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Citation: [Journal of Applied Physics](#) **117**, 17D511 (2015); doi: 10.1063/1.4916023

View online: <http://dx.doi.org/10.1063/1.4916023>

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Magnetic behavior of La-doped Fe₃O₄ studied by perturbed angular correlation spectroscopy with ¹¹¹Cd and ¹⁴⁰Ce

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(Presented 4 November 2014; received 22 September 2014; accepted 9 November 2014; published online 20 March 2015)

In this paper, the local magnetic properties of La-doped Fe₃O₄ (5% and 10%) bulk and Nanoparticles (NPs) samples were studied by measuring hyperfine interactions in a wide range of temperature from 10 to 900 K with perturbed γ - γ angular correlation spectroscopy using ¹¹¹In(¹¹¹Cd) and ¹⁴⁰La(¹⁴⁰Ce) as probe nuclei. Results for the temperature dependence of the magnetic hyperfine field (B_{hf}) for bulk and NP samples, pure and doped with La show that its behavior follows a second order Brillouin-like transition from which the Curie temperature (T_C) was determined ($T_C \sim 855$ K). Results also show two different regions in NP samples: the core where a minor fraction of probe nuclei with well defined magnetic dipole frequency was observed and the shell where a major fraction with broad distributed electric quadrupolar frequency (surface effect in NP) was observed. The Verwey transition $T_V \sim 120$ K, due the order disorder phase, was also observed in all samples. The results are discussed in terms of the magnetic exchange interaction between Fe²⁺ and Fe³⁺ ions in the two regions of NP. © 2015 AIP Publishing LLC.
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I. INTRODUCTION

Nanoparticles (NPs) are a class of structured materials that currently has a great interest due to the wide variety of their possible technological and biomedical applications. Among these materials, Fe₃O₄ magnetic NPs (MNPs) have been intensively investigated due to their non-toxic, biocompatibility characteristics, and magnetic properties when exposed to a magnetic field, making them good candidates for biomedical application, which include drug delivery, imaging, and labeling.^{1,2} The Fe₃O₄ is a ferrimagnetic oxide with a cubic inverse spinel structure with two different cations sites (labeled as A and B cations site, respectively). A sites have a tetrahedral coordination of oxygen and are occupied only by Fe⁺³, whereas B sites have octahedral coordination of oxygen and are occupied by Fe⁺² and Fe⁺³ ions in equal proportions.^{3,4} The magnetic and electric properties of this system may be controlled through chemical substitutions such as transition metals. When structured in the form of NP, Fe₃O₄ properties are sensitive to the ratio between atoms located at the surface of grains and those at the core of NP.^{2,5} For this reason, currently different methods used to prepare NP aiming at controlling the grain size and morphology of the NP as well as the doping with other metals have been improved. Hyperfine Interactions Techniques (HI), which are based on the interaction between the nuclear moments and their surroundings electronic charges and spins, are very efficient and accurate methods that can provide valuable information to nanoscopic materials due to the short range of the hyperfine interaction, which makes the hyperfine interactions to have a local character at the atomic scale and have been used very successfully to investigate the

different sources of magnetism in nanostructured materials.⁵ Among the nuclear techniques, those based on resonance, such as Mössbauer spectroscopy (MS), has been little applied to the study of magnetic transitions in Fe₃O₄ due the high temperatures of such transitions in oxides and because the contribution from the core polarization of the Fe ions is, by far, the highest contribution to the total magnetic hyperfine field (which prevents the investigation of the effect of defects and doping on the magnetism of the lattice as well as the contribution from the lattice itself to the magnetic hyperfine field). These drawback, in measuring hyperfine interactions with accuracy in compounds as in the case of Fe₃O₄, is overcome by using perturbed angular correlation spectroscopy (PAC) since this technique permits to study local properties in a wide temperature range. In this paper, bulk and NP samples of Fe₃O₄ and Fe₃O₄ doped with La prepared using co-precipitation methods and characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM), had the behavior of the hyperfine field as a function of temperature measured by PAC spectroscopy using ¹¹¹In(¹¹¹Cd) and ¹⁴⁰La(¹⁴⁰Ce) probe nuclei.

II. EXPERIMENTAL PROCEDURE

Samples (Fe₃O₄) were prepared by using co-precipitation methods. The formation of Fe₃O₄ is described by the following equation: $Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O$.

