I. INTRODUCTION

Spintronics is currently an active area of research because spin-based multifunctional electronic devices have several advantages over the conventional charge-based devices regarding data-processing speed, nonvolatility, higher integration densities, etc.\(^1\) The impending need to obtain such devices has led to the growing interest in developing and designing new spintronic materials. Starting from the initial works of Ohno et al.\(^2\) on Mn-doped GaAs, which is a ferromagnetic semiconductor with \(T_c \approx 110\) K, there have been continuous efforts to obtain such systems with high \(T_c\), preferably close to room temperature,\(^3\)–\(^5\) and also to provide a thorough understanding of the origin of ferromagnetism\(^6\)–\(^8\) in systems like Mn- and Cr-doped GaAs, InAs, GaN, and AlN. Earlier studies\(^9\) on some (II-VI)-based doped semiconducting systems like Mn-doped ZnTe and CdTe were not successful and resulted in \(T_c\) values only of the order of a few kelvin.

The possibility of designing a suitable spintronic material having simultaneously the properties of room-temperature ferromagnetism and 100% spin polarization or half metallic character has brightened after the advent of transition-metal-doped semiconductors like ZnO,\(^10\) SnO\(_2\),\(^11\) and TiO\(_2\).\(^12\) A wide range of contradictory experimental results, debating the success\(^13\)–\(^18\) versus failure\(^19\)–\(^23\) of obtaining a \(T_c\) above room temperature based on such dilute magnetic oxide systems, have injected much excitement about the origin of ferromagnetism in these systems. Among all these systems, ZnO belongs to the list of the most suitable candidates for spintronics application due to its abundance and environment-friendly nature and also due to its potential as a suitable optoelectronic material with a wide band gap (\(\sim 3.3\) eV) and high exciton binding energy of 60 meV. Earlier first-principles electronic structure calculations by Sato et al.\(^24\),\(^25\) suggested that transition-metal (TM) doped (TM=Ti, V, Cr, Mn, Fe, Co, Ni, Cu) ZnO compounds are ferromagnetic provided the TM doping produces carriers forming a partially filled spin-split impurity band. Theoretical calculations also indicate the possibility of designing a ZnO-based room-temperature ferromagnet obtained by n-type carrier doping (Ga\(_{1-x}\)Zn\(_x\)O),\(^25\) as well as by p-type carrier doping (Zn\(_{1-x}\)N\(_x\)),\(^26\) Most of the experimental results show that, among transition-metal dopants, Co-doped ZnO systems are ferromagnetic in both thin films as well as bulk materials.\(^13\),\(^16\),\(^17\) Also, there have been few reports of ferromagnetism in Mn\(_{1-\delta}\)Ga\(_\delta\)O.\(^27\) The ferromagnetism in the Mn-doped system is yet to be understood, as Mn in the +2 valence state does not dope any carrier into the ZnO system and hence, by first-principles studies,\(^24\) must lead to an antiferromagnetic ground state. However, the experimental success with a <4% Mn-doped ZnO thin film\(^28\) has posed a challenge to the theoretical understanding of ferromagnetism for such systems. Further experimental studies reveal the importance of defects such as interstitials and zinc and oxygen vacancies for the magnetic ordering in such systems.\(^14\),\(^13\) Regarding the experimental studies, it can be commented that the presence of long-range ferromagnetic ordering, especially the magnetic moment per cation and \(T_c\) depend largely on critical details of the sample preparation. Hence, in order to understand the exact ferromagnetic mechanism in such systems, there are several important issues to be resolved. First, the existence of room-temperature ferromagnetism must be related to some intrinsic origin and
it must not be due to some impurity phase or TM magnetic clusters. There are studies that advocate the presence of a segregated inverted-spinel phase in oxide-based dilute magnetic nanoparticle systems. This phase segregation apparently supports a magnetic network over the dimension of the crystal, resulting in a high-temperature ferrimagnetic phase. Some of the earlier studies correlate the existence of some such codoping cases with the observed results. Second, in most of the thin-film studies like Ref. 11, the magnetic moment per TM atom exceeds the spin-only moment for the corresponding pure TM atom. However, the nonreproducibility of some such studies in obtaining giant magnetic moments has strengthened the need for a proper explanation of the observed experimental results. Finally, the exact nature of the ferromagnetic interaction between the TM atoms must be probed both experimentally and theoretically.

