Magnetic Phase Separation in Diluted Magnetic System: $\text{Zn}_{1-x}\text{Fe}_x\text{O}$

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Abstract Single-phase diluted magnetic systems $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ have been prepared by chemical route. Structural and spectroscopic (UV–Vis and Mössbauer) studies indicate the incorporation of Fe^{3+} ions in the lattice sites. The UV–Vis results point to a systematic increase in the band gap with increasing Fe doping. The room temperature magnetization of $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ indicates a paramagnetic behavior which is in accordance with the Mössbauer results, illustrating quadrupolar doublet. At low temperature, the zero-field-cooled (ZFC) magnetization shows a cusp and this temperature increases systematically with decreasing particle size. The weak exchange bias effect manifested by a M – H loop shift is observed for $x = 0.03$. This shift is accompanied by the enhancement of coercivity. The dc magnetization results suggest the coexistence of ferromagnetic and antiferromagnetic exchange interactions for low doping of Fe, i.e., for $x = 0.03$.

KEY WORDS: Diluted magnetic system; Optical band gap; Mössbauer; Exchange bias effect

1 Introduction

Diluted magnetic semiconductors (DMSs) have attracted much interest for a decade due to their possibility of manipulating charge and spin degrees of freedom in a single material. DMSs are semiconducting materials where magnetic atoms at small (<10%) concentrations are distributed at the cation sites of the host semiconductor. These DMSs are potential candidates for technological applications in magneto-optics as well as spintronics because of their both semiconducting and ferromagnetic properties [1, 2]. Marcel et al. [3] have theoretically predicted that

ZnO doped by the transition metal ions (TM = Ti, V, Cr, Mn, Fe, Co, Ni, Cu) is ferromagnetic at room temperature. A number of experimental reports available on ZnO doped by transition metal ions propose different opinions. For example, different groups [4–7] reported room temperature ferromagnetism in ZnO implanted with Fe ions, while Janisch et al. [8] reported that Fe-doped ZnO showed a paramagnetic behavior. Several attempts have been made to explain the room temperature ferromagnetic behavior with Zener double exchange, super-exchange, direct exchange, carrier-mediated exchange [8], F-center exchange (FCE) mechanism proposed by Coey et al. [9], etc. However, the origin of ferromagnetism remains controversial and is often attributed to the fabrication artifacts of these systems. For very small Fe dopings, which are beyond the X-ray diffraction (XRD) detection ability, sometimes it is difficult to identify the presence of phase separation of Fe or Fe oxide clusters. In order to avoid this problem, we have restricted the Fe concentration in $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ within the range $0.03 \leq x \leq 0.13$. Samples are unambiguously characterized to be single phase where Fe enters into the ZnO lattice by Zn^{2+} substitution. The

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absence of any segregation of Fe/Fe oxide is confirmed by both macroscopic (XRD) and microscopic tools such as Mössbauer study. Both $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ [10] and $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ [11] systems show ferromagnetic (FM) behavior at room temperature and approach a paramagnetic behavior with an increase in the concentration of Fe or Ni with $x \leq 10\%$. These results could be explained with the simultaneous presence of FM and antiferromagnetic (AFM) exchange where the later one increases with the increase in the doping concentration [10]. The coexistence of two exchange interactions, namely FM and AFM [10] or FM and spin glass (SG) [5], has been proposed in Fe-doped ZnO.

The exchange bias (EB) effect is observed in systems composed of ferromagnetic and antiferromagnetic substances where the Curie temperature of the FM component is greater than the Néel temperature of the AFM component [12]. Later, this effect has been explored in various combinations between FM, AFM, canted AFM, SG and disordered magnetic components which have been reviewed by different groups [13–15]. Here, the EB effect has been revealed as a shift of the hysteresis loop (H_{ex}) in the diluted magnetic system $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ with $x = 0.03$. $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ ($0.0 \leq x \leq 0.13$) samples have been prepared by chemical route. The successful incorporation of the Fe ions in the lattice sites rather than the formation of a separate phase has been established from both XRD and Mössbauer studies. The horizontal shift of the hysteresis loop along with the increment of coercivity supports the exchange bias effect which is a fingerprint of the coexistence of two magnetic phases.

