Temperature dependence of the EPR spectra for the $Ni_{1-x}Co_xFe_2O_4$ nanoparticles

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Abstract. Electron Paramagnetic Resonance (EPR) was used to study the temperature dependence of the magnetic behavior of $Ni_{1-x}Co_xFe_2O_4$ with $0.0 < x < 0.5$, in the temperature range $80 < T < 700$ K. Nanoparticles of sizes between 30 and 40 nm were obtained using the sol-gel method. The results show that the resonance field ($H_R$) decreases while the linewidth ($\Delta H_{PP}$) increases, in the temperature range studied, when $x$ is increased. The $H_R$ values for $x = 0$ are in agreement with a superparamagnetic phase in the temperature range studied, while for $x = 0.2$, $H_R$ and $\Delta H_{PP}$ are in accordance with a ferrimagnetic to superparamagnetic transition at $T \approx 350$ K, where $T$ is related to the EPR blocking temperature of these samples. For sample with $x = 0.5$ this temperature is $T \approx 470$ K. These results are in good agreement with the magnetization and MOKE results. MOKE measurements as a function of temperature were made to corroborate EPR results.

1.- Introduction

The magnetic properties of nanoparticles are of great interest, due to the enormous development of devices of large storage capacity [1]. Their magnetic properties are strongly dependent on size, shape, preparation and composition [2]. The reversal of spontaneous magnetization in such particles is of particular interest, since this determines the stability of kept information and limits the density of the storage. The nanoparticles of $NiFe_2O_4$ has been broadly studied [3,4] and it has been found that its magnetic properties depend strongly on the preparation method, being noticed big changes in the hysteresis loops. In the same way, the cobalt nanoferites $CoFe_2O_4$ are interesting, due to its optical, electronic and magnetic properties, which frequently differ from the volumetric compounds. Besides that they present high coercivity and moderate magnetization. These properties, and the great physical and chemical stability, make of the cobalt nanoparticles very good candidates for applications of magnetic recording, just as audio, video and digital recordings of high density [5,6]. EPR is a broadly used technique to study the magnetic properties of magnetic systems [7,8], allowing us determine the magnetic anisotropy of the system and identify possible magnetic phase transitions and its thermal dependence.

In this work the temperature dependence of the magnetic properties of mixed ferrites nanoparticles of Co-Ni prepared by the sol-gel method are studied.

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2.- Experimental Detail
The samples were prepared using the sol-gel method, with nitrates of Ni, Co and Fe as precursors. The samples were characterized using X-ray diffraction (XRD) and Scanning electron microscopy (SEM), to determine the lattice parameters and the average size of the nanoparticles. The magnetic $M(T)$ and $M(H)$ measurements were carried out in a MPMS XL-7 SQUID magnetometer. The EPR measurements were carried out in a BRUKER EMX spectrometer at the X band in the temperature range $80 < T < 700 \, K$. MOKE measurements were carried out using a homemade MOKE setup with a $4 \, mW (\lambda = 635 \, nm)$ solid state laser, a photoresistance and two linear glass polarisers with and extinction ratio of 10,000:1. The optical geometry of the MOKE consists in a mixed disposition between POLAR and LONGITUDINAL setups i.e. the magnetic field applied to the sample surface have both normal and perpendicular components.

3.- Experimental Results
The XRD results showed that the systems crystallize in a spinel cubic structure. The table 1 shows the lattice parameters obtained for all the samples studied [9].

| $x$  | Cell Parameter ($\AA$) | Volume ($\AA^3$) | Average size (nm) |
|------|------------------------|------------------|-------------------|
| 0.0  | 8.327 (1)              | 577.39           | ~20-30            |
| 0.2  | 8.342(3)               | 580.51           | ~30-40            |
| 0.5  | 8.359(3)               | 584.07           | ~30-40            |

An increment in the cell parameter, as the concentration of cobalt ions increase, is appreciated and it is reasonable because of the cobalt ($Co^{2+}$) ions have a bigger ionic radius that the nickel ($Ni^{2+}$) ions. These results are in good agreement with those reported in the literature [10]. The SEM results show the presence of nanoparticles of different sizes as can be appreciated in table 1.