The present theoretical understanding of ferromagnetism in zinc-oxide-based dilute magnetic oxide systems is far from complete. The currently existing explanations of the nature and origin of ferromagnetism in dilute magnetic oxide systems can be categorized as follows.

(a) The spin-split donor impurity band model proposed by Coey et al., where the longer ferromagnetic exchange can be mediated by polaronic percolation of bound magnetic polarons formed by point defects like oxygen vacancies. The defect-induced shallow donor levels get hybridized with the TM d band and thus stabilize the ferromagnetic ground state for such materials. This model can explain the giant magnetic moment observed for thin films and also the ferromagnetism observed for samples with extremely diluted concentrations of TM impurity, where there is no possibility of nearest-neighbor interaction and the ferromagnetic interaction must be mediated by some other agents.

(b) On the other hand, a recent first-principles-based study suggests that long-range ferromagnetic coupling can be obtained even in the absence of defects. In this study, the explanation of the observed ferromagnetism is given by a hybridization picture of super- and double exchange, where the interaction is mediated by the delocalized Zn s states. These authors could improve long-range ferromagnetic ordering in the Co-doped ZnO system by codoping it with Li, which induces a non-spin-polarized s-like state. Li codoping improves the ferromagnetic ordering by bringing the d band of the TM atom to the optimal position to initiate double exchange. So, according to this study, spin-split defect bands are not essential for ferromagnetism.

The above discussion suggests that the mechanism behind ferromagnetism in TM-doped ZnO is not yet fully understood. In the present work, we have investigated the nature of magnetism in the Fe-doped ZnO system, both experimentally and theoretically. In the Fe-doped ZnO system, there are very few evidences of ferromagnetism except with codoping. However, some such codoping cases are proved to be associated with the formation of nonstoichiometric spinel ferrite phases. From some recent studies, the magnetic anisotropy of the dopant cation is suggested to be a signature of intrinsic ferromagnetism in dilute magnetic oxide materials. From the studies of Venkatesan et al., it is evident that, next to Co, Fe doped in ZnO is also highly anisotropic in nature. This suggests the possibility of obtaining high-temperature ferromagnetism in Fe-doped ZnO. Hence, magnetism in Fe-doped ZnO seems to be both a promising and an interesting issue to investigate. Instead of bulk material, we concentrate on the magnetic properties of Fe-doped ZnO in nanocrystalline form, since a clear understanding of finite-size effects on the magnetic mechanism of such systems is essential for the development of high-density magnetic storage media with nanosized constituent particles or crystallites. The effective storage density in a particular device is mostly determined by the stability of the stored information in it, which is largely limited by the spontaneous magnetization reversal in the constituent nanoparticles. Earlier studies in the literature on the Co- (Ref. 43) and Mn-doped ZnO nanoparticles were mostly dominated by superparamagnetism, a widely studied finite-size effect.

In our studies, we have mainly focused our investigations in the following categories. We have prepared Fe-doped ZnO nanocrystals by the chemical pyrophoric reaction technique and carried out structural characterization with x-ray diffraction (XRD) and transmission electron microscopy (TEM), resulting in a clear nanocrystalline phase without any segregated impurity phase. Different magnetic measurements on this sample reveal a Tc > 450 K with a well-defined hysteresis loop at 300 K. We have tried to understand the obtained ferromagnetism in terms of the core-shell structure of the underlying nanoparticle system where the spins on the shell adjacent to the surface are in a canted disordered state and the shell is in a perfectly ordered ferromagnetic phase. For nanocrystalline systems, due to their high surface to volume ratio, a critical observation of surface microstructure and behavior of individual atomic (ionic) moments is essential to analyze the underlying magnetic mechanism. We have tried to explain the observed magnetism in terms of a model where surface defects (vacancies) mediate the intercore (interparticle) ferromagnetic exchange. We have also carried out electron paramagnetic resonance (EPR) and Mössbauer studies on the same sample to clarify issues like the percentage of aligned moments and the valence state of the TM ions.

