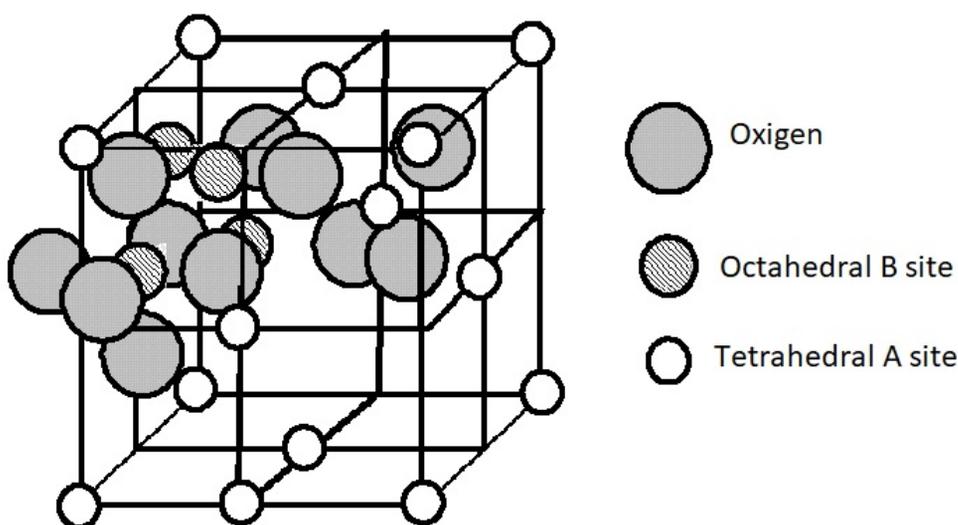
Source: Adapted from (MARTINS, 2008).

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.

$NiFe_2O_4$ nanoparticles studied in this work were prepared by chemical co-precipitation method using an aqueous solution of $Ni(NO_3)_2.6H_2O$ and $Fe(NO_3)_3.9H_2O$ 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.

2 MATERIALS AND METHODS

$NiFe_2O_4$ nanoparticles were prepared by the chemical co-precipitation method using an aqueous solution of $Ni(NO_3)_2.6H_2O$ and $Fe(NO_3)_3.9H_2O$ and the $NaOH$ solution as the precipitating agent. The precipitate was calcined at 500 °C (ALBUQUERQUE *et al.*, 2001). They were studied using magnetic measurements, ^{57}Fe Mössbauer spectroscopy, X-ray diffraction, and transmission electron microscopy.

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) 1.9×10^5 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).

Figure 2: Log-Normal size distribution, P(D).
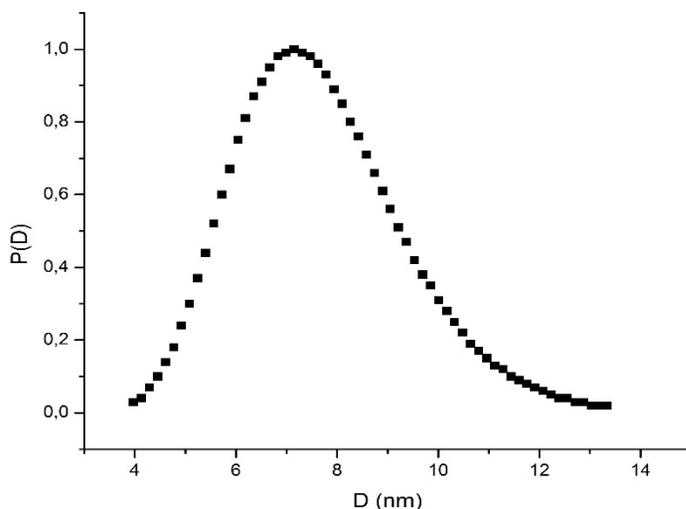
Source: The authors.

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

where D is the particle diameter, σ is the standard deviation, D_0 is the average size.

