

## STUDY OF HYPERFINE INTERACTIONS IN $\text{Fe}_3\text{O}_4$ AND $\text{LaMnO}_3$ OXIDES BY PERTURBED GAMMA-GAMMA ANGULAR CORRELATIONS

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### ABSTRACT

Nuclear techniques have been shown to be very useful tools to investigate fundamental properties in materials science and condensed matter physics. Among them the perturbed gamma-gamma angular correlation (PAC) spectroscopy has the advantage to be temperature independent e very sensitive to the crystalline array of constituent elements such as phase transitions, point defects, diffusion process, etc. PAC spectroscopy is based on the angular correlation between nuclear radiations emitted by radioactive nuclei, which is a well established method in nuclear spectroscopy. Perturbation occurs in this correlation by electromagnetic interactions external to the nucleus when it is inserted in a material, which can provide information on the electronic distribution of the neighborhood. In the present work two important materials were investigated by PAC spectroscopy using  $^{111}\text{In}$ , which decays to  $^{111}\text{Cd}$  by electron capture, as probe nuclei.  $\text{Fe}_3\text{O}_4$  nanoparticles, a superparamagnetic oxide which have biomedical applications, were prepared by co-precipitation method and  $^{111}\text{In}$  ( $^{111}\text{Cd}$ ) was added to the samples by annealing of the pellet samples at different temperatures.  $\text{LaMnO}_3$ , a ferromagnetic perovskite oxide, which has promising technological applications, was prepared by sol gel technique and  $^{111}\text{In}$  ( $^{111}\text{Cd}$ ) was introduced during preparation. Similar samples were prepared without radioactive  $^{111}\text{In}$  to be characterized by X-ray diffraction and results were analyzed by Rietveld method. Results showed that  $^{111}\text{Cd}$  nuclei substitutes Fe and La sites and, in the case of  $\text{LaMnO}_3$  the oxygen excess, which causes structural defects, are very small.

Keywords: Perturbed Angular Correlation, perovskites, nanoparticles.

### 1. INTRODUCTION

Magnetic oxides are very important material for the development of new technologies in engineering and medical applications. For instance,  $\text{LaMnO}_3$  exhibits colossal magnetoresistance, unusually large effect an external magnetic field has on their ability to transport electricity and heat[1]. The reason of such a importance is because these materials exhibit a wide variety of magnetic and electric properties, for example some materials can have antiferrimagnetic or ferromagnetic structures with possible application for spin electronics as well as some oxides can be good conductors, superconductors or good insulators depending on their electric properties. On the other hand, when the grain size is reduced, some magnetic oxides exhibit important properties that can be used in medical treatments and technologic application. For example, magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles have shown super-paramagnetic properties which are very important for hyperthermia application

of tumoral cancer treatment or drug delivery [2]. As the size of nanoparticles is less than 50 nm, they can pass through the capillaries and practically reach any internal organ, settling in those with tumor cells [3].

All such properties have motivated extensive researches in physics, chemistry and biology to investigate magnetic oxides using different scientific methods. In the work reported in this paper, a nuclear technique is used to study local properties in two important oxides,  $\text{LaMnO}_3$  (with space group  $R\bar{3}c$ ) which shows important magnetic properties and  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles by measuring hyperfine interactions. This nuclear technique is the perturbed angular correlation (PAC) spectroscopy. PAC spectroscopy requires the introduction of radioactive nuclei, which emit gamma rays in cascade, into the samples of different materials to be characterized in order to carry out measurements.

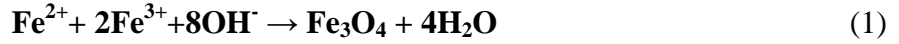
In the work reported here, probe nuclei were added after preparation of the materials using thermal procedures. Local investigation in magnetic materials is very important to magnetically characterize them because it permits to understand and describe the magnetic lattice. If the nucleus inside the material is subject to hyperfine interactions due to spin and charges from its neighborhood, these interactions cause a time change in the population of the magnetic substates of the intermediate state in the gamma-gamma cascade modifying the direction of the second gamma ray emission. Because the nucleus has electric quadrupole moment and a magnetic dipole moment [4], it is, therefore, possible to detect electric and magnetic fields generated, respectively, by charges and spins of the material. As a consequence, it is possible to study different properties of the material from an atomic view.