2 Experimental

The chemical reagents, like zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), ferric chloride (FeCl_3), sodium hydroxide (NaOH) and polyvinylpyrrolidone (PVP), used in the present case were analytical reagent grade. ZnO nanoparticles doped with iron (i.e., $\text{Zn}_{1-x}\text{Fe}_x\text{O}$) with different Fe contents (x) were synthesized in a deionized water ambience. To prepare $\text{Zn}_{1-x}\text{Fe}_x\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and FeCl_3 were taken in stoichiometric ratio. In a typical experiment, to prepare $\text{Zn}_{0.97}\text{Fe}_{0.03}\text{O}$, 50 ml aqueous solution of 0.31 mol/l of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was added slowly with 25 ml aqueous solution of 0.02 mol/l of FeCl_3 . One gram of PVP in 50 ml deionized water was added to the mixture. The mixture was then stirred magnetically at 80 °C for 2 h to make it homogeneous. Then, 50 ml aqueous solution of 0.4 g of NaOH was added dropwise to the above mixture. NaOH did not react with other precursors, it only helped to accelerate the reactions, and a yellow voluminous precipitate appeared after the NaOH injection. The NaOH dissolved easily in

deionized water and ethanol. The obtained precipitate having residual NaOH as impurities was washed and separated out by centrifuging it against deionized water and ethanol for several times. The product was dried in hot air oven at 120 °C for 2 h. In this way, $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ samples with $x = 0.0, 0.03, 0.06, 0.09, 0.13$ were prepared. The XRD patterns of these samples were recorded at room temperature in a powder X-ray diffractometer (Bruker D8 Advance) using the CuK_α radiation. The morphology of the nanoparticles was studied by field emission scanning electron microscopy (JEOL, JSM-7610F, FE-SEM). The optical transmission spectra were measured in the wavelength region 200–800 nm by using UV–Vis a diffuse reflectance spectrophotometer (Shimadzu, UV 2401PC). The Mössbauer studies were performed in a constant acceleration mode spectrometer (WissEl GmbH, Germany) using a 5-mCi ^{57}Co source. The electron paramagnetic resonance (EPR) spectra were measured by using a Varian E-109-X band spectrometer. Measurements of magnetization were taken using a commercial SQUID magnetometer (Quantum Design, MPMS-7).

3 Results and Discussion

3.1 Structural Characterization

Fe-doped ZnO nanoparticles are characterized by XRD. Figure 1a illustrates the diffraction peaks of $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ ($0.0 \leq x \leq 0.13$) which exhibit a single-phase Wurtzite structure (space group $p63mc$, JCPDF #36-1451). This clearly infers a successful incorporation of the Fe ions in the ZnO lattice sites. The Rietveld refinements of the XRD data for $x = 0.03$ and 0.13 are shown in Fig. 1b. This analysis reveals that the crystal structure of $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ remains same as that of ZnO even for $x = 0.13$. The lattice parameters are obtained from the Rietveld refinements, and the variation of the lattice parameter with Fe doping (x) is shown in Fig. 1c.

Figure 1d shows that the XRD line arising from the $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ (1 0 1) plane gradually shifts toward higher diffraction angles with the increase in the Fe doping. This gradual shift of the XRD line toward higher diffraction angles may be associated with the valence state of the Fe ions in ZnO which can exist in the form of Fe^{2+} as well as Fe^{3+} . The ionic radii of Fe^{2+} , Fe^{3+} and Zn^{2+} are 0.078, 0.068 and 0.074 nm, respectively. The replacement of Zn^{2+} in the ZnO lattice by Fe^{2+} or Fe^{3+} ions will lead to a lattice distortion. Chen et al. [16] and Wang et al. [17] showed that the Fe ions exist in the form of Fe^{2+} in the Fe-doped ZnO thin films prepared by magnetron sputtering. Kim and Park [18] also prepared Fe-doped ZnO thin films by magnetron sputtering, but they found that Fe^{2+} or Fe^{3+} coexist in the

