Mössbauer spectroscopy: An essential tool for nanoparticle magnetism in \( \text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4 \) ferrite

R N Bhowmik* & R Ranganathan†

Experimental Condensed Matter Physics Division, Saha Institute of Nuclear Physics, Calcutta 700 064

Received 15 February 2007; revised 25 July 2007; accepted 14 August 2007

Magnetism in \( \text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4 \) nanoparticles, prepared by mechanical activated process and chemical (co-precipitation) process has been reported. Experimental data showed that magnetic behaviour in mechanical activated nanoparticles (MANP) is drastically different in comparison with the nanoparticles (CPNP) prepared by chemical route. For example, MANP exhibited enhancement in both magnetization and ferrimagnetic order, whereas CPNP shows the reduction in both magnetization and magnetic order. The magnetic evolution during thermal activated grain growth process is also different for samples with smaller particle size, whereas magnetic behaviour for larger particle size is similar for both nano particles and approaching to the properties of bulk system. We have understood the co-existence of various competitive effects during grain growth process employing Mössbauer spectroscopy, \( dc \) magnetization and \( ac \) susceptibility measurements.

Keywords: Mössbauer spectroscopy, Nanoparticle magnetism, \( \text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4 \) ferrite

IPC Code: G01J3/28, H01F41/30

1 Introduction

Spinels belong to a special class of magnetic materials, which is represented by formula \( \text{AB}_2\text{O}_4 \). The anions (O\(^2\)- ions) form an fcc cubic lattice structure. The cations (M\(^{2+}\), Fe\(^{3+}\)) occupy two interstitial sublattices A (tetrahedral) and B (octahedral), respectively. The interactions between the cations (magnetic moments) of intra-sublattice and inter-sublattice are superexchange type via O\(^2\)- ions. There are three types of superexchange interactions, viz. \( J_{AB} \) (A-O-B), \( J_{BB} \) (B-O-B) and \( J_{AA} \) (A-O-A). The magnetic order depends upon the competition between these superexchange interactions. The essential condition for exhibiting collinear (long range ferrimagnetic) spin structure in ferrites is \( J_{AB} >> J_{BB} >> J_{AA} \). In such ferrites, the ferrimagnetic ordering temperature \( (T_C) \) is proportional to the strength of \( J_{AB} \). It is possible to change the relative strengths of superexchange interactions either by the substitution of (magnetic or non-magnetic) cations or by the gradual decrease of particle size. Although many substitution works on spinel ferrites have been studied for the last few decades, the interest for nanoparticle ferrites is creeping up in recent times only owing to their applications in nano-science and technology. In most of the cases, either the substitution work or the particle size effect has been investigated on the collinear (long range ferrimagnetic) bulk ferrites. Total magnetization per formula unit of a collinear (ferromagnetic) ferrite can be written as \( M = M_B - M_A \), where \( M_B \) and \( M_A \) are magnetization of B and A sublattices, respectively. The collinear spin structure at B sublattice, as well as ferromagnetic order in the ferrite, is no longer maintained for the A sublattice magnetic concentration below 0.33. Mössbauer Spectroscopy work by Petitt et al.\(^2\) showed the decrease of total magnetization in \( \text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4 \) for \( x \geq 0.6 \). A systematic increase of \( x \) essentially reduces the A sublattice magnetic moment \( (M_A = \text{Fe}^{3+}) \), and one could expect more magnetization per formula unit by applying \( M = M_B - M_A \). The decrease in M has been attributed to the increase of B site spin canting (\( \theta \)). In such non-collinear ferromagnetic structure, total magnetization per formula unit can be modified as \( M = M_B \cos \theta - M_A \). The work by Petitt et al.\(^3\) has established the inverse relationship between B site spin canting and magnetization. Recently, many studies also confirmed a possibility of exchanging cations among A and B sublattices in ferrite nanoparticles. It could be more interesting and relevant for the understanding of ferrite nanoarticles.
to investigate the relationship between the B site spin canting and particle size effect. In this aspect, we have studied the nanoparticles of Co$_{0.2}$Zn$_{0.8}$Fe$_{2}$O$_{4}$ ferrite. If the site exchange of cations (Zn$^{2+}$ and Fe$^{3+}$) with more A site magnetic population (Fe$^{3+}$) happens in Co$_{0.2}$Zn$_{0.8}$Fe$_{2}$O$_{4}$ nanoparticles, there is a possibility of decreasing of B site spin canting. Hence, an increase of magnetization in Co$_{0.2}$Zn$_{0.8}$Fe$_{2}$O$_{4}$ nanoparticles is expected. This concept may apparently contradict the general belief that more A site magnetic population effectively decreases the magnetization of ferrite. This contradiction will be removed, if we take into account the important contribution of cos$\theta$ terms. Mössbauer spectroscopy is used to study the local magnetic ordering as well as site exchange of cations in nanoparticle ferrites.