## 2. EXPERIMENTAL

### 2.1 Sample preparation and experimental methods

$\text{LaMnO}_3$  samples were prepared using the well-known Pechini method, popularly known as Sol-Gel method, which is based on metal citrate polymerization with ethylene glycol. In this process, high purity metals were used, La (99,9%) and Mn (99,99%) in stoichiometric proportions. These elements were dissolved in concentrated nitric acid following the reactions  $\text{La}(\text{NO}_3)_3 + 6\text{H}_2\text{O}$  and  $\text{Mn}(\text{NO}_3)_2 + 3\text{H}_2\text{O}$ . Both resulting aqueous solutions were mixed. A hydrocarboxylic acid, such as citric acid, in the ratio of 2:1 to metal ions was added to the aqueous solution to chelate metal ions. The addition of a polyalcohol, such as ethylene glycol, was added to this solution to promote the formation of an organic ester. Every step mentioned above was accompanied by constant magnetic stirring to make the solution transparent and homogeneous. Polymerization was promoted by heating at around 100 °C on a hot plate resulting in a homogeneous gel with metal ions uniformly distributed throughout the organic matrix. Subsequently, the gel was slowly heated to 820 K and calcined for 30 h in air. The resulting powder was pressed in a pellet and sealed in an evacuated quartz tube which was annealed for around 40 hours at 1100 K. Phase purity of the pellet sample was investigated by X-Ray diffraction (XRD) using  $\text{Cu K}\alpha$  radiation. The obtained XRD pattern was analyzed by Rietveld method with the FULLPROF software.

$\text{Fe}_3\text{O}_4$  nanoparticles were synthesized by co-precipitation method [5] in the Hyperfine Interactions Laboratory at IPEN following the chemical reaction:



In order to prepare the samples, a volume of Milli-Q water was deaerated with nitrogen gas for 10 minutes in a three neck flask. After that,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (pure granulated 99%) and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (pure granulated 99%) were added to the flask in the ratio 1:2 respectively. Ammonium hydroxide was added to the solution, which was homogenized by constant magnetic stirring to obtain a 10% ammonia hydroxide solution. At this step the color of the resulting solution became black. This reaction was performed for another 30 minutes under inert atmosphere of  $\text{N}_2$  gas. A black and magnetic precipitate was obtained which was washed four times with Milli-Q water. After this step, the washed solution was transferred to a beaker and dried in a desiccator using a vacuum pump for 12 hours. A black and magnetic powder was obtained. This powder was stored in an evacuated sealed quartz to avoid oxidation. At the time of PAC measurements the  $\text{Fe}_3\text{O}_4$  powder was pressed in a pellet in order to add the radioactive solution containing the  $^{111}\text{In}(^{111}\text{Cl})$  PAC probe.  $^{111}\text{Cd}$  probe nuclei were introduced into  $\text{LaMnO}_3$  and  $\text{Fe}_3\text{O}_4$  samples following the same procedure. Approximately 20  $\mu\text{Ci}$  of carrier-free  $^{111}\text{In}$  in the form of indium chloride ( $^{111}\text{InCl}_3$ ) solution was deposited on the surface of the pellets and dried under a infrared light. Each pellet was sealed in an evacuated quartz ampoule and sintered at 850 °C for 16 h. Two samples were prepared which, after the diffusion of  $^{111}\text{In}$ , were annealed at different temperatures, 950 °C and 450 °C, hereafter named SAMP950 and SAMP450, respectively.

Measurements of samples were carried out in the Hyperfine Interaction Laboratory at IPEN by perturbed gamma-gamma angular correlation (PAC) technique using a spectrometer consisting of four conical  $\text{BaF}_2$  detectors arranged in a planar 90°–180° geometry with a conventional slow–fast coincidence set-up. The time resolution of the detector system was of the order of 0.7 ns. The well known gamma cascade of 172–245 keV, populated from the electron capture of  $^{111}\text{In}$  with an intermediate level with spin  $I = 5/2^+$  at 245 keV ( $T_{1/2} = 84.5$  ns) in  $^{111}\text{Cd}$  was used to investigate the hyperfine interactions. Measurements for  $\text{LaMnO}_3$  were performed in the temperature range of 15–1100 K, while  $\text{Fe}_3\text{O}_4$  samples were measured at room temperature. The PAC method is based on the observation of hyperfine interaction of nuclear moment with extra-nuclear magnetic field ( $B_{hf}$ ) or electric field gradient ( $V_{ii}$ ). The technique measures the time evolution of the  $\gamma$ -ray emission pattern caused by hyperfine interactions. A description of the method as well as details about the PAC measurements can be found elsewhere [5, 6].