Next, we have tried to put forward an explanation of the origin of ferromagnetism by analyzing the electronic structure of the studied system. The theoretical investigations of electronic structure are carried out in the framework of the tight-binding linearized muffin-tin orbital method in the atomic sphere approximation (ASA) within the local spin density approximation (LSDA). The effects of point defects such as oxygen vacancies and cation vacancies on the ferromagnetic properties of such systems are also investigated.

The paper is organized as follows. In Sec. II, we describe the preparation and structural characterization of the sample. In the succeeding Secs. III, IV, and V, we describe, respectively, magnetization measurements and EPR and Mössbauer studies. Possible explanations toward the observed results are provided in Sec. VI. Section VII is devoted to theoretical calculations and discussion of the results. The last section summarizes all the results with a conclusion.

II. SAMPLE PREPARATION AND STRUCTURAL CHARACTERIZATION

Most of the bulk studies on TM-doped ZnO polycrystalline materials reported in the literature were carried out by the chemical pyrophoric reaction technique.
ried out on materials prepared using the solid-state reaction technique. In the present work, we utilized chemical route for sample preparation, which, being a comparatively low-temperature technique, is useful to prepare single-phase nanocrystalline samples.

Nanocrystalline 10%-Fe-doped ZnO powders are synthesized by using the chemical pyrophoric reaction method. Requisite amount of \( \text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \) and \( \text{Fe(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \) are dissolved in distilled water depending on the percentage of Fe doping. This solution was heated at 190 °C with constant stirring. After some time triethanol amine is added in a ratio 4:1 with the metal ions in order to precipitate the metal ions with the amine. At the same temperature HNO\(_3\) is added to dissolve the precipitate and the resulting clear solution was allowed to evaporate with continuous stirring at 190 °C. After complete dehydration, we got the precursor powder, which after grinding was calcined at 350 °C. The calcination temperature was optimized by repeated investigations such that secondary iron oxide phase formation could be avoided. In a previous study, the optimization procedure for preparing single-phase nanocrystalline systems revealed that both the percentage of TM dopant and the calcination temperature are appropriate for avoiding secondary phase formation. The secondary phase in the present case was identified with \( \text{Fe}_3\text{O}_4 \). Transmission electron microscopy reveals that the powder samples are nanocrystalline in nature with a broad size distribution from 2 to 30 nm with an average size of 7 nm. The structural characterizations have been carried out by using a standard x-ray diffractometer (Philips, PW-1729) with monochromatic Cu Ka radiation and by a high-resolution transmission electron microscope (JEOL, JEM-2010, 200 kV).

Powder x-ray diffraction patterns for pure ZnO and 10%-Fe-doped ZnO are presented for comparison in Figs. 1(a) and 1(b), respectively. Due to the smaller particle size, the XRD peaks of the doped sample are broadened. The profile fitting of the data was performed by the Le-Bail method using the GSAS program to find out changes in the unit cell volume for different compositions of Fe. The fitted and the observed data along with the difference between them are indicated in Figs. 1(a) and 1(b). To investigate the solubility of Fe in ZnO, we have studied the XRD for four different compositions of \( \text{Zn}_x\text{Fe}_y\text{O} \) with \( x=0.0, 0.05, 0.1, \) and 0.15. Since, in this paper we concentrate on 10%-Fe-doped ZnO, the XRD data and the fits are shown for \( x=0.0 \) and 0.1 only. Except for \( x=0.15 \), none of the samples in the compositional range have shown any evidence of impurity phases. All the data can be fitted in the hexagonal wurtzite structure. With the increase of Fe content, the x-ray peak widths increase, suggesting a decrease in crystalline correlation. By cell parameter refinement using the Le-Bail method, we have calculated the evolution of the cell volume as a function of Fe concentration, plotted in Fig. 2. For the first three concentrations, the cell volume increases almost linearly, whereas for the fourth one (15%), it decreases, indicating that the limiting composition must be less than that. The situation is quite similar to results in Refs. 20 and 22.