2 Experimental Details

2.1 Sample preparation and characterization

The details of the sample preparation and characterization are given in Refs (3-5) for mechanical milled, mechanical alloyed, and coprecipitation samples respectively. The bulk sample (S$_0$) after 24 h mechanical milling produces particle size~20 nm (MM$_0$ sample). On the otherhand, 100 hours mechanical alloying produced Co$_{0.2}$Zn$_{0.8}$Fe$_{2}$O$_{4}$ nanoparticles with average particle size~21 nm. We have used a mixed solution of 0.02 mol/l of CoCl$_2$, 0.08 mol/l of ZnSO$_4$, and 0.2 mol/l of Fe(NO$_3$)$_3$ to prepare nanoparticles in co-precipitation method. The as prepared sample was divided into different portions and each portion was heat treated (annealed) at different temperatures to investigate the magnetic evolution with grain growth process. The heat treated samples at different temperatures (T$_{AN}$) are denoted as MMX, MAX and CPX for mechanical milling, mechanical alloying and co-precipitation methods, respectively. Here, X = 0 for as prepared sample and without annealing, 2 for T$_{AN}$ = 200°C, 10 for T$_{AN}$ = 1000°C, and so on. XRD spectra indicated cubic spinel structure of all the nanoparticle samples, whereas transmission electron microscope (TEM) data confirmed the thermal activated grain growth process. The dc magnetization ($M$) as a function of temperature ($T$) and magnetic field ($H$) was measured using SQUID (quantum design) magnetometer. $M(T)$ data were recorded under zero field cooled (ZFC) and field cooled (FC) modes, respectively. Mössbauer spectra of the samples were recorded in transmission geometry, using constant acceleration drive (CMTE-250) with a 5 mCi $^{57}$Co source in Rh matrix. The Mössbauer spectra were fitted, wherever possible, with a least-squares fitting programme with Lorentzian profiles.

3 Results and Discussion

Figure 1(a) compares the $M(T)$ data at 100 Oe for bulk sample (S$_0$), mechanical milled (MM0) and heat treated mechanical milled (MM10) samples, respectively. Bulk sample shows magnetic irreversibility between zero field cooled magnetization (MZFC) and field cooled magnetization (MFC) below 260K. On further decreasing the temperature, MZFC decreases below 100K into a Cluster-Spin glass State, whereas the MFC shows saturation at lower temperatures. Over all, the bulk sample shows coexistence between paramagnetic state and short range interacting clusters between 260-300 K, and a mixture of cluster glass and short range ferrimagnetic order between 100-260 K. When the bulk sample is mechanical milled for 24 h (MM0 sample, average particle size~20 nm), there is an enhancement in both magnetization and magnetic ordering temperature in