Initially, 250 ml of deaerated and deionized water was prepared using nitrogen gas. In a three neck flask, 150 ml of water and 1 ml of ammonium hydroxide were mixed. Thereafter, Fe⁺² and Fe⁺³ were added (with Fe⁺²:Fe⁺³ = 1:2) and followed by addition of 100 ml of deionized water and 3 ml of ammonium hydroxide, thereby samples were alkaline

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with $\text{pH} = 8$. The resulting mixture was stirred for 30 min at a speed of ~ 450 rpm under N_2 flow and dried under vacuum for 24 h.

Nanoparticles doped with Lanthanum (NP-La) were prepared by the same procedure to obtain pure magnetite, using the co-precipitation method. Specifically, the dopant La was introduced using $\text{LaCl}_3 + \text{H}_2\text{O}$ to dope the samples with 5% and 10% at. wt. of La^{+3} in stoichiometric proportions to substitute Fe^{+3} ions. To obtain bulk samples, Fe_3O_4 powders were pressed in pellets and sealed in a quartz ampoule under helium at low pressure and sintered at 700°C for 15 h. After preparation, all samples had their structural properties checked by conventional θ - 2θ XRD scans using $\text{Cu K}\alpha$ radiation and their morphology characterized using TEM.

PAC measurements were carried out in a standard setup with four BaF_2 -detector spectrometer by measuring the delayed γ - γ coincidence spectra. The hyperfine field, parameters were obtained using the γ - γ cascades of 171–245 keV and 328–486 keV for ^{111}Cd and ^{140}Ce , respectively. PAC spectra were recorded at several temperatures in the range of 10–900 K. The PAC method is based on the observation of hyperfine interaction between nuclear moments with extranuclear magnetic fields (B_{hf}) and electric field gradient (efg). More details about the PAC technique as well as experimental details can be found elsewhere.^{6,7} Specifically, the perturbation factor $G_{22}(t)$ of the correlation function $R(t) = A_{22}G_{22}(t)$ contains detailed information about the hyperfine interaction and its measurement allows the determination of the Larmor frequency $\omega_L = \mu_N g B_{hf} / \hbar$, the nuclear quadrupole frequency $\nu_Q = eQV_{ZZ} / h$, and asymmetry parameter η . Carrier free ^{111}In (^{111}Cd) probe nuclei were added to the samples using $^{111}\text{InCl}_3$ solution and ^{140}La (^{140}Ce) probe nuclei were obtained by irradiating La-doped Fe_3O_4 samples for 5 min in a neutron flux of about $6 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ in the IEA-R1 nuclear reactor. This method was possible because natural lanthanum is present in samples, natural La contains 99.9% of the ^{139}La isotope which when irradiated with neutrons produces the ^{140}La radioisotope that decays to ^{140}Ce isotope.

III. RESULTS AND DISCUSSION

The XRD patterns for all samples, bulk and NP samples showed the peaks corresponding to the face centered cubic

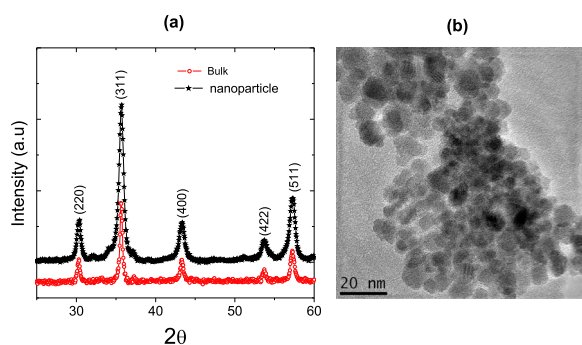


FIG. 1. (a) X-ray diffraction patterns for bulk and NP samples doped 10% La, the main peaks for Fe_3O_4 are indicated by arrows. (b) TEM micrographs of Fe_3O_4 nanoparticles.

phase of Fe_3O_4 ($Fd\bar{3}m$) as can be seen in Figure 1(a) for samples doped with 10% of La. TEM micrograph for the NP sample is displayed in Figure 1(b), indicating that the particles are spherical in shape with a diameter around ~ 12 nm.

