

Chapter VIII: Conclusions

In this thesis, we examined the structure, microstructure and magnetic properties of CoCr_2O_4 and Zn doped CoCr_2O_4 nanoparticles. 10 and 50 nm CoCr_2O_4 particles were synthesized using chemical co-precipitation method and the size dependent structure and magnetic properties were discussed. In comparison with CoCr_2O_4 , the structure and magnetic properties of $\text{Zn}_x\text{Co}_{1-x}\text{Cr}_2\text{O}_4$ ($0.05 \leq x \leq 0.8$) particles of size 10 nm were demonstrated. X-ray diffraction (XRD) technique was used to verify the structure and phase formation of the sample. The distribution of cations among A and B sites using Extended x-ray absorption fine structure (EXAFS) were determined. The magnetic ordering temperatures like Curie temperature (T_C), spin-spiral transition (T_S) and lock-in transition (T_L) were discussed using temperature dependent magnetization and Diffused neutron scattering (DNS) using polarized neutrons. Further, field dependent magnetization was probed in order to find out the relative alignments of the spins and their magnitude. In order to examine the magnetically ordered state in these nanoparticles, ac susceptibility measurements (χ' and χ'') with varying temperature and frequency were undertaken and results were discussed. The important findings of the present work were outlined below:

1. CoCr_2O_4 particles of different sizes were synthesized through coprecipitation technique by varying calcination temperature. The samples were calcined at 500°C and 900°C for 4 hours. The pure phase of the powders were confirmed from the X-ray diffraction. The X-ray diffraction patterns were fitted by standard Fullprof profile fitting with Fd3m space group using Fullprof program. The mean crystallite diameter estimated using Scherrer's formula after correcting the instrumental broadening along

(311) were found to be ~ 10 and 50 nm for sample calcined at 500°C and 900°C respectively. Although size reduced to nanometer range, Extended x-ray absorption fine structure (EXAFS) showed no change in cation distribution among A and B sites of CoCr_2O_4 unlike in spinel ferrites. Upon cooling, bulk cobalt chromite showed paramagnetic to collinear ferrimagnetic transition at Curie temperature (T_C) and to a short range non-collinear spiral ordering at T_S and finally to a lock in transition, T_L . Though T_C and T_L varied with size of the particle, T_S remained independent confirming the persistence of strong B-B interaction even in nanoparticles. Polarized neutron scattering further showed while para to ferrimagnetic transition was continuous in both samples, spin-spiral ordering was sharp, short range and commensurate in 50 nm particles. Splitting of ac susceptibility peak, increase in peak position with frequency and non saturation of magnetization at high field indicated the core-shell structure where core spins contributed to the ferrimagnetic phase and the disordered spins at the surface showed spin glass behavior. The memory experiment further confirmed the spin-glass behavior of surface spins in 50 nm particles.

2. The exchange bias, training effect and temperature dependence of memory effect were studied in 50 nm core-shell particles. The interaction between core and surface spins contributed to high exchange bias (EB) below spin-spiral transition, T_S , 30 K. The EB decreased with increasing temperature and vanished nearly at 50 K as core-shell interactions decreased due to unblocked surface spins. The high exchange bias of two orders of magnitude more than the bulk CoCr_2O_4 observed at lowest temperature was not only due to the contribution of interface interaction between collinear and non-collinear spins, but also due to spiral ordering observed below 30 K which was confirmed