![Fig. 1](image-url)
comparison with the bulk sample. In addition, MM0 sample shows a typical superparamagnetic blocking of the magnetic clusters below ~300K. Interestingly, the thermal activated grain growth kinetics has shown a tendency to restore the magnetic behaviour of bulk sample, as seen for 1000°C annealed sample (MM10 with particle size ~ 62 nm). The magnetic evolution is further confirmed from the Mössbauer spectra [Fig. 1(b)]. The $M(H)$ data [Fig. 2(a)] also indicate better ferrimagnetic order in MM0 in comparison with the bulk sample. The lack of saturation of magnetization at higher fields (H > 40 kOe) is reduced in the as milled (MM0) sample in comparison with bulk sample. This is attributed to the reduction of strong B site spin canting effect of bulk in the as milled nanoparticle. We have found that coercivity of MM0 sample is greater than the bulk sample throughout the temperature range below 300K (Fig. 2b). This indicates an enhancement of anisotropy in mechanical milled sample. Even though the preparation technique of mechanical alloyed (MA) nanoparticles is slightly different with respect to the mechanical milled nanoparticles, we have seen that magnetic evolution with particle size of the mechanical alloyed samples [8] is identical with respect to that seen in MM nanoparticles [3]. Both nanoparticles exhibit enhancement of magnetization, ferromagnetic order, and anisotropy energy, which are confirmed from the Mössbauer spectra at 300 K. The room temperature spectra of mechanical alloyed nanoparticles [3,8] (Fig. 3) reveal two different types of magnetic behaviour, depending on the annealing temperature ($T_{AN}$), i.e., size of the particle. The spectra for $T_{AN} \geq 700$°C (MA7, MA10) samples showed a typical paramagnetic doublet at RT, whereas the increase of line broadening associated with superparamagnetic relaxation effect, is becoming prominent in the samples (MA4 and MA2) of smaller particle size. The room temperature spectrum of MA2 sample also shows a weak magnetic component coexisting with the dominating central peak, appearing due to superparamagnetic fluctuation effect [Fig. 3(d)]. Therefore, room temperature Mössbauer spectra confirmed (and also consistent with dc magnetization data) that enhancement of ferrimagnetic order occurs for mechanical alloyed samples with smaller particle size. The magnetic evolution with grain growth kinetics of mechanical alloyed sample is shown in the Arrott plot [$M^2$ versus $H/M$] of $M(H)$ data at 300K [Fig. 4(a)]. The obtained values of spontaneous magnetization ($M_S$) are shown in Fig. 4b. Detailed analysis of the room temperature Mössbauer spectra of MM3 sample (annealed at 300°C for different annealing time) and mechanical alloyed samples [8] indicated that more Fe$^{3+}$ ions are occupied at A sites for lower particle size of mechanical activated (milled/alloyed) sample. We, then, explained the enhancement of both magnetization and magnetic ordering temperature in mechanical activated
nanoparticles (MANP) by inversion of spin canting model\textsuperscript{3}. The model states that the reduction of B site spin canting, associated with the site-exchange of cations, results in the enhancement of both magnetization and ferrimagnetic order.

