Competing interparticle interactions and surface anisotropy in NiO nanoparticles

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We report unconventional magnetic properties on NiO nanoparticles of an average diameter ~5.8(7) nm obtained by coprecipitation method. To investigate the effect of the intra and interparticle interactions in the magnetic properties nanoparticles were dispersed in a polyvinyl-pyrrodone matrix at two different concentrations. X-ray, ac, and dc magnetization and ferromagnetic resonance experiments were carried out on powder and dispersed NiO systems. Our results show that dispersed and concentrated samples exhibit following two different magnetic behaviors: (i) a high temperature peak related to the blocking of the particle core and (ii) a low temperature maximum likely related to the freezing of the frustrated spins on surface particle. Besides, we have observed that the low temperature maximum is not field-dependent and depend strongly on the distance among particles. This result can be understood taking account the decreasing of the dipolar interaction to more dispersed samples. © 2010 American Institute of Physics. [doi:10.1063/1.3459890]

I. INTRODUCTION

In the last few decades, studies on magnetic properties of fine particles with dimensions in the nanometer range have been the subject of intense theoretical and experimental investigations.1–6 In this sense, magnetic nanoparticles (NPs) have gained an increasing interest owing to their unique physical properties as compared to their bulk counterparts. It is well known that below a critical size, magnetic NPs behave as a single-domain, in contrast with the multidomain structure observed in their bulk form. In a rough approximation, the energy states of the magnetization vector of the particles can be modeled as a two level system separated by barriers that depend on their size and magnetic anisotropies.7–12 In the most general case the magnetic NPs can present following two different magnetic regimes as a function of temperature: (i) Below a critical temperature, so-called blocking temperature $T_B$, ($T < T_B$) the energy barriers can trap the magnetization vector in two or more metastable orientations, giving rise to hysteresis and (ii) for $T > T_B$ the thermal energy $k_B T$ becomes large enough (when compared to the energy barrier) leading to the so-called superparamagnetic (SPM) regime. Additionally, unusual magnetic behavior has been observed in the low temperature regime, which can be interpreted as a result of their finite size, that is, the breaking of a large number of exchange bonds for surface atoms driving the spins to a strongly frustrated state on particle surface. For example, small core moment antiferromagnetic (AFM) and ferromagnetic (FM) amorphous NPs (Refs. 2, 4, 6, 9, and 13–16) presents an additional maximum in the low temperature region of the magnetization curve. On the other hand, to best of our knowledge, there are not reports in literature about this unusual magnetic peak to FM crystalline NPs.

Among a variety of such materials, nickel oxide (NiO) NPs have been a subject of avid research due their finite size effects, small moment core, and strong surface effects. Several models which consider different interparticle interactions4,9,16–19 have been suggested to explain the experimental data. Recently, Winkler et al.9 have reported the complexity of the magnetic properties of NiO NPs with an average particle size of 4 nm. They explained their results as a consequence of the competition among size core effects, surface anisotropy and interface interaction. Additionally, theoretical calculations and experimental data have shown that NiO NPs ranging from 1 to 50 nm can present both AFM and FM couplings. This magnetic behavior appears to be linked with uncompensated surface moments.19

The main goal of this work is understand the role of the strengths of interparticle interactions in the magnetic properties of NiO NPs. In this sense, for using the same batch, we have prepared three NPs systems at following three different conditions: (i) concentrated (powder form) and (ii) two dispersed NPs systems. The results show to all samples a high temperature peak related with blocking effects of the NiO and a low temperature maximum likely related with the high degree of frustration of the spins on the particle surface. We also observed that the low temperature peak is strongly de-

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dependent on the distance among particles in contrast with the field-dependent behavior generally presented for the blocking temperature.

II. EXPERIMENTAL PROCEDURES

NiO NPs were prepared using coprecipitation method for mixing NiCl$_2$·6H$_2$O and gelatin aqueous solution with NaOH at temperature of 60 °C. In order to control the size and minimize the coalescence effect of our particles system we have used gelatin as dispersant agent. The agglomeration is slowly reduced as can be visualized in the Fig. 1 if we compared with others works that NiO NPs only using coprecipitation method without addition of any organic precursor. The precipitated solution Ni(OH)$_2$ and disnaturized gelatin were slowly cooled up to room temperature and then dried at a temperature of 80 °C for 36 h. The precipitated material was annealed in air at 350 °C for 3 h to obtain NiO NPs. The fine powder was washed several times with acetone in order to remove the chloride ions completely. Additional preparation details can be found elsewhere.

NiO powder was taken as the most concentrated sample (labeled as SP). The diluted NPs systems were obtained after centrifugation and dispersion of NiO NPs in polyvinyl-pyrrolidone (PVP) at following two concentrations: (a) 16% NiO/PVP in mass (labeled as S1) and (b) 1.8% NiO/PVP in mass (labeled as S2).