Fig. 1 **a** XRD patterns of Zn_{1-x}Fe_xO (where $0.0 \leq x \leq 0.13$) nanoparticles. **b** Rietveld refinements for Zn_{1-x}Fe_xO with $x = 0.03$ and 0.13 . **c** Unit cell parameter of Zn_{1-x}Fe_xO nanoparticles (where $0.0 \leq x \leq 0.13$) as a function of Fe doping (x). Inset shows the variation of c/a with x . **d** Peak position of Zn_{1-x}Fe_xO (101) XRD line with $0.0 \leq x \leq 0.13$. Inset shows the shifting of XRD line with x . **e** Variation of the particle size of Zn_{1-x}Fe_xO ($0.0 \leq x \leq 0.13$) nanoparticles, obtained from Williamson–Hall plot with x

films. Karmakar et al. [5] found the presence of Fe in both valence states Fe²⁺ or Fe³⁺ in Zn_{1-x}Fe_xO synthesized by chemical route. Xu and Li [19] showed the presence of only Fe³⁺ in Zn_{1-x}Fe_xO even if prepared by the chemical route. The above-reported results show that the valence state of the Fe ions in Zn_{1-x}Fe_xO is complicated and very much synthesis sensitive. If the Fe ions exist in ZnO mainly in the form of Fe²⁺, due to their larger ionic radius as compared to that of Zn²⁺, this would lead to tensile strains in the film [17]. A manifestation of this situation in the XRD patterns is a shift of the (101) peak toward smaller angles. On the contrary, if the Fe ions exist in ZnO lattice mainly in the form of Fe³⁺, due to its smaller ionic radius than that of Zn²⁺, this would lead to compressive strains. A manifestation of this situation in the XRD patterns is that the (101) peak shifts toward larger angles. In the present case, the (101) peak (Fig. 1d) shifts gradually toward higher angles with an increase in the Fe concentration. The inset shows clearly the variation of the (101) peak position (2θ) of Zn_{1-x}Fe_xO with x . Based on the above analysis, we suggest that the Fe ions in these Zn_{1-x}Fe_xO samples may exist mainly in the Fe³⁺ state. The optical band gap results obtained from UV–Vis spectroscopy measurements, and Mössbauer studies also support this conjecture.

The crystallite size (D) has been estimated using Scherrer's formula, $D = \frac{0.89\lambda}{\beta \cos \theta}$, where β is the full width half maximum (FWHM) of the diffraction line at diffraction angle θ and λ is the wavelength of the CuK α radiation. The D values determined from the low-angle and high-angle peaks differ considerably, and the difference between the two estimates of the particle size probably originates from the broadening of peaks due to microstrains in the samples. Williamson and Hall's [20] modified Scherrer's formula for microstrain in the form (as)

$$\beta \cos \theta = \frac{0.89\lambda}{D} + 2\varepsilon \sin \theta,$$

where ε is the microstrain. From a plot of $\beta \cos \theta$ versus $\sin \theta$, it is possible to calculate the microstrain from the slope and the crystallite size from the intercept. The microstrain (ε) comes out to be 0.0052 for $x = 0.03$, a value larger than that reported by Biswas et al. [21], where Fe did not enter into the ZnO lattice. The particle sizes calculated from the intercept of the plot of $\beta \cos \theta$ versus $\sin \theta$ for different Fe loadings are shown in Fig. 1e. The particle size does not vary in regular manner with x . The FE-SEM images elucidate the morphology and size of the particles. The FE-SEM image of Zn_{1-x}Fe_xO for $x = 0.13$

along with the particle size distribution is shown in Fig. 2. This is in accordance with the XRD results.