FIG. 1. (a) Experimental (×) and Le-Bail fitted XRD data (solid line) for pure ZnO nanocrystalline sample. (b) Same graph for 10%-Fe- doped ZnO. For each case, the difference plots are shown below.

FIG. 2. Using the cell parameter refinement with Le-Bail fitting, the evolution of the cell volume is plotted as a function of Fe concentration to indicate the solubility of Fe in the ZnO matrix.

Figures 3(a) and 3(b) show the results of TEM characterization. Figure 3(a) shows a low-magnification TEM micrograph for the 10%-Fe-doped ZnO sample. The micrograph reveals a broad particle size distribution with the diameter of the particles ranging from 2 to 30 nm. High-resolution TEM micrographs are presented in Fig. 3(b), which shows that all the nanoparticles are single crystalline and free from any major lattice defects. The crystallinity and preferential orientation of each nanoparticle in the sample are confirmed from the selected area diffraction (SAD) patterns shown in Fig. 3(c). The SAD patterns obtained by focusing the beam on a few nanoparticles of the sample clearly indicates the single-crystalline nature of each nanoparticle. Also, it confirms that the nanocrystals are indeed in the wurtzite phase. The particle diameters are estimated from the low-resolution TEM data using the standard software (IMAGE-J) and the particle diameter histogram is fitted with a log-normal distribution.
With a successful synthesis and structural characterization, we proceed with the magnetic measurement for the 10%-Fe-doped ZnO nanocrystals. The percentage of doped TM is, of course, slightly on the higher side toward the cationic percolation threshold for this material. The average particle size, as obtained from the low-resolution TEM data, is around 7 nm, whereas a broad particle size distribution exists within the material. In the present situation, on average, surface atoms constitute nearly 15% of the total number of atoms, the percentage being more (≈25%) for smaller sizes of particles (1–7 nm). Hence, the influence of surface atoms on the magnetic behavior is not negligible. We have attempted to understand the observed behavior in terms of the core-shell structure for each nanoparticle. The surface atoms are different from the core ones, as the total number of exchange interactions will be less for them due to their lower coordination (fewer nearest neighbors). Moreover, there can be broken exchange bonds on the surface due to cationic vacancies, oxygen vacancies, or the presence of organic surfactant molecules. As proposed by Kodama et al., these broken exchange bonds are largely responsible for the surface spin disorder, the percentage of which is higher for smaller sizes of particles. Further, the basic reason for irreversibility in the magnetization is due to magnetocrystalline, magnetostatic, and shape anisotropies. Magnetocrystalline anisotropies for the surface and the core atoms are different due to the easy-axis nature of the anisotropy for the surface, as proposed by Néel, in contrast with the easy-plane anisotropy for the core. Hence, the magnetic behavior will be different for the surface and core atoms and will be dominated either by the core or by the surface depending on factors like the applied field, temperature, percentage of aligned spins, etc.

Earlier studies on Co-doped ZnO nanoparticles prepared by the vaporization condensation method and on Mn-doped ZnO nanoparticles prepared by the coprecipitation technique have observed a ferromagnetic behavior at low temperature and superparamagnetic behavior at high temperature. For some of the samples, depending on the preparation procedure, Curie-Weiss behavior is observed, confirming an antiferromagnetic ground state.