The powder x-ray diffraction (XRD) data were obtained with a Rigaku diffractometer using the Bragg–Brentano geometry in continuous mode with a scan speed of $1/4°$/min in the 2θ range from 30° to 90° using Cu $K\alpha$ radiation. Rietveld refinements were performed using the software DBWS9807, as described by Young et al. The full width at half maximum obtained from this refinement was used to calculate the particle size and microstrain for {1 1 1}, {0 0 2}, {0 2 2} crystallographic families. The details of estimated particle size and strain can be found in Ref. In order to analyze the structure and morphology of the samples transmission electron microscopy (TEM) images were taken in a high resolution 200 keV JEM 3010 microscope at the Laboratório de Microscopia Eletrônica at Laboratorio Nacional de Luz Sincrotron (LNLS, Brazil).

Superconducting quantum interferometer device MPMS XL7 was used to characterize the magnetic properties as function of temperature (2–300 K), time and applied magnetic field (up to 6 T). AC susceptibility measurements as a function of temperature (2–300 K) and frequency ($10^2$–$10^4$ Hz) were performed in a commercial PPMS magnetometer (Quantum Design). To study the thermal evolution of the anisotropy FM resonance (FMR) spectra were taken (10–300 K) using a Bruker ESP300 spectrometer.

III. RESULTS AND DISCUSSION

A. Structural analysis

Figure 1 shows the Rietveld refinement XRD pattern for the as-prepared NiO NPs. The analysis of the positions and relative intensities of the diffracted lines confirms the presence of single phase cubic structure of NiO with a space group $Fm\bar{3}m$ and cell parameters $a=4.184(2)$ Å. The results obtained through Rietveld refinement show a goodness of fit $\chi^2=1.03$. From the Rietveld refinement, we are able to estimate the average particle size of NiO NPs around 5.8(7) nm and a strain of 0.5% for using Williamsom–Hall plotting as discussed in Ref. This value for strain is related to internal disconnections among the crystalline planes. According Rojas et al. and Nunes et al. this factor can strongly influence the local magnetic ordering of these materials to TbAl$_2$ alloys and Ni NPs. TEM images [see Fig. 2(a)] for the SP sample show that our NPs system consist of homogeneous particles of nearly spherical shape with an average size of 6.4(8) nm and a log-normal distribution (not shown here) which is further verified using investigation of zero-field-cooled (ZFC)-field-cooled (FC) curves presented below. Another noteworthy point is that our high resolution TEM (HRTEM) image shown in Fig. 2(b) clearly demonstrates the highly crystalline nature of the NiO NPs.

B. Magnetic properties

Figure 3 shows the magnetization as a function of temperature for the as-prepared (SP) and dispersed NPs measured in ZFC and FC conditions in an external magnetic field of 100 Oe. It is evident that as-prepared (SP) sample exhibits
a typical SPM behavior in the high temperature regime and a blocked state in the low temperature regime (below around 75 K). In addition, the curve also indicates a wide distribution of energies barriers that can be associated to the particles sizes distribution. Therefore, for some case of interacting magnetic metallic NPs, it is almost impossible to see SPM behavior and estimate particles size distribution due to agglomeration of the particles doing that the set of particles behaviors as grain, and consequently, it present to be a multidomain system,\(^\text{28,29}\) differently of our system. But when these NPs are diluted in some matrix nonmagnetic, they begin appear SPM behavior.\(^\text{29}\)

The \(M_{\text{ZFC}}\) measurements show to all samples an increase in the magnetization in low temperatures region (below 20 K), presenting a peak to SP and S1 samples. This kind of behavior was also observed previously for both crystalline as well as amorphous NPs systems.\(^\text{3,9}\) The origin of such maximum can be associated to the ordering of small magnetic clusters at the particle surface, inducing strong intraparticle interactions, which leads to a frustrated magnetic state.\(^\text{20}\)

As it has been observed to various magnetic NPs systems the high temperature peak is field-dependent, that is, it shifts to lower temperatures for increasing the magnetic external field. However, a careful analysis of the position of the low temperature maxima reveals that the peaks shift to lower temperatures for decreasing the strength of the interparticle interactions, being 11 K for powder samples, 9 K for sample S1, and it is not observed for sample S2. The observation of the low temperature peaks to the SP and S1 samples, their shift into lower temperature region and the continuous increase in \(M_{\text{ZFC}}\) around 2 K to S2 sample allow us to conclude that the dipolar interaction take an important role in determining the surface effects in the low temperature region. Winkler et al.\(^\text{30}\) (2005) have observed similar effects to NiO noninteracting NPs. Their results indicate that the magnetic behavior dominated by an uncompensated AFM particle core moment contribution that thermally fluctuates at high temperature and a low temperature behavior determined by surface cluster spins whose thermal fluctuations freeze in a cluster-glass-like state. Here, we have observed that the surface effects become more and more pronounced as function of dilution, that is, when the particles are continuously diluted in the matrix, the surface effects become stronger and the low temperature maximum is decreased.