In our experiment, the ^{111}In (^{111}Cd) nuclear probe was introduced into bulk samples by two methods: (a) thermal diffusion, where a small amount of $^{111}\text{InCl}_3$ solution was dropped on the pellets, which were then annealed for 12 h at 750°C to diffuse probe nuclei into the sample lattice; and (b) a small volume of $^{111}\text{InCl}_3$ was added during sample preparation, in the nucleation process of co-precipitation method, and the pellets obtained were annealed by thermal processes for 20 h at 750°C to grow the size of the grains. PAC spectra in both cases showed similar behavior.

All samples were fitted by a model that considers two hyperfine interactions corresponding to probe nuclei occupying two different site fractions. Results for bulk samples show one major site fraction ($f_1 \sim 80\%$) with well-defined frequency (frequency distribution $\delta_1 \sim 4\%$) corresponding to probe nuclei substituting one cation position in the crystal lattice (see Figure 2(a)). The minor fraction ($f_1 \leq 20\%$) with broad frequency distribution is due to probe nuclei at non substitutional sites most probably at the grain boundary. Conversely, results for NP samples (see Figure 2(b)) show a major fraction ($f_2 \sim 75\%$) corresponding to a broad frequency distribution ($\delta_2 \sim 60\%$) and a second site fraction with the well-defined ($\delta_1 \sim 5\%$) frequency and low population $f_1 \sim 25\%$. This difference between the fraction values ($f_2 > f_1$) is because in NP one can define two regions, the shell, corresponding to the region near the surface with deformed crystal structure (less crystalline), where probe nuclei will produce broader distributed hyperfine frequencies, and the core, corresponding to inner region of particles with well structured crystal lattice, where probe nuclei produce well-defined hyperfine frequencies.

The major fraction in bulk samples corresponding to a pure magnetic dipole interaction that allowed the determination of the Larmor frequency (ω_L). Some PAC spectra for Bulk samples at different temperatures are shown in Figure 3

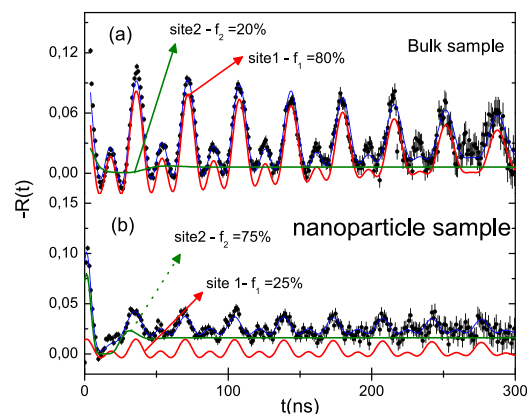


FIG. 2. PAC spectra at 250 K for bulk and nanoparticle to $\text{Fe}_3\text{O}_4 + 5\%$ La sample. The experimental data were fitted by a model with two site fractions (f_1 and f_2) for the probe nucleus occupation. (a) Bulk sample, where $f_1 > f_2$ and hyperfine frequency distribution $\delta_1 < \delta_2$. (b) NP sample with $f_2 > f_1$ and $\delta_1 < \delta_2$.

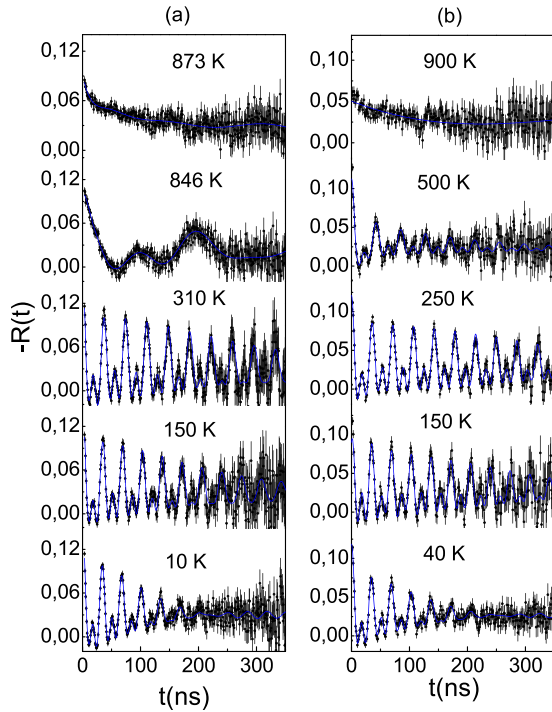


FIG. 3. PAC spectra for bulk samples using $^{111}\text{In}(^{111}\text{Cd})$ as probe nuclei at indicated temperatures. (a) Fe_3O_4 and (b) Fe_3O_4 doped with 10% of La. Solid lines are least-squares fits of the perturbation functions with pure magnetic dipole interactions to experimental data.

for pure Fe_3O_4 and Fe_3O_4 doped with 10% of La. At low temperatures, below 120 K, the amplitudes of PAC spectra were observed to decrease with time for all samples (see spectra at 10 K and 40 K in Fig. 3). This phenomenon can be attributed to the spin dynamics due the order-disorder phase transition known as the Verwey transition at 120 K.