$$T_N(D) = -A_1 \times e^{\left(-\frac{D}{A_2}\right)} + T_{bulk}, \qquad (2)$$

where T_{bulk} is the bulk magnetic transition temperature of the sample, and A_1 and A_2 are parameters to be found.
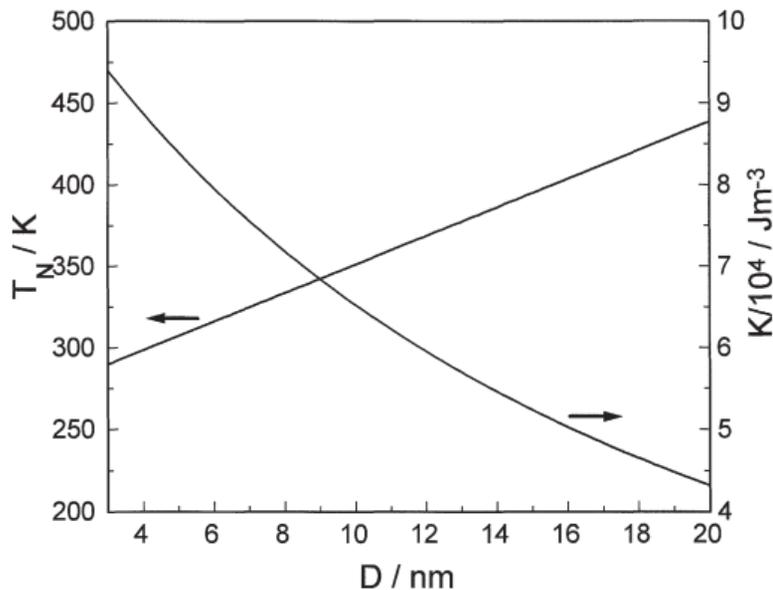
$$K(D) = AN_{01} + \frac{AN_{02}}{(D \times AN_{03})}, \qquad (3)$$

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

$$BR1\left(\frac{T}{T_N}\right) = BR_{11} \times \left[1.0 - BR_{12} \times \left(\frac{T}{T_N}\right)^{BR_{13}}\right], \qquad (4)$$

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

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

Figure 4: Reduced Internal Field [H_{int}/H (4.2K)] vs. reduced temperature (T/T_N).
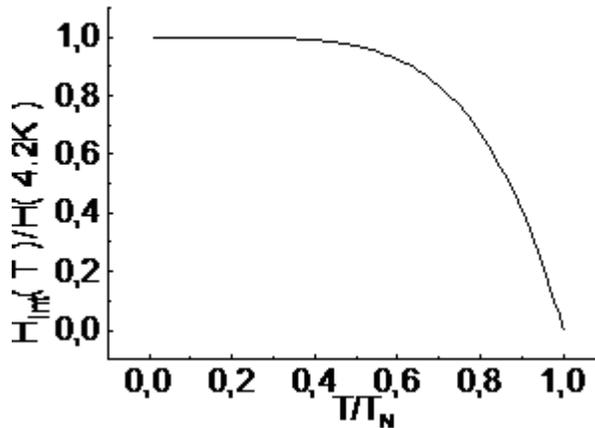

Source: (PFANNES *et al.*, 2001).

language. 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).

Figure 5: Typical experimental arrangement for Mössbauer spectroscopy (scheme) and an outline of a transmission spectrum.
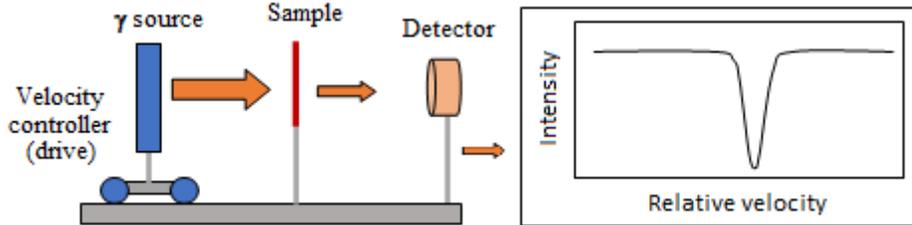
Source: Adapted from (PIRES, 2014).

