RF Dynamics in Nanoparticle Systems With Tuned Strength of Interactions

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***Abstract*—The dynamic response in a large experimental time window (10^{-6}–10^{2} s) of Co and CoPt nanoparticle systems is reported. In order to reveal the dynamics effects, along with classic experiments as a.c. susceptibility and static magnetic measurements, a rf temperature dependent transverse susceptibility experiment is used. To study the effect of interaction between particles, samples of Co and CoPt nanoparticles dispersed in an insulated matrix in different volume fractions were investigated.**

***Index Terms*—Dynamic properties, interparticle interactions, magnetic nanoparticles, transverse susceptibility.**

I. INTRODUCTION

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], [3]. The transverse susceptibility (TS) 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 [3]. In previous treatments of the transverse susceptibility in particulate magnetic systems, relaxation phenomena arising from temperature dependence of TS were not considered, and only recently we have pointed out the importance of magnetic relaxation in transverse susceptibility experiments on nanoparticle systems [2]. Two different magnetic systems were considered in our study: CoPt and Co nanoparticle systems. In order to investigate the role of the dipolar interactions, we performed TS experiments at various temperatures on the nanoparticle samples dispersed in different concentrations in an insulated matrix. The degree of dilution in the matrix controls the average particle distance and therefore the strength of dipolar interactions.

II. EXPERIMENTAL

Cobalt–platinum alloy nanoparticles were obtained [4] by reduction of $CoCl_2$ and $PtCl_2$ with sodium naphthalide in N–methylpyrrolidone solution in presence of dioctylamine. The room-temperature reaction was followed by heating the solutions at 180 °C. Solid products were isolated from colloidal solutions by adding hydrocarbon nonsolvent. The transmission electron microscopy (TEM) experiments indicated the nanoparticles of 5 nm average diameter with low crystallinity; EDAX analysis confirmed the atomic ratio $\mathrm{Co:Pt} = 2:1$. The synthesis of cobalt nanoparticles was carried out reducing organo–cobalt salt in a nonpolar solvent at relatively high temperature, capped/stabilized by some organic compounds [5]. The obtained Co nanoparticles are spheroidal with an average diameter of 6 nm as determined by TEM. In order to study the effect of interactions, samples of nanoparticles dispersed in an insulated matrix were prepared. Due to different solubility properties of the two considered magnetic systems, two different matrix were used. The diluted CoPt samples were prepared by dissolving the nanoparticles powders in molten myristic acid, that ensured a homogenous dispersion of CoPt nanoparticles without aggregates. The dispersion of Co nanoparticles was carried out in a wax matrix 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 magnetic component was determined based on the real amount of Co or CoPt used and amount of myristic acid or wax. The nanoparticles in

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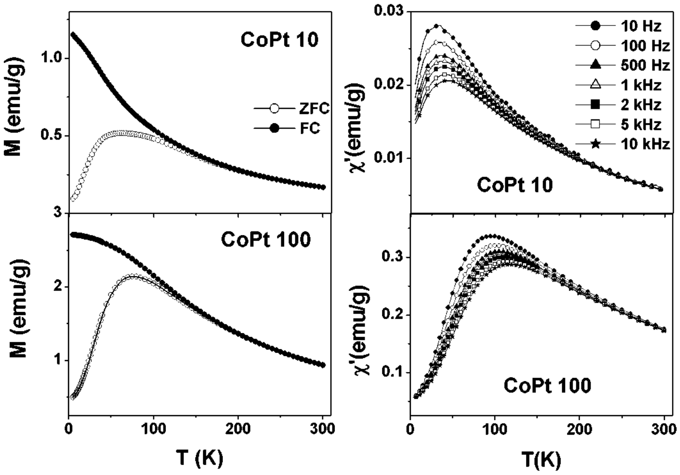

Fig. 1. Thermal variation of magnetization ZFC and FC, and a.c. susceptibility at different frequencies for CoPt100 and CoPt10 samples.

diluted samples, for both Co and CoPt samples, were from the same batch of pure Co and CoPt nanoparticles, to make sure that we preserve the same size distribution ($\sigma < 10\%$ std. dev.) in concentrated samples and diluted ones. The volume fraction in both diluted samples, Co and CoPt was about the same, $C_V = 0.01$.

