Investigation of magnetic anisotropy in Co nanoparticles using ferromagnetic resonance technique

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Using ferromagnetic resonance (FMR) technique, we have investigated the temperature dependence and angular dependence of line width and resonance magnetic field of Co nanoparticles capped with novel alkane carboxylic acids of varying chain lengths. The magnetic properties such as blocking temperature and anisotropy sensitively depend on the chain length as evidenced by the temperature dependence of line width. These results indicate that the magnetic properties of these samples are critically governed by the interparticle interactions which are decided by the chain length. The presence of anisotropy even up to very high temperature above the blocking temperature observed in these studies confirms the presence of inter-particle magnetic interactions as well as intra-particle exchange interaction between the core and shell regions as evidenced by our earlier ac susceptibility and transverse susceptibility measurements on similar system.

Introduction

Magnetic nanoparticles have gained a lot of interest in recent years both due to their technological applications in nanoscale devices and also for fundamental research [1]. For nanomaterials the surface to volume ratio is sizeable and the surface effects play an important role in deciding the different physical properties. Co nanoparticles have attracted significant interest due to their technological significance and fundamental physics and have been investigated by a number of groups. We have reported a large magneto caloric effect associated with surface spin disorder in these nanoparticles [2]. Recently we investigated the static and dynamic magnetic properties including magnetic relaxation and memory effect of Co nanoparticles through a variety of experimental techniques such as bulk magnetization, ac susceptibility and transverse susceptibility [3]. Magnetic anisotropy which is crucial for various applications depends sensitively on the shape, size and interface of magnetic nanoparticles.

Ferromagnetic resonance (FMR) is a local probe that enables us to determine the saturation magnetization, linewidth and effective anisotropy [4]. In the literature there are reports on FMR studies on Co nanoparticles coated with polymer shell to study the influence of polymer shell on the magnetic properties. Room temperature FMR studies were reported on Co and Ni nanoparticles with the core shell structures and the line width was found to depend on the material chosen for shell formation [5]. Many of these investigations reveal the presence of interparticle interactions in these superparamagnetic nanoparticles. However, there are no investigations reported on the interaction between these superparamagnetic particles as a function of interparticle distance. The unavailability of stabilizing ligands that can be used to systematically vary distance between the particles could be one reason for the lack of such studies. To this effect we have recently embarked on the synthesis of new ligands with a suitable design element that can act as good capping agents and allows us to systematically vary the interparticle distance as described above. The ligands designed and synthesized are R-O-CH$_2$-COOH with R$_{12}$ = C$_{12}$H$_{25}$ and R$_{18}$ = C$_{18}$H$_{37}$. The –O-CH$_2$-COOH group here act as the capping agent and R$_{12}$=C$_{12}$H$_{25}$ and R$_{18}$=C$_{18}$H$_{37}$ provide the variation of alkyl chain length. In the case of these synthesized acids, the –O-CH$_2$-COOH group binds to the nanoparticle surface exposing the
long chain to the exterior. Thus the particle separation can be systematically varied if the different chain length acids are used. In this paper we report the temperature dependence of FMR line width and the resonance field on the nanoparticles capped by these ligands. For the sake of clarity the particles capped by C_{12}H_{25}-O-CH_2-COOH are abbreviated as R_{12}Co and those capped with C_{18}H_{37}-O-CH_2-COOH are termed as R_{18}Co.

**Synthesis and characterization of Co nanoparticles**

Cobalt nanoparticles of various interparticle distances are synthesized by soft chemical route by reducing an appropriate cobalt precursor (CoCl_2 for eg.) with NaBH_4 in the presence of any of the ligands mentioned above. Structural and transmission electron microscopy (TEM) images of as-synthesized Co-nanoparticles are presented in Figure 1. TEM analysis reveal that the bulk of the particles have mean size of ~25 nm. The image also shows that the particles are well separated from each other presumably due to the surfactant coating. Both the synthesized particles are characterized structurally using XRD that reveal the formation of ε-phase Co particles [6] with some contribution of CoO (probably on the surface of the particles).