Figure 6: Scheme of nuclear energy levels (^{57}Fe) for electric monopole interaction (causing isomer shift, left), pure magnetic dipole interaction (causing magnetic splitting, middle), and combined electric quadrupole and magnetic dipole interactions.
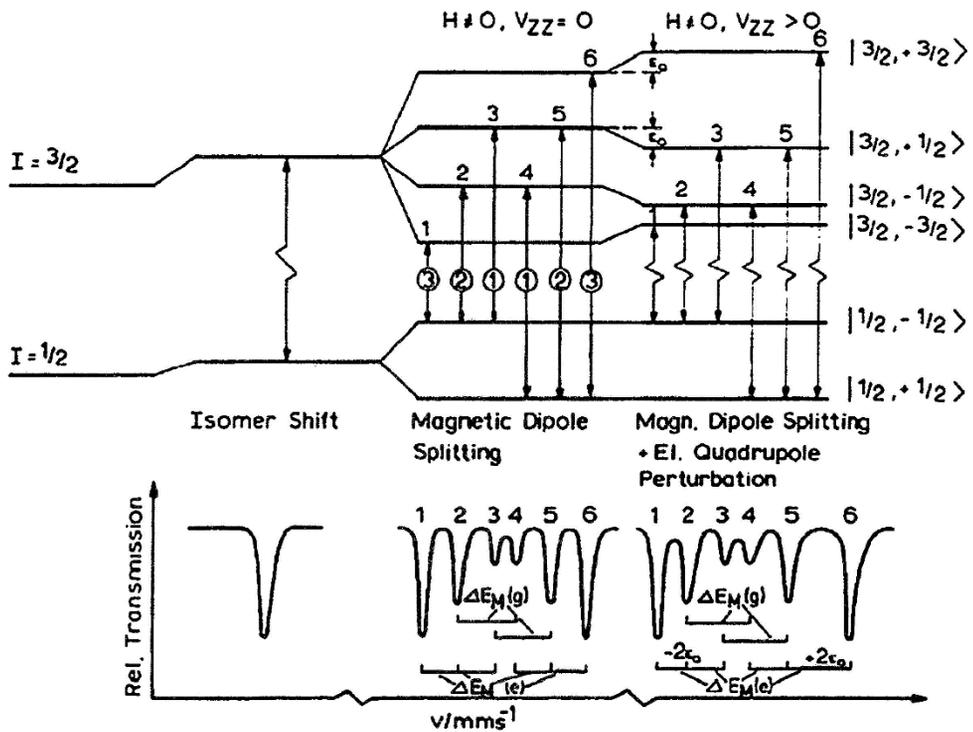
Source: (YOSHIDA; LANGOUCHE, 2013).

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.

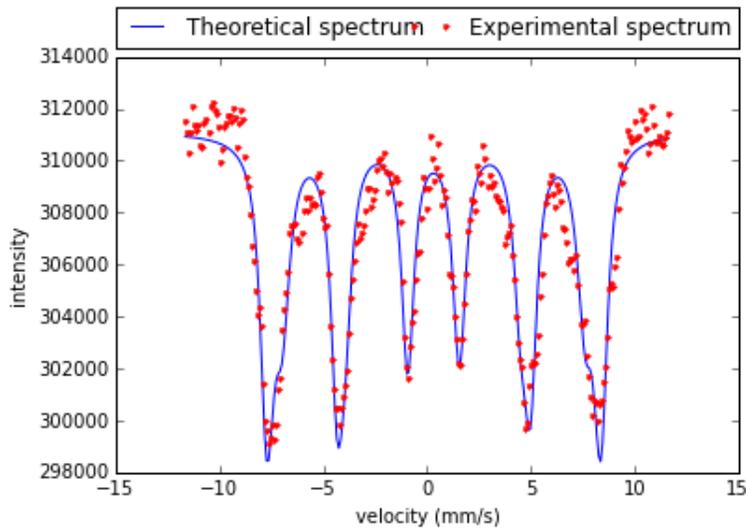| Parameters	Values found
AN_{01}	4641.009
AN_{02}	279736378.496
AN_{03}	20.000
BR_{12}	4.500
BR_{13}	5.600
BR_{21}	-0.200
BR_{22}	5.499
BR_{23}	2.224

Source: The authors.

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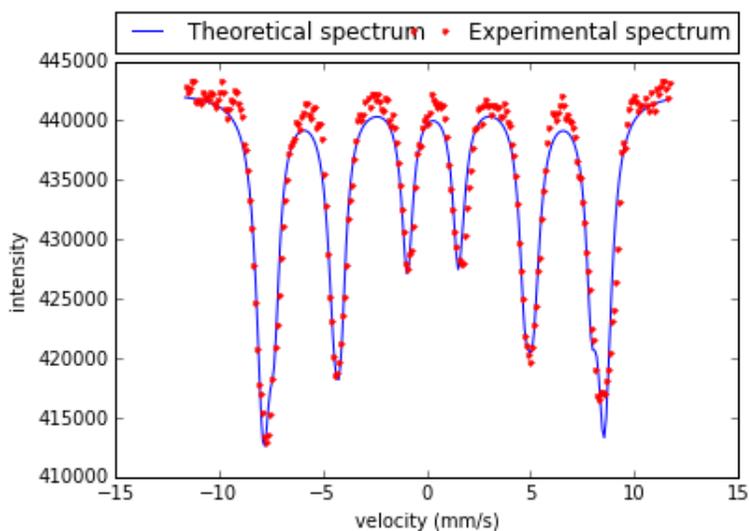
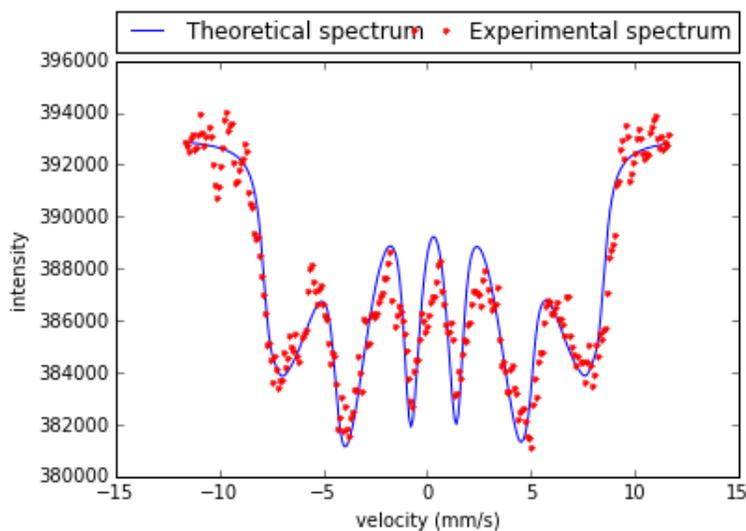**Source**: The authors.