3.2 Optical Characterization

To investigate the Fe doping-induced change in the optical band gap of ZnO, UV–Vis absorption experiments have been performed. The fundamental absorption, which corresponds to the transition from the valence band to the conduction band, can be used to determine the optical band gap of a material. For direct band gap systems, the absorption coefficient is related to the incident photon energy by the equation $(\alpha h\nu)^2 = A(h\nu - E_g)$, where E_g is the band gap of the material. Using this relationship, the band gap of ZnO is evaluated in the standard manner from a plot of $(\alpha h\nu)^2$ versus $h\nu$ as shown in Fig. 3. The monotonous increase in the band gap with x is shown in the inset of Fig. 3. Similar trends of band gap enhancement in Fe-doped ZnO films and nanocrystals have been reported by Xu and Li [19], Murugadoss [22] and Parra-Palomino et al. [23], respectively. In fact, both positive and negative values of change in a band gap corresponding to a band gap enhancement and decrement with respect to an undoped ZnO have been reported. Chen et al. [16] reported that the band gap E_g of $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ thin films shows a red shift with the increase in the Fe concentration. A similar red shift down to 2.23 eV has also been observed in $\text{Zn}_{1-x}\text{Fe}_x\text{S}$ ($x = 0.3$) thin films by Selmani and Abdullah [24]. The change in the optical band gap of Fe-doped ZnO is bound up with the valence state of the Fe ions. If the Fe^{3+} ions go into the lattice sites by replacing Zn^{2+} ions, they will provide additional free carriers which cause the Fermi level to move into the conduction band. The enhancement of the

Fig. 3 Plot of $(\alpha h\nu)^2$ versus $h\nu$ of $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ nanoparticles where $0.0 \leq x \leq 0.13$. Inset shows the variation of band gap with x

optical band gap has been explained through Burstein Moss shift when the carrier concentration is found to increase in Fe-doped ZnO [19, 25] and Co-doped ZnO [26]. Thus, the enhancement of the optical band gap of $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ compared to ZnO also supports the existence of Fe as Fe^{3+} . As more doping by Fe^{3+} contributes additional free carriers causing the Fermi level to shift, this explains the monotonous increment of the optical band gap with x . Thus, the linear increment of the band gap suggests a far higher solubility limit of Fe in ZnO.

3.3 Mössbauer Studies

To probe the local magnetic environment prevailing around the Fe sites and also to determine the oxidation state of Fe, Mössbauer spectra have been recorded for $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ ($x = 0.03, 0.06, 0.09$ and 0.13) nanoparticles at 300 K. Figure 4 shows the Mössbauer spectra recorded for the Fe-

Fig. 2 FE-SEM image of $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ nanoparticles where $x = 0.13$. Inset shows the particle size distribution following Lorentz distribution shown by continuous fitted line

Fig. 4 Mössbauer spectra of $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ nanoparticles ($0.0 < x \leq 0.13$) at 300 K. The solid lines indicate the satisfactory fits. Right inset confirms the absence of magnetic hyperfine split sextet pattern at 300 K. Left inset shows the variation of quadrupolar splitting (QS) and isomer shift (IS) with x

doped ZnO nanoparticles. A magnetic hyperfine split sextet pattern is absent. The appearance of a quadrupole doublet confirms the paramagnetic relaxation at 300 K which is consistent with the magnetization results as discussed below. The isomer shift $IS \sim 0.35$ mm/s as obtained from the fit indicates that the Fe exists in +3 oxidation state [27] in $Zn_{1-x}Fe_xO$ in the range $0.03 \leq x \leq 0.13$. The inset of Fig. 4 depicts that the quadrupolar splitting (QS) remains almost same in the range of Fe doping $0.03 \leq x \leq 0.13$.