The spin rotation spectra  $R(t)$  obtained in the measurements were fitted by using a model that takes into account the fractional site populations ( $f_i$ ):

$$R(t) = A_{22} G_{22}(t) = A_{22} \sum_i f_i G_{22}^i(t), \quad (1)$$

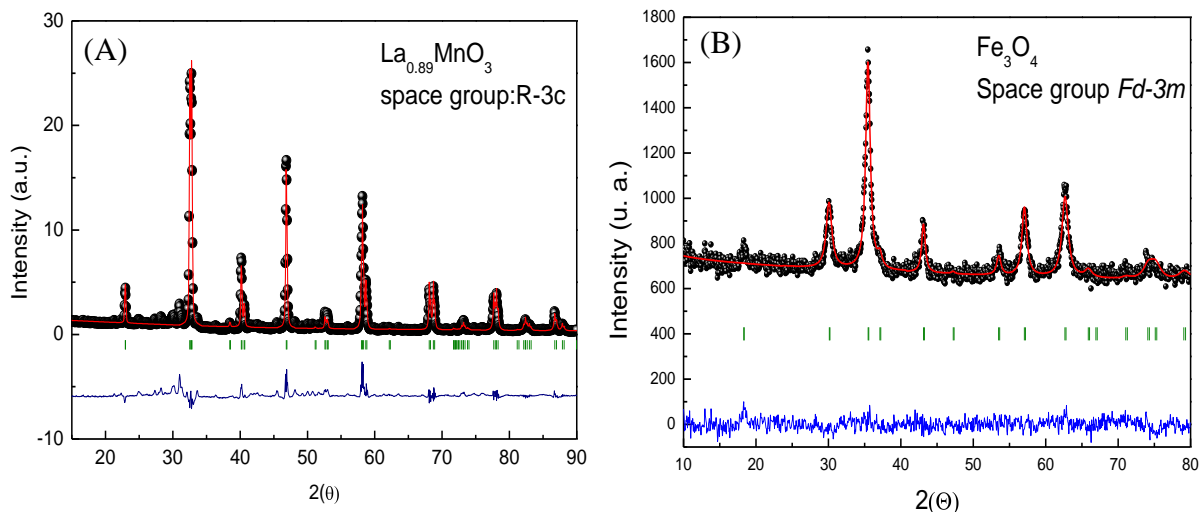
Where  $A_{22}$  is the unperturbed angular correlation coefficient and  $G_{22}(t)$  is the perturbation factor, which contains information about the hyperfine interaction. Measurement of  $G_{22}(t)$  allows the determination of the Larmor frequency  $\omega_L$ , which is proportional to the magnetic hyperfine field, the quadrupole frequency  $\nu_Q = eQV_{zz}/h$  as well as the asymmetry parameter  $\eta = (V_{xx} - V_{yy})/V_{zz}$ , where  $V_{xx}$ ,  $V_{yy}$  and  $V_{zz}$  are the components of the electric field gradient tensor in its principal axis system.

### 3. RESULTS AND DISCUSSIONS

The x-ray diffraction pattern of polycrystalline  $\text{LaMnO}_3$  and  $\text{Fe}_3\text{O}_4$  samples at room temperature were analyzed using the Rietveld refinement method. The analysis of  $\text{LaMnO}_3$  evidenced the formation of pseudo-cubic crystal structure with space group R-3c space group where La atoms occupy 4e positions with lattice parameter  $a = 10,44 \text{ \AA}$ . Impurity phases  $\text{Mn}_3\text{O}_4$  and  $\text{La}_2\text{O}_3$  with a little percent were also observed. The analysis of  $\text{Fe}_3\text{O}_4$  shows that samples present a inverse cubic spinel structure with spatial group Fd3m. From XRD line broadening, the average crystal size of the nanoparticles of 9.75 nm was deduced using Scherrer's equation.