Figure 4 shows the temperature dependence of the real \(\chi'(T)\) and imaginary \(\chi''(T)\) parts of the ac susceptibility, measured to SP sample at different frequencies in the range from \(10^2\) to \(10^4\) Hz using the same conditions of the ZFC magnetization curves measurements. It is clearly seen that \(\chi'\) increases as the temperature increases up to the proximity of \(T_B\) (\(\sim 75\) K) and shows a frequency-dependent variation but decreases rapidly below 50 K and finally becomes frequency independent below 40 K. This suggests that the sample exhibits a blocking phenomenon at region high temperature. The weak dependence of the frequency at low temperatures (around 11 K) is a typical behavior of strong surface effects.

The relaxation time calculated to both high and low temperature peak (see insets of Fig. 4) is characteristic of a blocking phenomena and spin-or-cluster-glass-like state, respectively. It can be assumed that the reversal of the particles is due to thermal activation effects over a distribution of energy barriers (\(\Delta E\)). The relaxation over a single barrier for noninteracting particles with uniaxial anisotropy is described by the Néel–Arrhenius law given by \(\tau = 1/f_0 \exp[-\Delta E/k_BT]\), where \(\tau\) is the measurement time, \(f_0\) is the attempt frequency to reversal, normally taken to be \(10^9\) s\(^{-1}\), \(k_B\) is the Boltzmann constant, and \(T\) is the measurement temperature. Assuming a grain volume dependence of the energy barriers to reversal of the form \(\Delta E = K_A V\), where \(K_A\) is the magnetocrystalline anisotropy of the NiO particles and \(V\) is the median of the particles volume distribution, and a typical measurement time of 100 s, we obtain an expression of the form, \(K_A V = 25k_BT_B\), where \(T_B\) is the median blocking temperature. We can estimate the value of \(K_A(T_B)\) using the approximation that the AF moment \(m_{AF} = (T_N - T)^{\frac{1}{3}}\) and \(K_A = m_{AF}^3\) for uniaxial anisotropy, i.e., \(K_A(T_B) = K_A(0)(T_N - T_B/T_N)\), with \(K_A(0)\) the bulk NiO value (4.96 \times 10^6\) erg/cm\(^3\)) (Ref. 30).

![FIG. 3. (Color online) ZFC-FC magnetization curves to applied field (100 Oe) for samples (a) as prepared, (b) S1 sample, and (c) S2 sample.](image)

![FIG. 4. (Color online) Imaginary components of the ac susceptibility as functions of temperature for samples (a) as prepared and (b) S2 sample. The inset is a close up to the behavior near maximum (40 K).](image)
and \( T_N \sim 520 \) K,\(^{31}\) hence \( K_{Ap}(T_B) \) is \( 4.2 \times 10^6 \) erg/cm\(^3\). Therefore, the value of \( V \) obtained from this framework is 4.9 nm that is rather lower than the value obtained by x-ray and TEM analysis (5.8 nm). This find should be associated to the disordered structure in the surface of the NPs.

Figure 5 shows the \( M-H \) hysteresis curves taken at temperatures nearly above the irreversibility temperature for the as-prepared as well as for the dispersed NPs samples. One can clearly observe a linear dependence of magnetization even at high fields, whose slope increases with the decrease in strength of interactions. Interestingly, the curves for the as-prepared (SP) and S1 samples display following two different regimes: (a) one linear region, dependent on \( \chi(T,H) \) that can be attributed to the partially oxidized surface and gives rise to a nonsaturating component of the magnetization\(^{9,32}\) and (b) one second component that shows a typical SPM trend, following a Langevin-like function, reaching a saturation. On the other hand, sample S2 exhibits only a linear region throughout. This fact reflects a characteristic behavior of strongly frustrated systems in which there is a large number of uncompensated spins on the surface of the particles.

In order to get further insight into the nature of this anomalous behavior, hysteresis loops were measured in the ZFC condition at different temperatures around the low temperature peaks. Figure 6 shows the \( M-H \) curves recorded at temperatures 2, 11, and 25 K to as-prepared, S1, and S2 samples after subtracting the diamagnetic contribution from the PVP. It can be clearly seen that a large magnetic moment and coercivity are observed in the case of as-prepared sample [see Fig. 6(a)]. These results confirm that these particles display a weak-FM-like\(^{33}\) behavior, which is reduced after the dispersion. It is also evident that, to as-prepared sample, the hysteresis curves measured close to low temperature maxima, the coercive field \( H_C \) and remanent magnetization \( M_R \) are strongly narrowed. In fact, these results are well established and corroborated to the uncompensated spins systems either on the surface or in the core of the NiO NPs.\(^{2,9,13,14}\) However, due the decrease in the contribution from dipolar interactions, the surface effects turn out to become dominant when the particles are more disperse. In this scenario, the freezing of such uncompensated spins at the shell is more difficult, consequently it is necessary to de-
increase the temperature enough to envisage better the surface, as observed in the ZFC-FC magnetizations and ac susceptibility measurements.