As it was mentioned above, for NP samples, PAC spectra were fitted using a model with two site fractions at all temperatures. The major fraction ($f_2 \sim 75\%$) corresponds to an electric quadrupole interaction with quadrupole frequencies in the range from $\nu_Q = 154$ MHz to $\nu_Q = 168$ MHz with broad distribution ($\delta_2 \sim 60\%$ for all temperatures). The minor fraction observed ($f_2 \sim 25\%$) was fitted with a well-defined magnetic dipole interaction. Some PAC spectra for pure Fe_3O_4 and Fe_3O_4 doped with 5% of La samples at different temperatures are shown in Figure 4.

Bulk samples were measured using ^{140}Ce probe nuclei. Due to the short half life of the parent nuclei, it was only possible to obtain two spectra: at room temperature and at 77 K. Both PAC spectra were fitted using a single site with pure magnetic dipole interactions.

IV. DISCUSSIONS: HYPERFINE FIELD BEHAVIORS

The temperature dependence of the hyperfine field for all bulk and NP samples is shown in Figure 5. The B_{hf}^{Cd} was calculated using the equation given above using the experimental Larmor frequencies. In this figure, the behavior of B_{hf}^{Cd} was observed to follow a second-order Brillouin-type transition both for bulk and NP samples. These results agree with the literature when the Curie temperature ($T_C \sim 855$ K) is compared. It was observed only one discrepancy to NP of

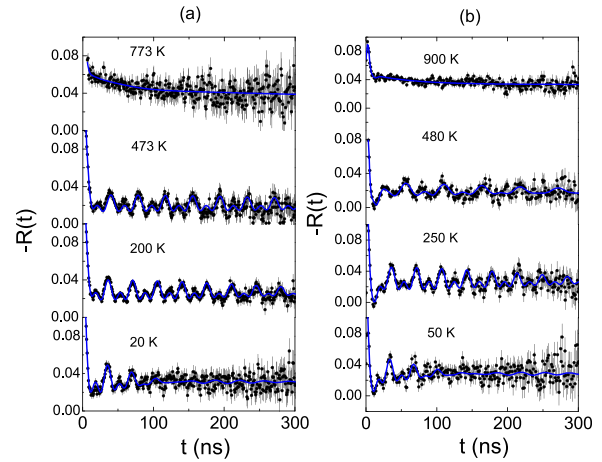


FIG. 4. PAC spectra for NP samples using $^{111}\text{In}(^{111}\text{Cd})$ as probe nuclei at indicated temperatures. (a) Fe_3O_4 and (b) Fe_3O_4 doped with 5% of La. Solid lines are least-squares fits of perturbation functions with two site fractions as described in the text.

Fe_3O_4 to which was estimated the $T_C \sim 722$ K. For the Brillouin functions, the spin $S = 2$ was used corresponding to Fe^{2+} ions because only the spins of Fe^{2+} contribute to the total magnetic moment on the host, since the contributions due to Fe^{3+} ($S = 5/2$) located at site A and site B are oriented anti-parallel to each other. Also, this is the reason because the magnetic moment of $4.1 \mu_B$ was observed by experimental measurements. This value is close of the $4.0 \mu_B$ due to Fe^{+2} ions.^{8,9}

But one question is still open: What is the location of probe nuclei $^{111}\text{In}(^{111}\text{Cd})$ inside of lattice? This question is not trivial due to the existence of two possible sites. The assignment of probe nuclei into lattice was made by comparison of our data with the work reported by Inglot *et al.*,⁴ where probe nuclei were introduced by implantation methods. PAC spectra after implantation were fitted considering that probe nuclei replace the two Fe sites into the lattice, Fe^{+2} and Fe^{+3} . This approach is possible because the implantation forced the radioactive ions to replace different position into lattice. In our experiment, the radioactivity