We, now, plot the $M(T)$ data for different particle size of coprecipitation nanoparticle (CPNP) sample (Fig. 5). The magnetic evolution with reduction of particle size is as usual, i.e. the smaller particle shows superparamagnetic blocking below the blocking temperature $T_B$. The blocking temperature as well as the magnetization of the system increases with the increase of particle size. The sample with larger particle size is also approaching to the mixed magnetic order of bulk, as also seen in MANP nanoparticles. The $M(T)$ behaviour is also supported by the Mössbauer measurements. We also find from the analysis of the Mössbauer spectra, more A site population of Fe$^{3+}$ ions in CPNP samples of smaller particle size, as seen in mechanical activated nanoparticle (MANP) samples. Comparing the magnetic states (Fig. 6) of mechanical activated nanoparticles (MANP) and coprecipitation nanoparticles (CPNP), the question may naturally arise: why MANPs show enhancement of magnetization and magnetic order, whereas CPNPs show the decrease of magnetization on decreasing the particle size, since both are showing the site exchange of cations in the Co$_{0.2}$Zn$_{0.8}$Fe$_2$O$_4$ nanoparticles? First of all the decrease of magnetization in CPNPs may be consistent with the conventional core-shell model\textsuperscript{3}, which is not applicable to MANPs. This suggests that
the combined effect of the site exchange of cations and the inverse of spin canting may not be sufficient for the complete understanding of the enhancement of magnetization in ferrite nanoparticles, unless some other origin (driving force) contributes to the total magnetization of nanoparticle. Therefore, it is an open problem to identify the driving force (mechanism) that shows drastically different properties of mechanical milled activated nanoparticles in comparison with particles prepared by chemical route. First, we have compared the TEM pictures of mechanical alloyed nanoparticles and coprecipitation nanoparticles with particles size nearly in the same range of magnitude. We expect same order of surface anisotropy for the particles of identical microstructure, (i.e., shape and size) and magnetic structures (i.e., spin configuration both at grain boundary and inside grain). This should be independent of preparation techniques. We have seen that CPNPs are nearly spherical in shape, but MANPs are well deviated from the spherical shape. This is shown schematically in Fig. 7. In this aspect, magnetic contribution from grain boundary (surface) spins, which are largely controlled by total surface anisotropy energy of the particle, should be taken seriously into account. Some typical magnetic behaviour of chemical route prepared nanoparticles, such as: (i) reduction of magnetization, (ii) decrease of superparamagnetic blocking temperature ($T_B$) and (iii) large value of irreversibility field, are consistent with dominating canting effect among surface spins\(^9\). The increase of surface spin canting decreases particle magnetization, effectively we call it a negative contribution of surface spins (also known as magnetically dead) to total particle magnetization. On the otherhand, Fig. 8 shows an extra anisotropy contribution in mechanical alloyed nanoparticles in comparison with the chemical route nanoparticles for smaller particles. However, coercivity (proportional to anisotropy) in both NPs are almost independent of particle size, and nearly same in magnitude for larger particles. The extra anisotropy in mechanical alloyed sample is contributed from the mechanical strain, including non-spherical shape of the nanoparticles. Extra anisotropy alongwith distinct magnetic features in mechanical alloyed nanoparticle suggest that its grain boundary structure is not identical with that of chemical route sample. It is expected that large strain induced anisotropy, distributed mainly in grain boundary spins, plays a significant role to determine the magnetic order in mechanical alloyed system. We have shown by detailed analysis\(^8\) that preferential magnetic ordering of grain boundary spins, activated by strain induced anisotropy, gives some (positive) contribution to the total particle magnetization. It is positive in the sense that such ordering of grain boundary spins gives a magnetic contribution to the total particle magnetization, unlike the magnetic dead layer (or negative magnetic contribution) by grain boundary spins in chemical route nanoparticles.

### 4 Conclusions

The magnetic evolution with thermal activated grain growth kinetics in ferrites is a complicated process. This is associated with many concurrent effects. So far we have been able to identify three mechanisms in Co$_{0.2}$Zn$_{0.8}$Fe$_2$O$_4$ ferrite: (i) site exchange of cations, (ii) inverse of spin canting effect, and (iii) strain induced anisotropy effect on the grain boundary magnetic contribution. All of these
mechanisms are not dominating at the same time, rather they depend on the range of particle size, heat treatment, and preparation methods. Inverse of spin canting effect is associated with the exchange of cations ($\text{Zn}^{2+}, \text{Fe}^{3+}$) among A and B sites. Mössbauer spectroscopy revealed that site exchange of cations among A and B sites takes place during grain growth kinetics in both MANP and CPNP samples. This shows that site exchange of cations, and its associated inverse of spin canting effect are not the only mechanisms which can give rise to drastically different magnetic behaviour in MANP and CPNP samples. There are basically two competitive effects which determine the nanoparticle magnetism. First one is the surface spin canting effect which reduces the magnetization in CPNP. Second one is the inverse of spin canting effect, assisted by the strain induced anisotropy, which enhances the particle magnetization in MANP. Therefore, Mössbauer spectroscopy is essential to identify the site exchange of cations in both (MANP and CPNP) nanoparticles of $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ ferrite, whereas magnetic measurement is essential for the identification that strain induced anisotropy plays a vital role in partial magnetic ordering of grain boundary spins.

Acknowledgement
We thank Prof R Nagarajan, Prof C Bansal and S Kumar for their contribution in some of the measurements and useful discussions.

References