These anomalies are further confirmed from the dependence of coercive field \( (H_C) \) and remanent magnetization \( (M_R) \) as functions of temperature [Figs. 7(a) and 7(b), respectively]. As the demagnetizing and remagnetizing curves (see Fig. 6) change rapidly in low fields, both coercive field \( H_C \) and remanent magnetization \( M_R \) in as-prepared sample (SP) decrease with increasing temperature. Therefore, if one reduces the strength of dipolar interactions among the particles a maximum is observed at around 20 K for the \( H_C (T) \). This trend has already been reported for the NiO NPs of an average particle size 3 nm (Ref. 9) and single-domain particle systems.\(^5\) Also, another interesting behavior has been found in case of more diluted sample (S2). It is clear from Fig. 7 that the change in both \( H_C \) and \( M_R \) are more pronounced in the case of the more diluted sample S2. One can infer that the surface effects become dominating over the particle core and it is more difficult to align the uncompensated spins in the particle shell. Therefore, for decreasing the temperature, a strong contribution of the blocked particles increases the \( H_C \) values and consequently the \( M_R.\)\(^5\) Besides, it is not unreasonable to state that this increase the total magnetization can be related with the formation of the FM clusters of short-range.\(^32\)

In order to further understand and visualize the effect of anisotropy, we have also performed FMR spectra for the as-prepared and S2 samples in the temperature range 4.2–300 K at a frequency of 9.45 GHz (X-band). To measure the X-band spectra, the magnetic field was applied both parallel and perpendicular to the plane of the PVP matrix. However, no angular dependence was observed, suggesting that the samples are magnetically isotropic. Figure 8 shows the spectra derivative of the resonant absorption signal as functions of applied magnetic field for the as-prepared sample at different measuring temperatures. It can be clearly seen that the high temperature spectra exhibit a symmetric shape which gradually decreases with the reduction of sample temperature. Also, the line widths \( (\Delta H_{PP}) \) become broader with the decrease in the sample temperature \( (T<140 \text{ K}) \), as shown by the thermal dependence of \( \Delta H_{PP} \) and \( H_R \) (see Fig. 9). This \( T \)-dependence can be attributed to the thermal fluctuations of the magnetic moment with respect to the magnetic anisotropy axes and has been also reported in other NP systems.\(^3\)\(^9\)\(^,\)\(^11\)\(^,\)\(^34\) The shift in \( H_R \) (with respect to \( g=2.0023 \)) as well as the increase in \( \Delta H_{PP} \) with the decrease in temperature are clear signatures of the FM character of the signal. For decreasing the temperature, the magnetic moment of the particle experience with more intensity the effect of anisotropy. In fact, the presence of the large size distribution (as observed in the ZFC curves) as well as the random orientation of the easy axes is responsible for the increase in \( \Delta H_{PP} \). Indeed, this is behavior expected to a strongly interacting system (powder sample), that is, the dipolar and exchange interactions generate an effective local field over each resonance center that helps it to reach the resonance condition. Finally, within the accuracy of our experimental set-up, we can state that in the high temperature regime, we observe the FMR of the magnetic moment of the core, e.g., \( \Delta H_{PP} \) increases once the surface spins are in a paramagnetic state. Also, the formation of surface spin clusters creates an additional effective field on the core leading to both the shift in the resonant field and the broadening of the FMR linewidth.

IV. CONCLUSIONS

We have studied the magnetic properties of coprecipitated NiO NPs with different strength of interparticle interactions. X-ray and electronic microscopy probes confirm the
presence of single crystalline phase and a strain of 0.5% obtained through Williamson–Hall plotting, which can strongly influence the local magnetic ordering of these materials. Magnetization as a function of the temperature, magnetic field and time and FMR measurements show that for decreasing the temperature one can see first a progressive blocking process of the core particle moments and then, a strong surface effects (likely relate with formation of spin clusters at the particle surface) which is sensitive to the distance among particles. We argue that this fact is sufficient to explain the anomalies in the hysteresis loop shape and the behavior observed to $M_s$ and $H_C$ at low temperature. Our results also allow us to conclude that the NPs possess a high degree of spin surface disorder even with the decrease in the strength of interparticle interactions once we have observed that our systems turned out to be highly frustrated ones, displaying a spin-glass disorder to temperatures below 2 K for the sample with almost negligible interactions.

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