3.4 Electron Paramagnetic Resonance

Electron paramagnetic resonance (EPR) is an effective tool to investigate the nature of magnetic interactions in a material. Electron paramagnetic resonance measurements have been taken for $Zn_{1-x}Fe_xO$ ($x = 0.03, 0.09$ and 0.13) at room temperature. Typical EPR spectra recorded at room temperature, shown in Fig. 5, contain broad signals fitted with a single Lorentzian line with $g_{\text{eff}} = 2.01$. The line width (ΔH_{pp}) is found to be 1739 Oe in $Zn_{1-x}Fe_xO$ for $x = 0.03$. This may be attributed to the exchange coupled interaction between iron ions [26]. A similar broad EPR signal was observed in Fe-doped ZnO nanocrystals at 300 K by Karmakar et al. [5]. The inset of Fig. 5 indicates that the line width ΔH_{pp} decreases with the increase of x in $Zn_{1-x}Fe_xO$ within the range $0.03 \leq x \leq 0.13$. The change in the line width is a direct measure of the magnetic exchange interactions. The line width may decrease because of the weakening of the exchange field [28].

3.5 Magnetization

The magnetic properties of Fe-doped ZnO nanoparticles are studied by dc magnetization measurements. Figure 6a shows the temperature-dependent magnetization under zero-field-cooled (ZFC) and field-cooled (FC) protocol with $H = 100$ Oe for the $Zn_{1-x}Fe_xO$ ($x = 0.03, 0.06, 0.09$)

nanoparticles. The ZFC curve is obtained by initially cooling the sample from 300 K down to 2 K in the absence of magnetic field and recording the magnetization at 100 Oe field in the heating cycle. For the FC measurements, the sample is cooled under the same field and magnetization is recorded while heating from 2 to 300 K. A cusp is observed in the ZFC magnetization curve at $T = T_P$, which does not change systematically with x as depicted in the inset of Fig. 6a. Interestingly, T_P changes systematically with the particle size (D) as depicted in the lower inset of Fig. 6a. We note that T_P increases systematically with decreasing D . Further detailed experiments are required to confirm the underline mechanism. A similar peak in the ZFC curve was observed by Limaye et al. [10] and Karmakar et al. [5] in Fe-doped ZnO. Karmakar et al. have attributed the cusp observed in ZFC measurements to a transition from ferromagnetic to spin glass state. Limaye et al. [10] observed that at higher magnetic fields the cusp shifts toward lower temperatures. They ascribed these results to the presence of a weak ferromagnetic component. Several reported works [5, 6, 10, 27, 29] demonstrated the existence of room temperature ferromagnetism (RTFM) in Fe-doped ZnO. In the present case, the room temperature magnetization of $Zn_{1-x}Fe_xO$ ($x = 0.03, 0.06$ and 0.09) within $-50 \text{ kOe} \leq H \leq 50 \text{ kOe}$ indicates a paramagnetic behavior as illustrated in Fig. 6b. This is consistent with the Mössbauer results illustrating quadrupolar doublet at 300 K for all x values. The M - H loops measured at 2 K for $Zn_{1-x}Fe_xO$ are shown in Fig. 6c. Considering the molecular formula of $Zn_{1-x}Fe_xO$, the magnetic moment per Fe atom has been estimated for each sample. The inset of Fig. 6c, showing the variation of the magnetic moment per Fe atom measured at 50 kOe with x , reveals that magnetic moment per Fe atom in $Zn_{1-x}Fe_xO$ decreases with the increase in Fe doping. Such decrement of the magnetic moment in μ_B/Fe atom with an increase in x was also reported by Parra-Palomino et al. [23] and Limaye et al. [10]. This result is in agreement with the dominance of antiferromagnetic (AFM) exchange interactions over ferromagnetic (FM) ones.

These magnetic results can be explained by the F-center exchange (FCE) mechanism proposed by Coey et al. [9]. The results of XRD, UV-Vis spectroscopy, Mössbauer unambiguously indicate the incorporation of Fe^{3+} ions in ZnO lattice. Due to charge mismatch between Fe^{3+} and Zn^{2+} , more defects are produced in the sample and these can give rise to a large number of F-centers (electrons are trapped into the defects). According to the study of Coey et al. [9], the exchange interaction between two Fe^{3+} ions through the F-center is ferromagnetic in nature. This direct ferromagnetic coupling is also called as bound magnetic polaron [4, 9]. This mechanism leads to the ferromagnetic nature of the Fe-doped samples. The number of F-centers