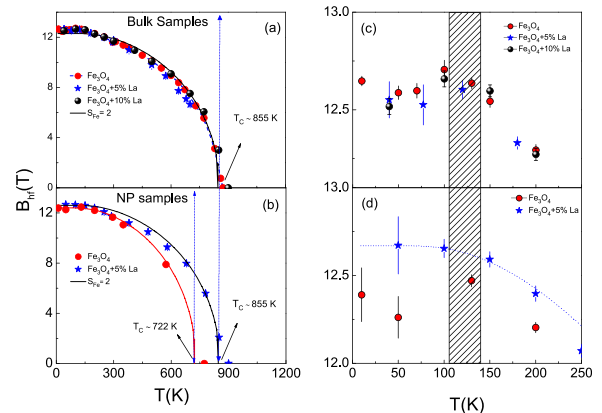


FIG. 5. Temperature dependence of B_{hf}^{Cd} for (a) and (c) Fe_3O_4 , Fe_3O_4 doped with 5% of La and Fe_3O_4 doped with 10% of La bulk samples and (b) and (d) Fe_3O_4 and Fe_3O_4 doped with 5% of La NP samples measured with $^{111}\text{In}(^{111}\text{Cd})$ nuclei probe. Solid lines fits represent the Brillouin functions to $S = 2$ (c) and (d) the behavior of B_{hf}^{Cd} below Verwey transitions for bulk and NP samples.

probe $^{111}\text{In}^{+3}$ was introduced during sample preparations by co-precipitation methods, therefore, the In^{3+} probe ions replace Fe^{+3} cations in octahedral site due to the chemical affinity between In^{+3} and Fe^{+3} , the preference for octahedral sites of In ions was observed also in different oxides.¹⁰ Another point that reinforces this idea is the behavior of the B_{hf}^{Cd} vs temperature below Verwey transition temperature around 120 K. For all samples, a decrease of B_{hf}^{Cd} values were observed (see Figure 5(c)). Similar to that observed to octahedral site by implantation methods. However, for NP samples of Fe_3O_4 doped with 5% of La, it was observed that the behavior of the B_{hf}^{Cd} follows the host magnetization (see Figure 5(d)). Therefore, we can say, that probes are located at octahedral sites and the local magnetic coupling between probe nuclei and Fe ions in octahedral sites is described by double exchange interaction model.¹¹

This study also support the idea that the magnetic properties of small particles are different for bulk samples because NP are strongly influenced by finite-size effects such as blocking temperature found by magnetic measurement. We found that on the region near surface of NP, a random distributions of atoms is present (less crystalline), whereas the core of NP preserves the crystal structure and the proprieties of magnetite samples. Therefore, it is possible that the blocking temperature could be due to interactions between Fe ions at surface and core in NP.

On the other hand, the preliminary results of hyperfine interactions using ^{140}Ce probe nuclei showed a small hyperfine field of $B_{hf}^{Ce} = 1.6(3)$ T at 77 K. This small value is due to the fact that probably the valence of ion Ce is +4, which was also found in other oxides.¹² This change of valence from +3 to +4 could modify the double exchange and indirect exchange interactions in octahedral and tetrahedral site, respectively. More macroscopic and local measurements are necessary to reveal the nature of the coupling mechanism between rare earth and iron in magnetite samples.

V. SUMMARY

The magnetic hyperfine field was characterized in a wide range of temperatures, and it was observed that its

behavior follows second order Brillouin-like transitions with the determination of the Curie temperature for bulk and NP samples of both pure and magnetite doped with La. Two different regions in NP were observed: The shell region where probe nuclei present a major site fraction with broad frequency distribution due to the random ion distributions (surface effect in NP), and the core region where a well defined magnetic dipole hyperfine frequency with minor fraction was observed. The Verwey transition was observed in all samples, except for NP doped with 5% of La to which was observed that the hyperfine field does not decreases below the temperature transition, however, PAC spectra for this sample, below Verwey transition, present a decrease in amplitude with time, which is probably due to the order-disorder phase, characteristic of Verwey transition.

ACKNOWLEDGMENTS

Partial financial support for this research was provided by FAPESP. Thankfully acknowledge the support provide by CNPq and CAPES.

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