# Comparative Study of Magnetic Property of Nanoparticles of $Fe_{2.9}Zn_{0.1}O_4$ and $Fe_{2.2}Co_{0.8}O_4$

**Dr. Subhash Chander**

Associate professor
Department of Physics
S S Jain Subodh PG College
Jaipur -302004 (India).

***Abstract*- Comparative magnetic studies of Zn-substituted spinel ferrite $Fe_{2.9}Zn_{0.1}O_4$ (Zn50) and $Fe_{2.2}Co_{0.8}O_4$ (Co50) of average size of ~5 nm are performed. The Zn50 sample shows the linear variation of the blocking temperature of 80K and M-H curve of Zn50 at 21 K suggests that there is a small but non-zero coercivity of 35 Oe. The 5 nm sample Co50 is largely in superparamagnetic state at 300 K and its blocking temperature is ~260 K in the presence of a low magnetic field. M-H curve of Co50 at 85 K suggests that there is a high non-zero coercivity as compared to Zn50.**

***Keywords*: Ferrites, Blocking temperature, Coercivity, Superparamagnetism, Nanoparticle.**

## INTRODUCTION

In the area of magnetism of fine particles, modifications in saturation magnetization and anisotropy as effected by reduction of particle sizes, magnetism of surface layers and the dynamic behaviour of magnetization have been the subjects of recent interest [1–8]. Studies, for example on $ZnFe_2O_4$, have shown that reduction of particle sizes may lead to reduction of saturation magnetization and changes in site occupation [7,8]. We have examined this question in a cobalt (for iron) substituted ferrite $Fe_{2.2}Co_{0.8}O_4$. In its bulk particle state this ferrite is known to exhibit[2] a much higher magnetic anisotropy (290 kJ/m$^3$) at room temperature than of $Fe_3O_4$ (-11 kJ/m$^3$). In the present work, we have undertaken to examine the question of modification in magnetic anisotropy when particles are sized down to nano-scale. For this purpose, we have chosen a Zn-substituted spinel ferrite, viz., $Fe_{2.9}Zn_{0.1}O_4$ and cobalt (for iron) substituted ferrite $Fe_{2.2}Co_{0.8}O_4$. Literature reports show that in bulk particle state of the samples, substitution of Zn causes the magnetic anisotropy to decrease. Also, for a composition close to the one undertaken for the present study, values of magnetic anisotropy are available in the literature in its bulk particle state and this would facilitate comparison.

Two multi-disperse nano-particle samples with average particle sizes of ~50 Å of $Fe_{2.9}Zn_{0.1}O_4$ and $Fe_{2.2}Co_{0.8}O_4$ have been prepared. DC magnetization measurements have been made at different temperatures for examining the modification in magnetic properties like disordered spin surface and freezing of disordered spins.

## Experimental Details

Synthesis procedure of $Fe_{2.9}Zn0_{.1}O_4$ and $Fe_{2.2}Co_{0.8}O_4$ ferrite nanoparticles is discussed in detail in papers published in peer-reviewed journals previously by us. The DC magnetization measurements have been made on a vibrating sample magnetometer (VSM; PARC make, model 155). For calibration of the VSM a small cylindrical piece (2.4 mm in diameter and 2.4 mm long) of pure nickel has been used. For sample measurements, the powder has been compacted to about the same height in a sample cup of identical inner diameter.

**Results and Discussion**

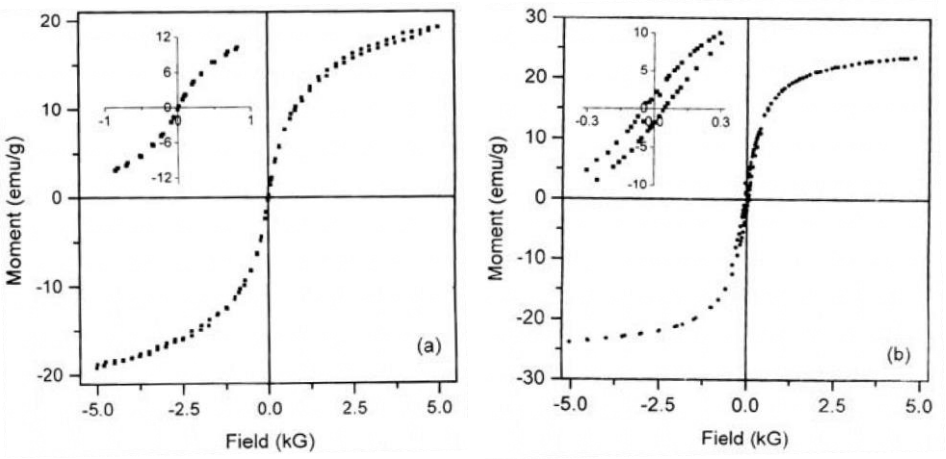


**Figure 1.** Magnetization–field curves of Zn50 sample recorded at sample temperatures (**a**) 295 K and (**b**) 21 K. Insets to figures show expanded low field region.