$$t = \frac{0.9\lambda}{B\cos\theta}, \quad (2)$$

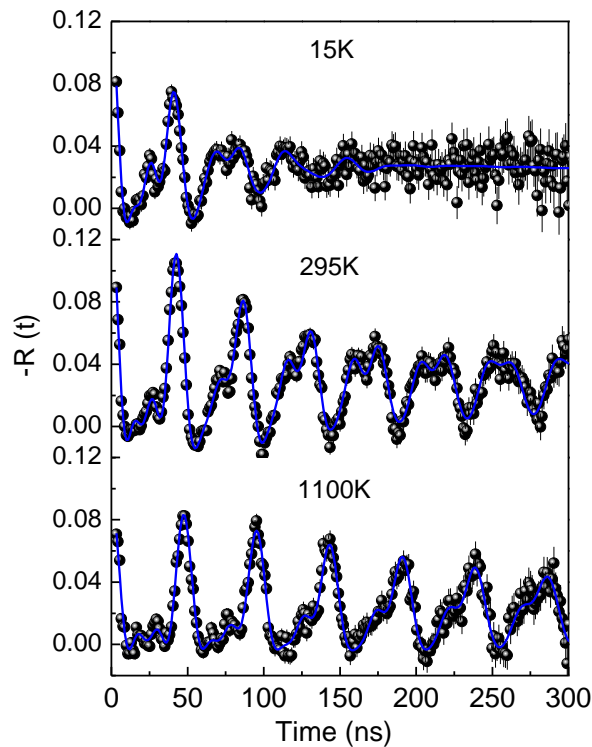
where  $t$  is the average crystallite size,  $\lambda$  is the X-ray wavelength ( $1.5418 \text{ \AA}$ . for Cu-K $\alpha$ ) and  $B$  is the full width at half maximum of the diffraction peak (fwhm).



**Figure 1: X-ray pattern of (A)  $\text{LaMnO}_3$  oxide and (B)  $\text{Fe}_3\text{O}_4$  nanoparticles at room temperature, the red lines represent calculated fit using the Rietveld method and the blue line represent de difference between the experimental and calculated data**

PAC spectra for  $\text{LaMnO}_3$  samples measured with  $^{111}\text{Cd}$  probes at different temperatures are shown in figure 2. The visual inspection of these spectra clearly show that the frequencies changes with temperature indicating a magnetic behavior of samples. The fit of the spectra above magnetic transition temperature  $T_C \sim 250 \text{ K}$ , which was observed before in similar compound reported in the literature [6] [8], was performed using a model considering only electric quadrupolar interactions (figure 2). For example, PAC spectrum measured with  $^{111}\text{Cd}$  at room temperature (295 K) shows only one site with quarupole frequency  $\nu_Q = 150 (2) \text{ MHz}$  and asymmetry parameter  $\eta = 0.2$ . This observed quadrupole interaction was assigned to  $^{111}\text{Cd}$  probe replacing La sites in  $\text{LaMnO}_3$ . This assignment is based on results of previous PAC

experiments for several rare-earth perovskites, for which similar frequencies were observed at rare-earth sites [7-9]. Below the magnetic transition temperature, spectra were fitted using a model which considers a combined magnetic dipole plus electric quadrupole interaction. The behavior of the hyperfine parameters indicates structural transition and magnetic transition in this compound. The temperature dependence of the magnetic hyperfine field ( $B_{hf}$ ) shows an unusual behavior, not consistent with the Brillouin function, which suggests a first-order magnetic transition.

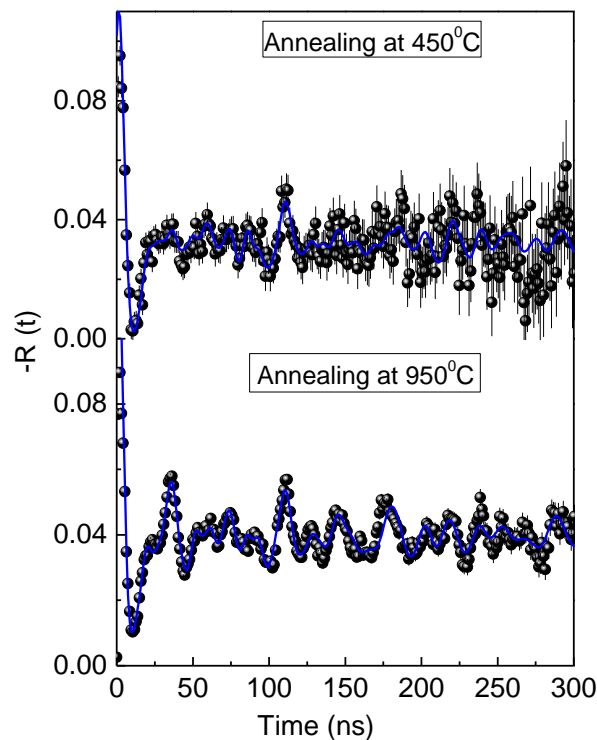


**Figure.2: PAC spectrum of  $\text{LaMnO}_3$  at different temperatures. below temperature (15K) room temperature 295K and high temperature 1000K, the blue lines represent fitting of spectra.**

Our PAC results agree with the work reported by G. Dezanneau, *et al* for  $\text{La}_{1-x}\text{MnO}_{3x}$  in which the magnetic transition temperature in  $\text{LaMnO}_3$  was observed between 210 K and 250 K [6]. Recently, lower magnetic transition temperature was reported by A.N. Ulyanov *et al.* [9]. We suggest that the observed magnetic and structural transitions are due to the presence of vacancies in the samples and also due to distortions observed at La sites due the Jan-Teller effect which change the typical chemical stoichiometry of the perovskite structure is  $\text{ABO}_3$ . Both effects may be due to the high mobility of oxygen two A-site (La 3b) ions and one B-site ion.