Figure 8: Nickel ferrite Mössbauer spectrum at 100 K (CHI2 = 3.32).

Source: The authors.
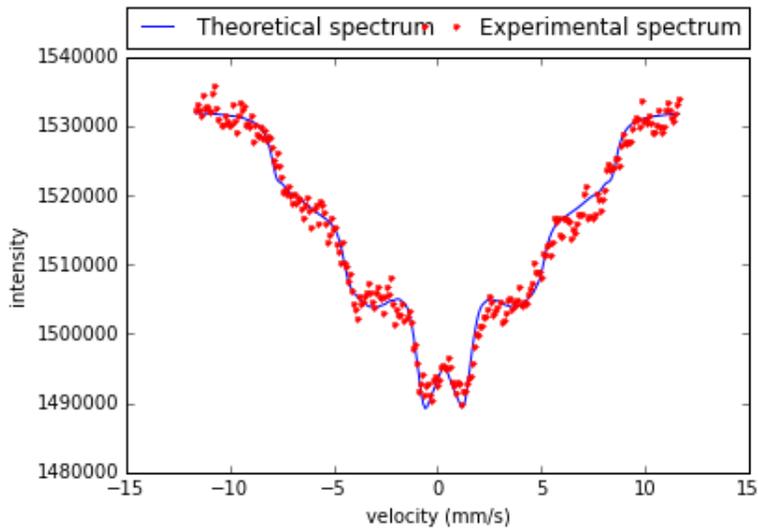
Figure 9: Nickel ferrite Mössbauer spectrum at 140 K (CHI2 = 2.98).
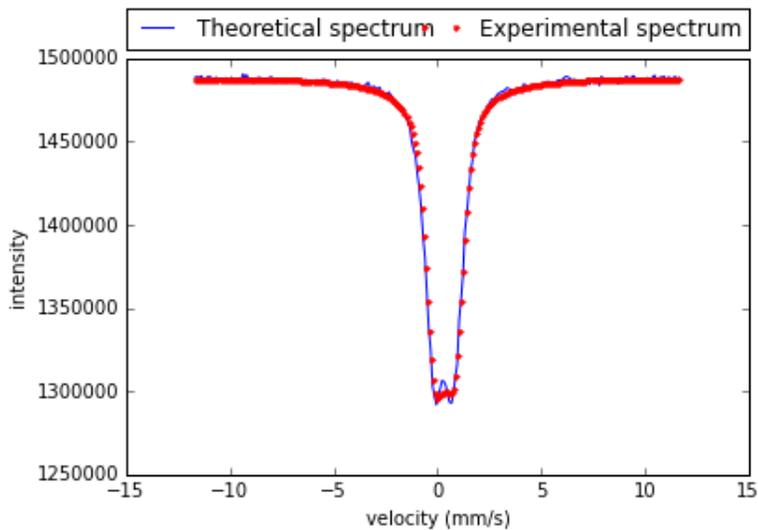

Source: The authors.

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 complexes 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.

Figure 10: Nickel ferrite Mössbauer spectrum at 180 K (CHI2 = 1.81).

Figure 11: Nickel ferrite Mössbauer spectrum at 300 K (CHI2 = 2.51).

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

approach commonly used in the Mössbauer fitting programs.

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.