Figures 1a and 1b show variation of magnetization *M* with magnetic field *H* recorded at 295 K and 21 K respectively; insets to the figures show expanded plots. The 21 K curve shows a small but non-zero coercivity of 35 Oe. At 295 K it is almost zero. The observations are suggestive of a superparamagnetic behaviour at 295 K and also that the blocking temperature is greater than 21 K. Further, the *M–H* measurements at 21 K suggest that saturation magnetization $M_s$ in the present sample should be much less than 98 emu/g whichis the value for $Fe_3O_4$ [9]. Extrapolation of *M* vs. 1 *H* curve to 1 *H* 0 gives a value of 26 emu/g for $M_s$. Now, $Fe_3O_4$ is an inverse spinel. If $Zn^{2+}$ goes to the tetrahedral site, it should result in an enhancement in magnetization as against an observed reduction and if it goes to an octahedral site there must be only 10% reduction in magnetization. The muchreduced $M_s$ in the nano-particle sample implies that outside a core of ordered moments, those in the surface layer are in a state of frozen disorder. Kodama and Berkowitz, in their study of nano-particles of $NiFe_2O_4$ and $\gamma$-$Fe_2O_3$, have found evidence for disorderedsurface spins [5].

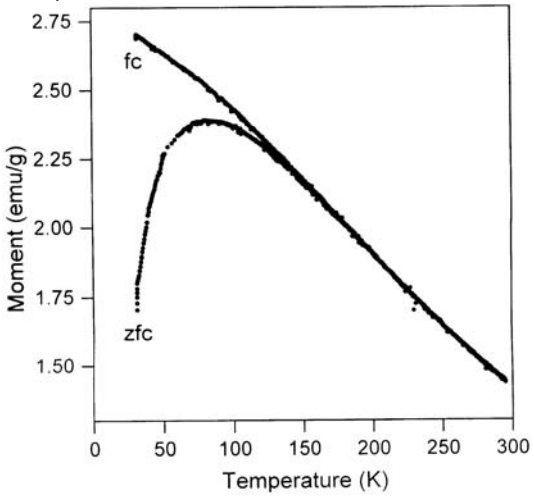


**Figure 2. Magnetization–temperature curve recorded in ZFC and FC modes inan external magnetic field of 50.8 Oe.**

Figure 2 shows a plot of magnetization vs. temperature (*M–T*) recorded in the zero field cooling (ZFC) and field cooling (FC) modes in an external magnetic field of 50.8 gauss. The ZFC pattern has been recorded by first cooling the sample from 295 K to 21 K in the zero magnetic field, then applying the magnetic field and warming the sample up to 295 K in the presence of the field and recording the moment in this warming cycle. Field-cooled patternhas been obtained by first cooling the sample from 295 K down to 21 K in the external field and then warming it up to 295 K and recording the moment. Two features are noticeable:

(i) the ZFC curve exhibits a peak at 80 K and (ii) the FC and ZFC curves considerably depart from each other below this peak temperature. Appearance of a peak in the ZFC curve owes to 'blocking' mechanism arising from a competition between the thermal energy and the magnetic anisotropy energy of the fine particles. Departure of fc curve from the ZFC one is suggestive of temporal relaxation, viz., evolution of magnetization with time.

Fig. 3 shows for Co50 the magnetization recorded as a function of magnetic field $H$ at 300 K and 85 K. At 300 K 'coercivity' $H_c$ and 'remanence' $M_r$ are negligible. This observation supports the conjecture of a largely superparamagnetic (SPM) state at 300 K.

