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Relaxation and interaction effects on transverse susceptibility measurements of nanoparticle systems

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Abstract

Dynamic properties of Co nanoparticle systems were investigated by means of RF transverse susceptibility. To study the effect of interaction between particles, samples of Co nanoparticles dispersed in a wax matrix in different volume fractions were studied. The evolution of interaction intensity in the Co nanoparticle systems as a function of temperature was determined by measuring the Integral Generalized DeltaM curves.

Keywords: Nanoparticles; Transverse susceptibility; Interaction effects; Relaxation effect

The dynamics of magnetic nanoparticle systems is a subject of considerable interest [1] due to their fundamental and technological interest. The properties of such systems are strongly modified compared to the bulk, due to granular texture and the small size of the grains. On one hand, thermal relaxation of the magnetic moment of the particles, i.e. superparamagnetic relaxation, can occur. Namely, due to thermal fluctuations the magnetic moment of particles can overcome the energy barrier even in the absence of an applied field, and as consequence above a certain temperature, T_B, the ensemble of single-domain particles behaves as a collection of independent super-spins. On the other hand, magnetic inter-particle interactions always exist in fine particle systems, and they can be best probed in particles dispersed in a matrix where the volume concentration can be systematically varied. The demand for high-density recording media requires high packing densities that make the role of inter-particle interactions very important. Consequently, many theoretical and experimental works were devoted to understanding the role of interactions on the magnetic properties of fine particle systems. Various time and temperature dependent experimental techniques have been used in order to study the magnetic properties of nanoscale systems [1]. Among them, the techniques involving small AC magnetic field excitations are very useful. A unique way to investigate the response of a magnetic system for an alternating field excitation is the method of transverse susceptibility [2]. The transverse susceptibility is defined as the variation of the magnetization due to a small magnetic field h_{AC} applied perpendicular to the main DC field, H, and measured along the h_{AC} direction. A very important advantage of transverse susceptibility is its capability of revealing the singularities in the field dependent magnetization curves at the anisotropy and switching fields in magnetic fine particle systems, which makes this technique very attractive. In previous treatments of the transverse susceptibility in particulate magnetic systems, relaxation phenomena arising from temperature dependence of χ_T were not considered, and only recently we have pointed out the importance of magnetic relaxation in transverse susceptibility experiments on nanoparticle systems [2]. Moreover, the combined effect of interactions and magnetic relaxation in the case of nanoparticle systems was not considered in

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χ_T experiments. In this paper we studied the effect of both, relaxation and interaction effects on transverse susceptibility experiments. In order to investigate the role of the interactions, we performed χ_T experiments at various temperatures on samples of Co nanoparticles, dispersed in different concentrations in a wax matrix. The degree of dilution in the wax controls the average particle distance and therefore the strength of interactions.

The synthesis of cobalt nanoparticles was carried out using standard organometallic reaction procedures with airless/moisture-less devices and commercially available reagents. The common approach for the synthesis of cobalt nanocrystallites is to reduce organo-cobalt salt in a non-polar solvent at relatively high temperature, capped/stabilized by some organic compounds. The experimental procedure is similar to that reported by Sun et al. [3]. The dispersion of Co nanoparticles in the wax matrix was carried out by ultrasonically mixing the concentrated cobalt nanocrystallites in hexane with wax-hexane solution, followed by increasing temperature of the system to remove the solvent. The ratio of cobalt was determined based on the real amount of cobalt used and amount of wax. The size and size distribution of each filtrated sample in as-prepared cobalt colloidal solution was monitored using light scattering technique (Dyna-Pro 99 Molecular Sizing Instrument). The obtained Co nanoparticles are spheroidal with an average diameter of 6 nm as determined by transmission electron microscopy. In order to study the effect of interparticle interactions two samples were considered for this study: a sample of $C_V = 0.011$ volume fraction of Co nanoparticles dispersed in wax (Co10) and a sample containing only Co nanoparticles (Co100). The nanoparticles in both samples were from the same batch of Co nanoparticles, to make sure the same size distribution in both samples.

To probe the dynamic transverse susceptibility in the radio frequency range we employed a very sensitive method based on a tunnel-diode oscillator (TDO) technique. A LC tank resonator is driven by a tunnel diode forward biased in its negative resistance region. This idea is the basis of the TDO measurement system whose circuit design and operation have been described elsewhere in detail [4]. The circuit is self-resonant with a typical resonance frequency of around 5 MHz. In the experiment, the measured quantity is the shift in resonant frequency as the static field is varied and this is proportional to the relative variation of transverse susceptibility, $\chi_T \equiv \Delta\chi_T/\chi_T(\%)$ [2]. The field-dependence of transverse susceptibility data at different temperatures for both samples, Co10 and Co100 are shown in Fig. 1. The left insets are the zero-field cooled (ZFC) and field-cooled (FC) magnetization curves for both Co nanoparticle systems measured using a commercial MPMS5 Quantum Design SQUID magnetometer. The