Fig. 5 EPR spectra of $Zn_{1-x}Fe_xO$ nanoparticles ($0.0 < x \leq 0.13$) at 300 K. Inset shows the variation of line width (ΔH_{pp}) with x

Fig. 6 **a** Temperature variation of ZFC and FC magnetization of $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ nanoparticles (with $x = 0.03, 0.06$ and 0.09) measured at 100 Oe. *Upper inset* highlights the cusp position T_p for different x . *Lower inset* shows a systematic variation of T_p with the particle size. **b** Magnetic hysteresis loop of $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ nanoparticles (with $x = 0.03, 0.06$ and 0.09) measured at 300 K. **c** Magnetic hysteresis loop of $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ nanoparticles (with $x = 0.03, 0.06$ and 0.09) measured at 2 K. *Inset* shows the variation of magnetic moment per Fe atom, measured at 5 T and 2 K, with x . **d** Hysteresis loop of $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ nanoparticles (with $x = 0.03$) measured in FC mode under different cooling field at 5 K. *Bottom right inset* highlights the central portion of M – H loop indicating exchange bias effect. *Top left inset* shows the variation of coercivity with cooling field (H_{cool})

and the interactions between two iron ions through F-centers are highly dependent on the concentration of iron doping [30]. As the Fe concentration increases, the anti-ferromagnetic ($\text{Fe}^{3+}\text{--O}^{2-}\text{--Fe}^{3+}$) exchange interactions [30] dominate the ferromagnetic interactions. The competition between the ferromagnetic and antiferromagnetic exchange interactions may be responsible for the gradual fall in the magnetic moment per Fe atom at 2 K with the increase of x . To confirm the presence of two different exchange interactions, an exchange bias experiment has been performed as it is the fingerprint of the coexistence of different exchange interactions. Samples have been cooled down to 5 K from 300 K in FC mode under different cooling fields (H_{cool}), and magnetization has been measured between ± 5 T. A small horizontal shift of the hysteresis loop has been observed, as shown in the inset of Fig. 6d, for $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ with $x = 0.03$ exhibiting the typical manifestation of EB effect. The magnitude of the horizontal shift of the M – H loop along the magnetic field axis is very small but it is systematic. This may not be an

experimental artifact rather, but must be genuine as the shift of M – H loop is undoubtedly absent while cooling under ZFC condition. Moreover, an increase in coercivity (H_c) with the increase in the cooling field is also observed, as depicted in the inset of Fig. 6d. In nanostructures, this behavior is most frequently associated [14] with the loop shift, i.e., the EB effect. In $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ with $x = 0.09$, the M – H loop shift is not observed. This is in agreement with the magnetization measurement which infers the dominance of the AFM state over the FM one.

4 Conclusion

Diluted magnetic systems $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ (with $x = 0.0, 0.03, 0.06, 0.09, 0.13$) have been prepared by chemical route. The successful incorporation of the Fe ions in the lattice sites rather than the formation of a separate phase has been confirmed from both XRD and Mössbauer studies. The incorporation of the Fe ions causes a gradual shift of the

XRD line toward high diffraction angles. Analysis of these XRD results together with that of the UV–Vis spectroscopy and Mössbauer data infers the presence of iron in the Fe^{3+} state. The UV–Vis results confirm the increase in the band gap with an increase in the Fe doping. The EPR studies demonstrate the existence of exchange coupled interactions between iron ions in the low doping regime. This exchange field gradually weakens with the inclusion of more Fe in the ZnO lattice. The ZFC magnetization curves depict a cusp at T_P . Even though T_P does not change in a regular manner with x , it interestingly decreases steadily with an increase in the particle size. A small horizontal shift of the hysteresis loop is observed in $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ with $x = 0.03$ in the FC mode. This shift, accompanied by the increment of coercivity with the cooling field, indicates an exchange bias effect which is a fingerprint of the coexistence of two exchange interactions. The exchange bias effect is not observed for higher doping of Fe.

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