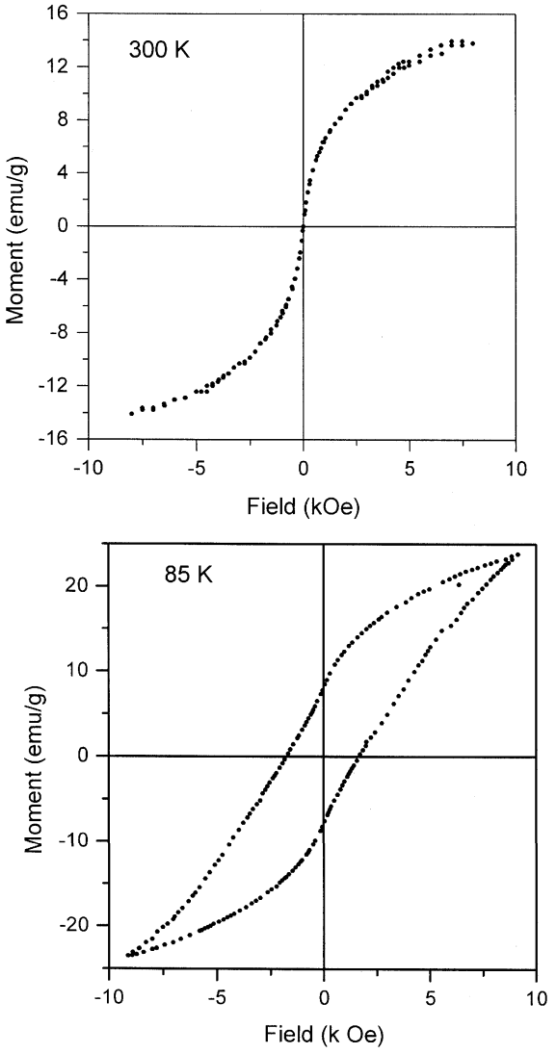


**Fig. 3: *M-H* curves for the sample Co50 at 300 K and 85 K**

Further, the facts of magnetic relaxation suggested by FC and ZFC curves departing considerably below 260 K (Fig. 4a) and shifting of the peak towards lower temperature (Figs 4a and 4b) with increasing field are suggestive of dynamic magnetic behaviour [10-12]. Such behaviour is characteristic feature of nano-particle state.

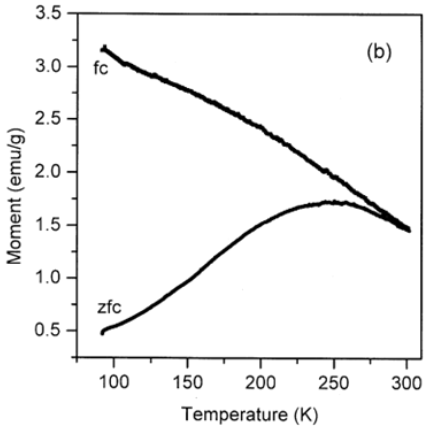


**Fig. 4 — *M-T* curves for the sample Co50 recorded in ZFC and FC mode in field of 5 Oe.**

Figure 4 shows variation of magnetization $M$ for the sample Co50 as a function of temperature, in the range 5-300 K,

recorded in zero field cooling (ZFC) and field cooling (FC) modes, in the presence of an external magnetic field of 5 Oe. *M-T* measurements were made under different magnetic fields in the temperature range 85-300 K. Fig. 4 shows, as a typical example, *M-T* curve recorded under a field of 94 Oe. Appearance of a peak at 260 K in *M-T* curve of Co50 is suggestive of blocking[7], arising from competition between thermal energy and magnetic anisotropy energy, at around 260 K. Above 260 K the sample would be largely in super-paramagnetic (SPM) state.

**Conclusion**

DC magnetization measurements have been made for Zn-substituted spinel ferrite $Fe_{2\,9}Zn_{0\,1}O_4$ Zn50 having an average particle size of 5 nm. The study shows interesting analogies with conventional spin glasses in the form of an observed linear variation of the blocking temperature of 80K. and M-H curve of Zn50 at 21 K suggests that there is a small but non-zero coercivity of 35 Oe. At 295 K it is almost zero. The observations are suggestive of a superparamagnetic behaviour at 295 K and also that the blocking temperature is greater than 21 K.

The 5 nm sample Co50 is largely in superparamagnetic state at 300 K and its blocking temperature, arising from competition between thermal energy and magnetic anisotropy energy, is ~260 K in the presence of a low magnetic field. Much smaller moments of the sample than the saturation magnetization for the bulk sample and a loop shift observed for *M- H* curves of Co50 recorded in zero field and field cooling modes are suggestive of spin disordered surfaces.

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