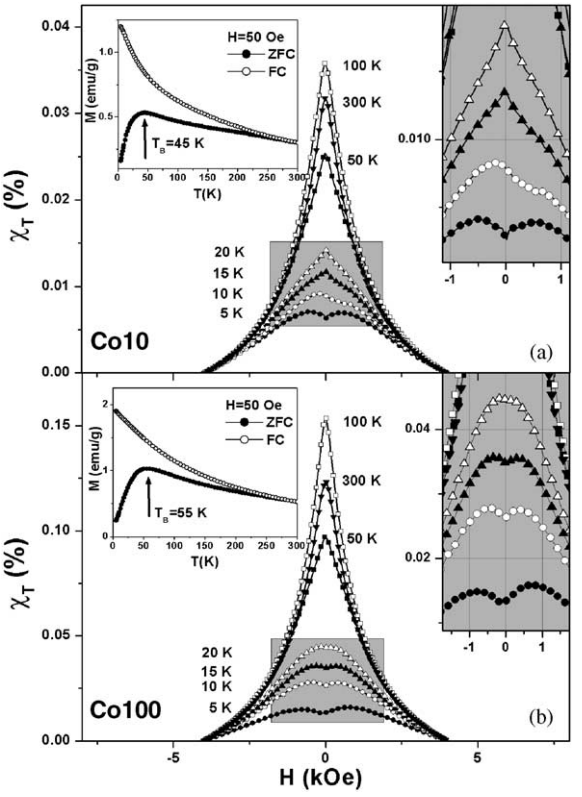

Fig. 1. Field-dependent RF transverse susceptibility of Co10 (a) and Co100 (b) samples at various temperatures (main panels); zero-field cooled (ZFC) and field cooled (FC) magnetization (left panels); zoom view of (χ_T,H) data marked by the shaded region (right panels).

ZFC and FC curves display the classic behavior due to relaxation effects, with the particles exhibiting superparamagnetic behavior for temperature above $\sim$45 and 55 K for Co10 and Co100 samples, respectively. The greater value in the blocking temperature, T_B, for the Co100 sample is consistent with stronger interactions in this sample comparing with Co10 [1]. One notices that the FC curves, for both samples are merging with the corresponding ZFC curves at higher temperatures than T_B. This is a reflection of the presence in both systems of a small fraction of particles with larger sizes, as indicated by light scattering experiments. For these particles the thermal equilibrium is achieved at a higher temperature than the average blocking temperature, T_B, of the system. The main panels of Fig. 1(a) and (b) show the χ_T data, as the field is swept from positive saturation to negative one, at seven different temperatures covering the region from 5 to 300 K. The shaded regions around zero field are blown up in the right panels to clearly depict the peak structure exhibited by the transverse susceptibility. A prominent feature that can be distinguished clearly (as seen in the right insets of Fig. 1), is

that for low temperatures, for both samples, Co10 and Co100, the χ_T curves show two peaks having different heights but located symmetrically about the origin of the field axis. As the temperature is increased, the peak heights become equal and eventually the double-peak structure becomes less pronounced and merges into a single central peak. This trend is observed for both samples Co10 and Co100, and is consistent with a gradual transition from a blocked state towards a superparamagnetic one in both samples. The difference is that for Co10 sample as the temperature increases, the double peak structure is replaced by the sharp central peak at a lower temperature than in the case of Co100 sample. This is a clear evidence for a faster magnetic relaxation occurring in the case of non-interacting or weak interacting magnetic nanoparticle systems (Co10) than in strong interacting ones (Co100). For both samples, one notices also an increase of the initial transverse susceptibility, $\chi_T(H\to 0)$, as the temperature is increased, followed by a decrease. This implies that the temperature variation of the initial transverse susceptibility $\chi_T(H\to 0)$, for this experimental time, $\tau_m = 1/f = 2\times 10^{-5}$ s, has a maximum between 100 and 300 K. As mentioned before, for DC magnetic measurements (ZFC/FC), where the experimental time is usually around $\tau_m = 10^2$ s, the blocking temperature is around $T_B = 45$ K for Co10 and $T_B = 55$ K for Co100. This is consistent with an increase in the blocking temperature, T_B, as the experimental time decreases, as it is typically observed experimentally in magnetic nanoparticle systems [1]. A precise value of the blocking temperature in the case of transverse susceptibility experiments can be obtained by a 3D mapping of χ_T in the (H,T) plane [2]. For Co10 the determined blocking temperature from χ_T experiments is ~ 130 K. This value is in very good agreement with the values determined from classical AC susceptibility experiments carried out in the frequency range (10 and 10^4 Hz) on the same sample [5]. A last analysis of the χ_T results for the two samples concerns the relative height of the peaks at low temperature. For Co10 sample one observes that as the applied magnetic field is decreasing, first a small peak appears around 700 Oe followed by a higher amplitude peak around -200 Oe. This is consistent with the results predicted by the classical model of χ_T for a random non-interacting uniaxial monodomain particles [6], where an anisotropy field distribution is present [7]. In the case of Co100 one notices that for the same positive to negative field sweep, first a higher amplitude peak appears followed by a lower amplitude one. This must be the consequence of the stronger interactions in Co100 sample, since only the volume fractions changed in the two cases.