PAC spectra for two  $\text{Fe}_3\text{O}_4$  samples (SAMP450 and SAMP950) prepared with different annealing temperatures measured with  $^{111}\text{Cd}$  probes at room temperatures are shown in figure 3. A visual inspection shows that a sharp difference in the spectra can easily be observed. The fit for both samples was performed using a model given by equation 1 considering three fraction sites. One fraction with pure dipole magnetic interaction with magnetic frequency  $\nu_M$   $\sim 27$  MHz for both samples, which was assigned to crystalline  $\text{Fe}_3\text{O}_4$ , based on the reported

PAC frequency found for bulk  $\text{Fe}_3\text{O}_4$ [10]. The abundance for this fraction site was around 15% and corresponds to  $^{111}\text{Cd}$  nuclei at Fe sites in crystalline  $\text{Fe}_3\text{O}_4$  formed at inner region of the particles. The second fraction with abundance around 67% was fitted with a pure electric quadrupole frequency  $\nu_Q \sim 210$  MHz with a broad distribution. This fraction was assigned to  $^{111}\text{Cd}$  probes at non-crystalline iron oxide in the outer region of nanoparticle, near the surface where defects are present. The third fraction with abundance around 18% was fitted with a combined electric quadrupole plus magnetic dipole frequencies with different values  $\nu_Q \sim 207$  MHz and  $\nu_M \sim 22$  MHz for SAMP950 and  $\nu_Q \sim 32$  MHz and  $\nu_M \sim 27$  MHz for SAMP450. Both quadrupole frequencies were also fitted with high asymmetry parameters  $\eta \sim 0.9$ . This fraction was assigned to probe nuclei occupying Fe sites in particles with strongly distorted  $\text{Fe}_3\text{O}_4$  structure which probably is a result of the preparation method.



**Figure 3: Analysis of these two PAC spectra of  $\text{Fe}_3\text{O}_4$  above shows that in annealing at  $900^\circ\text{C}$  is better than annealing at  $450^\circ\text{C}$  for introducing  $^{111}\text{Cd}$  into the sealed in vacuum pellet. Quadrupole frequencies were as-signed to  $^{111}\text{Cd}$  probe substituted at Fe site.**

The goal of the PAC measurements was to observe the annealing temperatures used in the  $\text{Fe}_3\text{O}_4$  particles. Analysis of the spectra obtained with  $^{111}\text{Cd}$  in both  $\text{Fe}_3\text{O}_4$  samples at room temperature shows that  $^{111}\text{Cd}$  replaces Fe sites in the cubic spinel structure in different regions of the particles (the core and the shell) and is also capable to distinguish the quality of the crystal structure of the core region in the particles. Interestingly, the amplitude of peaks in the PAC spectrum are higher for SAMP950 (annealing at  $950^\circ\text{C}$ ). This observation shows that the temperature of  $950^\circ\text{C}$  is probably better for probe diffusion and replacement of Fe into the particles to perform PAC spectroscopy measurements.

### 3. CONCLUSIONS

In this paper it is shown that PAC spectroscopy is a powerful tool to investigate magnetic oxide bulk as well as nanoparticle samples. In the case of bulk  $\text{LaMnO}_3$ , PAC spectroscopy corroborates the occurrence of phase transition at  $T \sim 250$  K and provides strong evidences the occurrence of magnetic-dipole interactions coexisting with electric-quadrupole interactions at the La sites below 250 K. The observed magnetic hyperfine field shows a temperature dependence which presents a first-order transition. Complementary measurement by Magnetic techniques and PAC using  $^{140}\text{La}$ ( $^{140}\text{Ce}$ ) are in progress to have a better understanding of the structural and magnetic behavior in this system. As for nanoparticles, PAC spectroscopy results showed the capability to distinguish different regions inside the particles (core and shell fractions) as well as it was able to give information about the quality of the crystalline part of the particles. Moreover, PAC results also showed that the annealing temperature is important in the diffusion and replacement of probe nuclei at Fe sites in  $\text{Fe}_3\text{O}_4$ .

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