The d.c. susceptibility, in zero-field-cooled (ZFC) and field-cooled (FC), of all samples was measured with a SQUID magnetometer, for temperatures between 5 K and 300 K. The a.c. susceptibility data were measured using the ac/dc magnetometer option of a Physical Property Measurement System from Quantum Design. The real and imaginary components were measured between 10 Hz and 10 kHz, for temperatures ranging from 5 to 300 K.

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. The circuit is self-resonant with a typical resonance frequency 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].

III. RESULTS AND DISCUSSION

The experimental determined a.c. and d.c susceptibilities for CoPt samples are displayed in Fig. 1. The ZFC and FC curves display the classic behavior due to relaxation effects, with the particles exhibiting superparamagnetic behavior for temperatures above ~60 K nd ~75 K for CoPt10 (diluted) and CoPt100 (concentrated) samples, respectively. The greater value in the blocking temperature, T_B, for the CoPt100 sample and the shape of FC curve is consistent with stronger interactions in this sample comparing with CoPt10 [1]. The a.c. susceptibility results at different frequencies display the same overall increasing of blocking temperature for CoPt100 sample compared to CoPt10. Also, the frequency (f) dependence of blocking temperature, as a consequence of different measuring times ($\tau_m = 1/f$) involved in a.c. experiments, is very well displayed in the right side panel of Fig. 1.

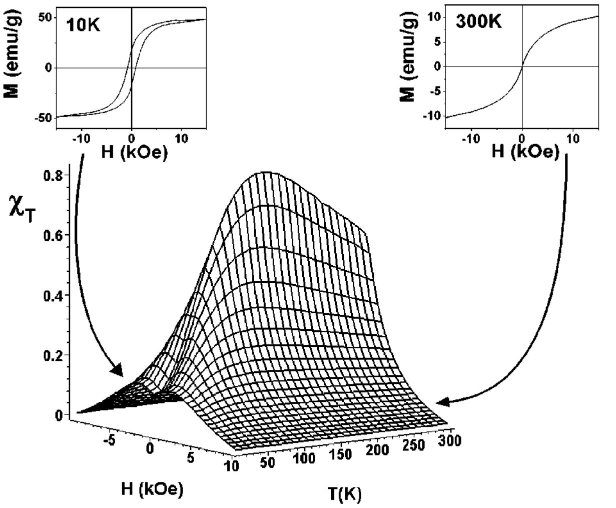

Fig. 2. The experimental determined transverse susceptibility for CoPt100 sample, represented as a landscape plot in the (H, T) plane. The insets are the hysteresis loops in the superparamagnetic state ($T = 300$ K) and blocked state ($T = 10$ K) of CoPt nanoparticles.

In order to extend our investigation of dynamic properties of magnetic nanoparticles in a larger time window we used systematic temperature dependent TS experiments. Fig. 2 shows a three dimensional landscape plot of TS data for CoPt100 sample with temperature as one of the axes. In the (χ_T, H) plane, one observes the field dependence of TS at different temperatures whereas in the (χ_T, T) plane one observes the temperature dependence of TS at different fields. A prominent feature that can be distinguished clearly is that for low temperatures, the TS 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 consistent with a gradual transition from a blocked state toward a superparamagnetic one. One notices also an increase of the initial transverse susceptibility, $\chi_T(H \rightarrow 0)$, as the temperature is increased, followed by a decrease. This implies that the temperature variation of the initial transverse susceptibility $\chi_T(H \rightarrow 0)$, for this experimental time, $\tau_m = 1/f = 2 \cdot 10^{-5}$ s (where $f = 5 \times 10^6$ Hz is the resonance frequency), has a maximum around 155 K, as can be easily observed in the (χ_T, T) plane. This temperature is exactly the blocking temperature corresponding to this measuring time. The variation of the blocking temperature as function of the experimental time can be represented in the classical plot $\log_{10}(\tau_m)$ versus $1/T_B$. Fig. 3 displays this plot for CoPt100 sample, including both, a.c. and TS data. One observes a fairly good agreement with the expected increase of blocking temperature as the measuring time is decreasing. Therefore systematic temperature dependent TS experiments, performed at RF frequencies provide an useful extension of the time window investigation of dynamic properties of magnetic nanoparticles systems.