An analysis of the inter-particle interactions in the two samples was done by measuring the remanent curves, DC demagnetization (DCD) and forward isothermal remanent magnetization curves (IRM). First of all in order to evaluate the evolution of interaction intensity in the systems as a function of temperature, we have measured the Integral Generalized DeltaM (IGDM) at 5, 10, 15, 20, 25 and 30 K [8]. We used this methodology to avoid the necessity to produce experimentally an accurate AC demagnetized state. The DCD and the forward IRM curves were measured for seven initial remanent states. The data for C100 at 5 K are presented in Fig. 2. For each forward curve the IGDM is calculated. In order to compare the IGDMs at different temperatures they were translated and normalized on the abscissa at the saturation remanent moment for each temperature. The translated IGDM curve was given by the formula:

$$m_{IGDM} = \int_0^{H_m} [m_{DCD^*}(H) - m_{DCD}(H)]\,dH, \qquad (1)$$

where H_m is the maximum field applied to the sample in the experiments, m_{DCD} is the magnetic moment in the well known DCD process and the m_{DCD^*} is the DCD-like curve calculated using the forward IRM curve, as described in detail in Ref. [8]. The moment m_{IGDM} is represented as a function of the initial remanent state used in the IRM forward curve. In Fig. 3 one presents the IGDM curves for the Co100 and Co10 samples as a function of temperature. The Co100 sample IGDMs have a clear central maximum which is characteristic to a system with important static statistic interactions [9]. The static statistic interaction intensity is decreasing with the increase of temperature, as expected. The asymmetry of the IGDM curve could be explained by the asymmetric coercive field distribution. The Switching Field Distributions (SFD), calculated as derivatives of the DCD curves, for different temperatures, confirm this asymmetry (see inset Fig. 2). The Co10 sample IGDMs are significantly different of the Co100 sample.

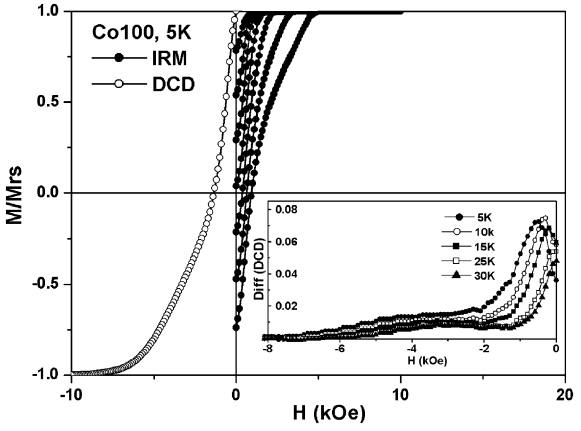

Fig. 2. The forward IRM and the DCD curve for the Co100 sample at $T = 5$ K. The inset shows the Switching Field Distribution for the same sample at various temperatures.

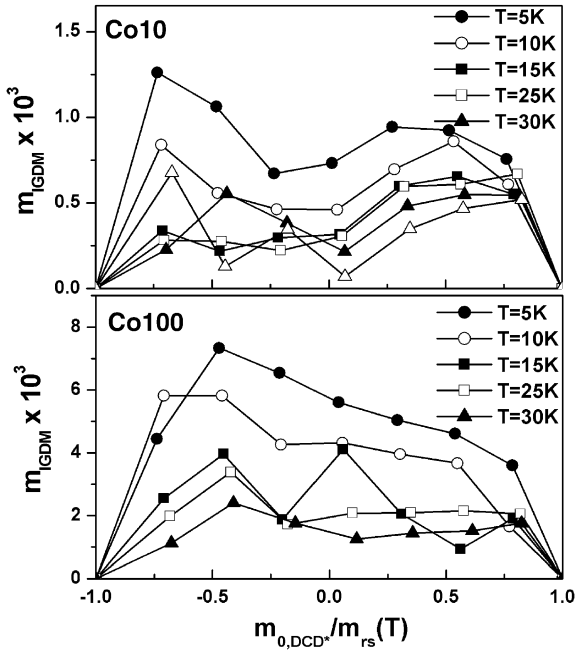

Fig. 3. The IGDM's for the Co100 (a) and Co10 (b) samples at various temperatures.

They show a central minimum that separates two maxima. This is characteristic for systems in which the mean field or exchange interactions are more important than the static statistic interactions. It is easy to understand that the statistic interaction intensity in the Co10 sample is less important than in the Co100 sample. The presence of exchange-type interactions in this sample is probably linked with the presence of clusters in the system. As in the other case, the static interaction intensity, measured by the IGDM, is decreasing with the temperature increase.

In conclusion, by RF transverse susceptibility experiments it was explored, the influence of interactions on dynamic properties of Co nanoparticle samples with different volume fractions. Also, using the Integral Generalized DeltaM plot method, it was possible to investigate the character of interactions, at different temperatures in the nanoparticle systems.

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