ACKNOWLEDGMENTS

REFERENCES

ALBUQUERQUE, A. S. *et al.* Structure and magnetic properties of nanostructured Ni-ferrite. *J. Magn. Magn. Mater.*, v. 226-230, p. 1379–1381, 2001.

BARBOSA, W. O. *Otimização de Parâmetros de Modelo Matemático da Forma de Linha Mösbauer Aplicado a Sistemas Magnéticos Granulares Nanométricos*. Dissertação (Mestrado) — Dissertação (Mestrado em Modelagem Computacional e Sistemas) – Universidade Estadual de Montes Claros – Unimontes, Montes Claros, 2017.

CHEN, Y.; YANG, D. *Mössbauer Effect in Lattice Dynamics*. [S.l.]: WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Deustcheland, 2007.

CIANCHI, L. *et al.* Mossbauer spectra in paramagnetic relaxing systems. *Rep. Progr. Phys.*, v. 49, p. 1243–1291, 1986.

CLAUSER, M. J.; BLUME, M. Stochastic theory of line shape: Off-diagonal effects in fine and hyperfine structure. *Phys. Rev. B*, v. 3, p. 583–591, 1971.

FILHO, J. H. D. *Relaxação de Spin em Partículas Magnéticas Nanométricas*. Tese (Doutorado) — Tese (Doutorado em Física) – Departamento de Física, Belo Horizonte, UFMG, 2001.

GOLDANSKII, V. I.; HEBER, R. *Chemical Applications of Mössbauer Spectroscopy*. [S.l.]: Academic Press, New York, 1968.

GÜTLICH, P.; BILL, E.; TRAUTWEIN, A. *Mössbauer Spectroscopy and Transition Metal Chemistry: Fundamentals and Application*. Berlin: Springer, 2011.

JONES, D. H.; SRIVASTAVA, K. K. P. A re-examination of models of superparamagnetic relaxation. *J. Magn. Magn. Mater.*, v. 78, p. 320–328, 1989.

KODAMA, R. H. *et al.* Surface spin disorder in $NiFe_2O_4$ nanoparticles. *Phys. Rev. Lett.*, v. 77, p. 394–397, 1996.

LÓPEZ, J. L. *et al.* Influence of particle size on superparamagnetic relaxation of $MnFe_2O_4$ particles in ferrofluids. *J. Magn. Magn. Mater.*, v. 226-230, p. 1878 – 1880, 2001.

MARTINS, M. L. *Síntese e Caracterização de Ferritas de Manganês e Zinco Visando Aplicação como agente de Contraste em Diagnóstico Médico*. Trabalho de Conclusão de Curso - TCC. Universidade Estadual Júlio de Mesquita Filho, Instituto de Biociências, Campus de Botucatu, Botucatu: [s.n.], 2008.

MEDRANO, J. J. A. *et al.* Evidence of particle-particle interaction quenching in nanocomposite based on oleic acid-coated Fe_3O_4 nanoparticles after over-coating with essential oil extracted from Croton cajucara Benth. *J. Magn. Magn. Mater.*, v. 466, p. 359–367, 2018.

PFANNES, H. D. *et al.* Mössbauer spectroscopy, superparamagnetism and ferrofluids. *Braz. J. Phys.*, v. 31, 2001.

PFANNES, H. D. *et al.* Study of ferrofluids by Mössbauer spectroscopy. *Hyperfine Interactions*, v. 113, p. 507–515, 1998.

PIRES, M. J. M. Espectroscopia Mössbauer: da física nuclear à verificação de efeitos relativísticos. *Gazeta de Física*, v. 37, p. 10–13, 2014.

RECHENBERG, I. *Cybernetic solution path of an experimental problem*. Relatório Técnico 1122, Franborough, Royal Aircraft Establishment: [s.n.], 1965.

SAHA, K. *et al.* Beauty is skin deep: a surface monolayer perspective on nanoparticle interactions with cells and bio-macromolecules. *Small (PMC)*, v. 7, p. 1903–1918, 2011.

SCHWEFEL, H. P. *Evolutionsstrategie und numerishe optimierung*. Tese (Doutorado) — Berlin, Technical University of Berlin, 1975.

TOURINHO, F. *et al.* Synthesis and magnetic properties of managanese and cobalt ferrite ferrofluids. *Prog. Colloid Polym.*, v. 79, p. 128–134, 1989.

YOSHIDA, Y.; LANGOUCHE, G. *Mössbauer Spectroscopy – Tutorial book*. [S.l.]: Nova Iorque, Springer Verlag, 2013.