![Figure 1](image1.png)

**Figure 1** A) and C) structures of the R-O-CH_2-COOH carboxylic acids used in this study. B) TEM image of Co nanoparticles synthesized with (A) as capping agent and D) Co nanoparticles synthesized with (C) as capping agent.

**Ferromagnetic Resonance (FMR) study**

Ferromagnetic resonance will occur when the energy of microwave power is equal to the Zeeman energy due to dc magnetic field. At resonance, the system absorbs the maximum microwave power till population equilibrium is reached. We used JEOL X band spectrometer with 9.2 GHz and recorded the derivative of power absorption (dP/dH) vs. applied dc magnetic field in the temperature range of 120 K to 320K. To investigate the effect of interparticle distance on the magnetic properties we have chosen two samples of Cobalt nanoparticles namely R_{12}Co and R_{18}Co. These samples were sandwiched in a groove between a quartz rod and half cut piece of the same material to arrest the physical moment of the sample during the sweeping of the magnetic field. FMR measurements were carried out not only on the 100% concentrated nanoparticles samples but also on different concentration of composite samples prepared by mixing with paraffin wax in the concentration range of 1% to 75%.
Figure 3: Temperature dependence FMR of $R_{12}$Co

Figure 4: Temperature dependence FMR of $R_{18}$Co

Figure 5: Line width vs. T (K) of $R_{12}$Co (50,100)

Figure 6: Line width vs. T (K) of $R_{18}$Co (5, 75,100)

Figure 7: Resonance field vs. T (K) of $R_{12}$Co (50, 100)

Figure 8: Resonance field vs. T (K) of $R_{18}$Co (5, 75,100)
All the samples show very broad and asymmetric resonance arising due to the Co nanoparticles. Figures 3, 4 shows the temperature dependence FMR spectrum of R12Co (100\%) and R18Co (100\%). In R18Co (100\%) the line width becomes larger and broadens compared to R12Co (100\%). It indicates that more the interparticle separation more will be the spin disorder. The temperature dependence of line width and the resonance field of these samples are shown in Figures 5-8.

RESULTS AND DISCUSSION

The temperature (T) dependences of the line width $\Delta H_{pp}$ (T) and the resonance field $H_{res}$ (T) is calculated for all the samples. The experimentally observed resonance field for the ensemble of particles is a resultant of average resonance field due to i) the random orientation of easy axis of different particles and ii) the distribution in size of the particles [7]. So the observed resonance for these particles is quite broad in comparison to that of a single particle or thin film.

The linewidth of R12Co sample at RT is 695 Oe, with decrease in temperature the linewidth increases and at 131 K linewidth is 1224 Oe. The linewidth of R18Co sample also follows similar trend. The value of linewidth at RT for this sample is 858 Oe and increases to 1460 Oe at 118 K. The resonance field ($H_{res}$) of R12Co sample at RT is 3250 Oe and there is a very weak temperature dependence (goes through a maxima) (Figure 7). Figure 8 shows the temperature variation of $H_{res}$ for the R18Co sample. It can be seen from the figure that the resonance field of R18Co, $H_{res}$ is 3080 G at room temperature (RT) and continues to decrease monotonically with decrease in temperature in the whole measured temperature range. $H_{res}$ and linewidth does not vary much with concentration for both R12Co and R18Co samples.

These results indicate that the magnetic properties of these samples depend very sensitively with the interparticle interactions which are decided by the chain length. The presence of anisotropy even up to very high temperature above the blocking temperature observed in these studies confirms the presence of inter-particle magnetic interactions as well as intra-particle exchange interaction between the core and shell regions as evidenced by our earlier ac susceptibility and Transverse susceptibility measurements on similar system. Due to the asymmetric nature of the FMR line shape we are not able to do the complete line shape analysis on these samples.

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