The field-dependence of transverse susceptibility data at different temperatures for both samples, Co10 and Co100 are

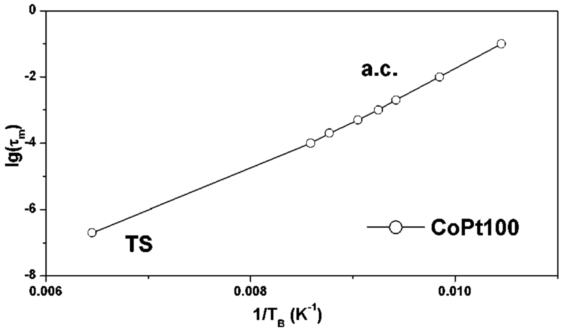

Fig. 3. Thermal variation of relaxation time for CoPt100 sample, including a.c. and transverse susceptibility data.

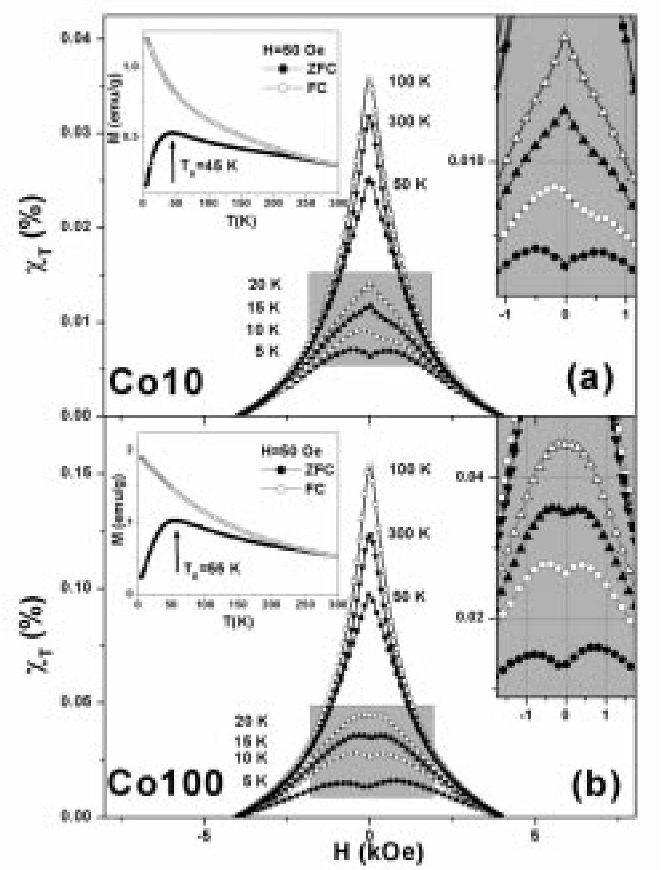

Fig. 4. Field-dependent RF transverse susceptibility of (a) Co10 and (b) Co100 samples at various temperatures (main panels); zero-field cooled (ZFC) and field cooled (FC) magnetization (left panels); zoom view of (χ_T, H) data marked by the shaded region (right panels).

shown in Fig. 4. The left insets are the ZFC and FC magnetization curves for both Co nanoparticle systems. The main panels of Fig. 4(a) and (b) show the TS data, as the field is swept from positive saturation to negative one, at seven different temperatures covering the region from 5 K 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. As in the case of CoPt samples, for Co samples one notices the same temperature dependence of anisotropy peaks. This trend is observed for both samples Co10 and Co100, and is consistent with a gradual transition from a blocked state toward 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 noninteracting or weak interacting magnetic nanoparticle systems (Co10) than in strong interacting ones (Co100). A last analysis of the χ_T results for the two Co 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 noninteracting uniaxial monodomain particles [3], [6] where an anisotropy field distribution is present [2]. 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.

IV. CONCLUSION

Various experimental techniques were used in order to reveal the dynamic properties of magnetic nanoparticles systems. The strength of interactions between particles was varied by dispersing the nanoparticles in different volume fractions in insulated matrix. RF transverse susceptibility experiments at different temperatures, provide not only an extension of the time window dynamics investigation in magnetic nanoparticle systems but also complementary information, such as the temperature variation of the anisotropy and switching fields.

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