from diffused neutron scattering using polarized neutrons. The microscopic origin of exchange bias was explained using training effect. With increase in number of loops, the percentage of training effect decreased and attained 60% after 7th cycle. The exchange bias between the first and second loop was higher than the subsequent loops indicating the relaxation of magnetization much faster from the first to the second loop than in the higher loops. During each cycle, the spin rearrangement took place and modified the exchange bias. This could be explained by considering fraction of rotatable spins and frozen spins in which rotatable spins dominated over the frozen spins. Hence, the frozen/pinned spins were unstable during each magnetization reversal and hence exchange bias was decreased. The depth of memory dip (ΔM) was high at halt temperature, 50 K which decreased with decrease in halt temperature and vanished at 30 K. Much below T_B , at 30 K, the drop in memory dip was less due to frozen shell spins. The amount of recovery in magnetization at every halt temperature depends on how fast the nanoparticles realign to the applied field. The most pronounced memory effect observed at 50 K, below T_B , could be due to the slow dynamics of the spin system. The less recovery of the spins could produce a large difference in magnetization between reference and memory, which showed a large memory dip at 50 K. The position of memory dip observed in our case did not vary with the halt temperature. The appearance of memory dip at 75 K for all halt temperatures could be due to chaotic nature of the spin glass equilibrium configuration. We concluded that while the behavior of the training effect controlled by the core to shell size ratio for a given nanoparticle size, the exchange bias was contributed by commensurate spiral ordering.

3. $\text{Zn}_x\text{Co}_{1-x}\text{Cr}_2\text{O}_4$ ($0.05 \leq x \leq 0.8$) particles of size 10 nm were synthesized through chemical co-precipitation technique. The structure, cation distribution and magnetic properties of the particles were discussed in comparison with CoCr_2O_4 . XRD patterns confirmed the cubic spinel structure without any impurity phase. Lattice parameter decreased with increase in Zn concentration, due to less ionic nature of Zn than Co, and/or due to decrease in A-B repulsion. Cation distribution of $\text{Zn}_x\text{Co}_{1-x}\text{Cr}_2\text{O}_4$ studied through EXAFS confirmed that while Cr^{3+} ions preferred B site, Zn^{2+} and Co^{2+} ions occupied the A site. It indicated that there is no effect on cation distribution by reducing the particle size. From dc magnetization and diffused neutron scattering, with increase in x from 0.05 to 0.8, we revealed that the paramagnetic to ferrimagnetic transition, T_C , decreased from 90 K to 67.4 K. The observed value of T_C is higher than T_C of bulk $\text{Zn}_x\text{Co}_{1-x}\text{Cr}_2\text{O}_4$. The increase in T_C by one fold at $x=0.8$ by reducing the particle size was ascribed to finite size effect. The spin-spiral transition, T_S decreased from 26 K to 24 K and the spin lock-in transition, T_L observed at 10 K remained unchanged with increase in x from 0.05 to 0.1. There was no evidence of T_S and T_L found in these nanoparticles for $x > 0.1$. Temperature dependent ac magnetic susceptibility measurement showed the dispersion behavior with frequency for $x=0.05$. However, no dispersion behavior was observed for $x > 0.05$ which confirmed the absence of superparamagnetic and/or spin-glass behavior in these particles. The phenomenological models like Vogel-Fulcher, power law were fitted and coexistence of spin-glass and cluster glass in $x=0.05$ was confirmed. Neel's two sub-lattice model failed to explain the decrease in saturation magnetization with increase in Zn concentration measured from hysteresis loop at 2 K. This was well explained by considering the three sub-lattice model suggested by Yafet-Kittel (Y-K).

The increase in Y-K angle with increase in Zn concentration further indicated the triangular spin arrangement in B site resulting in decreasing A-B exchange interaction hence decreased in T_C . In contrast to the ferrites which consists of Zn, the net magnetization of CoCr_2O_4 decreased with addition Zn upto 20 mol% and then increased upto 80 mol%. The experimental magnetization was found to be one order magnitude less than the theoretical one which could be due to the existence of random canting of spins at the surfaces due to nanometer size of the particles.

Our investigation on CoCr_2O_4 and Zn doped CoCr_2O_4 nanoparticles revealed several new and important findings. However, there are several open issues need to be clarified with proper experimentation as well as theoretical investigations. Few important suggestions for future work are appended below.

- The dielectric and multiferroic properties of Zn doped CoCr_2O_4 nanoparticles may be studied.
- The effect of addition of Zn on the exchange bias, training effect and memory effect of CoCr_2O_4 nanoparticles may be examined.
- The size dependent study of non-linear optical properties of ZnCr_2O_4 nanoparticles can be explored.