The figure 1 shows the temperature dependence of the magnetization, in the field cooled (FC) and zero field cooled (ZFC) cycles with $50 \, Oe$ of applied magnetic field, for the $NiFe_2O_4$ ferrite. As it can be seen it was not possible to observe the blocking temperature, since the measurements were carried out from 2K to room temperature. However, it is clearly observed the splitting of the magnetization curve below the blocking temperature. The behaviour of the FC and ZFC curves are the expected for the Ni ferrite nanoparticles. Similar behaviour was observed for the other samples. In the figure 2 the unnormalized EPR spectra at $T = 450 \, K$ for all the samples studied are shown. A well defined spectrum, centred around $g = 2$, for the $NiFe_2O_4$ sample is observed. The lineshape for this compound is consistent with the spectrum obtained for superparamagnetic particles with distribution density of the nanoparticles diameters in the Ni ferrite-sample [11]. When cobalt ions concentration is increased, the lineshape of the spectrum changes and becomes wider due to the dipolar interaction among the nanoparticles. A shift in the $H_R$ toward lowest values is also observed when increasing the cobalt content. In figure 3 the temperature dependence of the $H_R$ is shown for all the samples in the range of temperatures studied. When the temperature is decreasing from $T = 700 \, K$ it is possible to observe, that $H_R$ remains approximately constant for the sample with $x = 0$, the inset of the figure shows the $\Delta H_{pp}$ behaviour as function of the temperature. Besides that the linewidth for $x = 0$ shows a continuous increment, probably due to an increment of the dipolar interaction of the nanoparticles, this behaviour of the $\Delta H_{pp}$ and $H_R$ agrees with the presence of the superparamagnetic phase in the system [8] in the temperature range studied. This apparent contradiction between magnetic and EPR results can be explained because of the very different characteristic measuring times for a static magnetization and EPR spectra [12]. The $H_R$ for sample $x = 0.2$ remains approximately constant until $T = 350 \, K$, below this temperature $H_R$ quickly decrease until the EPR spectrum spreads to disappear due to the strong zero field absorption present in the sample; the inset shows that $\Delta H_{pp}$ for this sample increase very quickly until reaching a cusp at the same temperature. This abrupt increment in $\Delta H_{pp}$ could be
related with the fact that the $\text{Co}^{2+}$ ions generally occupy the tetrahedral places of the spinel structure and there exists an antiferromagnetic interaction between the ions in tetrahedral and the octahedral sites producing an increment in $\Delta H_{pp}$ [10]. It has been found that the $\text{Ni}^{2+}$ ions have preference for the octahedral sites, while the $\text{Co}^{2+}$ and $\text{Fe}^{3+}$ ions can occupy both, tetrahedral and octahedral sites [13]. The behaviour for the sample $x = 0.5$ is similar to that of the sample $x = 0.2$. $H_R$ decrease smoothly, almost constant when the temperature is decreased, and a marked decrease is seen around $T = 470 \, K$. $\Delta H_{pp}$ increase very quickly when the temperature is decreased, reaching a cusp at $T = 380 \, K$. These temperatures could be related with the EPR superparamagnetic blocking temperature, what allows us to assume that samples with $\text{Co}^{2+}$ ions present a ferri-superparamagnetic transition at these temperatures; in the case of the sample with $x = 0.5$ the critical temperatures for $H_R$ and $\Delta H_{pp}$ are not in accordance, this can be because as we increase the $\text{Co}^{2+}$ ions concentration also we increase the dipolar interaction among the superparamagnetic nanoparticles modifying the temperatures for the cusp in the $\Delta H_{pp}$. In order to corroborate the EPR results, the hysteresis loops at temperatures below and above the blocking temperature were measured. As we are interested in the shape of the loops at the two magnetic states, ferromagnetic and superparamagnetic, i.e. the presence or not of coercive field, the amount of magnetization of the sample is not relevant (calibration of the y-axis). Because of this, the MOKE measurement is an adequate method. The figure 4 shown the hysteresis loops taken by this method for the $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ compound which have an EPR blocking temperature about $470 \, K$, as it can
be see, the sample shown an hysteresis loop below this temperature ($T = 400 \, K$) and not observable hysteresis loop above ($T = 530 \, K$) in perfect accordance with the EPR results.

![Hysteresis loops for the sample at three different temperatures](image)

**Figure 4.** Hysteresis loops for the $Ni_{0.5}Co_{0.5}Fe_2O_4$ sample at three different temperatures

4.- **Conclusions**

Particles between 20 and 40 nm size of cobalt-substituted nickel ferrites have been prepared by sol-gel method. The magnetization measurements indicate a ferrimagnetic behavior with transition temperature above the room temperature for the samples containing $Co^{2+}$. The EPR measurements confirm the existence of superparamagnetic phase above 350 K for all the samples studied. Samples with cobalt ions present EPR superparamagnetic blocking temperatures at about $T = 350 \, K$ and 470 K for samples with $x = 0.2$ and 0.5, respectively. The nickel ferrite seems to show a superparamagnetic behavior below 700K, however more experiments of magnetic nature are in progress to elucidate that point. When the concentration of cobalt ions is increased, the EPR blocking temperature increase and $H_B$ decreases in agreement with an increment in the crystalline field due to the presence of $Co^{2+}$ ions. The MOKE results support quite well the EPR results.

**Acknowledgments**

The authors wish to acknowledge to Instituto Venezolano de Investigaciones Científicas and Universidad de Los Andes for financial support.

5.- **References**

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