In our experimental observation, we have obtained room-temperature ferromagnetism for 10%-Fe-doped ZnO nanocrystals. The magnetic measurements were carried out using a Quantum Design MPMS superconducting quantum interference device magnetometer and a vibrating sample magnetometer (VSM). The temperature dependence of the magnetization is investigated for the sample (in the form of a pressed pellet) in both (zero-field-cooled (ZFC)) and (field-cooled (FC)) conditions for four different field values \( H = 100, 1000, 1500, \) and \( 5000 \) Oe, as depicted in Figs. 4(a)–4(d). The outward concave nature of all these magnetization curves confirms the non-mean-field-like behavior for the presently studied system, where the magnetic behavior is explained in terms of carrier-induced effects. The concave shape confirms the low carrier density and the localized nature of the carrier as well. From Fig. 4(a), it is evident that the transition temperature is above 320 K, the maximum permissible instrumental limit for us. With the gradual increase of the applied field value, the meeting point of the ZFC and FC curves shifts toward lower temperature and at a sufficiently high field, there will be absolutely no irreversibility. Figure 4(a) indicates that the system will be weakly ferromagnetic even at room temperature, unlike the other two recent studies, where the superparamagnetism is the pre-
dominant magnetic mechanism at high temperature. The $M$ vs $T$ curves obtained in the present study have a basic difference in their nature from superparamagnetism-dominated curves in Ref. 43 for Co-doped ZnO nanoparticles and from those in Ref. 53 for highly reduced Co-doped TiO$_{2-x}$ thin films, where the FC and ZFC curves diverge substantially at low temperatures. From the first three graphs, Figs. 4(a)–4(c), the ZFC curves all have a cusp which with the increase of applied field shifts toward lower temperature. For a magnetic system, a cusp in the ZFC curve may appear due to various reasons. It may result from nanoscale-related superparamagnetic behavior or from field-induced crossover from the ferromagnetic (FM) to the spin-glass (SG) state as observed in mixed-valence manganites. 54 To investigate the actual reason for the appearance of the cusp, we have measured the relaxation in the thermoremanent magnetization. The sample is field cooled in a field of 1000 Oe to 5 K, which is below the peak of the cusp temperature corresponding to this field [as can be seen in Fig. 4(b)], and then the field is switched off. The magnetization of the sample is measured using a VSM, as a function of time. The magnetization vs time data are plotted in Fig. 5(a), which indicates a considerable amount of relaxation within a time period of 7000 s. This curve rules out the possibility of cusp behavior in the ZFC curve due to superparamagnetic behavior as for superparamagnetic systems the relaxation is very fast, within the experimental time scale of hundreds of seconds. 55 Also, the time dependence of the thermoremanent magnetization can be fitted well with a stretched exponential function $M(t) = M_0 + M_r \text{exp}[-(t/\tau)^{1-n}]$, where $M_0$ is related to the intrinsic ferromagnetic-like component and $M_r$ relates to a glassy component contributing to the observed relaxation effect. The time constant $\tau$ and the parameter $n$ are related to the relaxation rate. Stretched exponential functions are usually used to describe the magnetic relaxation in spin glasses and cluster spin glasses. 56 We have also measured the same relaxation at 50 K (not shown) and have not observed any relaxation as it is above the spin-glass transition temperature.

![Figure 4](image1.png)

**FIG. 4.** Magnetization vs temperature curves for Zn$_{0.9}$Fe$_{0.1}$O in the field-cooled (FC) and zero-field cooled (ZFC) conditions for the applied field value (a) 100, (b) 1000, (c) 1500, and (d) 5000 Oe. (a) indicates that the ferromagnetic to paramagnetic transition temperature is well above room temperature. For the first three graphs, the system undergoes a spin-glass transition in the low-temperature regime.

![Figure 5](image2.png)

**FIG. 5.** (a) Relaxation of thermoremanent magnetization for the sample after field cooling it at a field value 1000 Oe to confirm the spin-glass behavior at low temperature. (b) Spin-glass arrangement of the spins due to surface spin disorder and the field- or temperature-induced crossover from the spin-glass to the ferromagnetic state schematically explained by means of the simple core-shell model, which is diagrammatically presented in this figure.

The existence of this spin-glass state may be explained in terms of a core-shell-type model for the spin structure of the underlying nanoparticle system in the following way. For a particular temperature and applied field, the core spins are aligned in a particular direction. For a given orientation of the core magnetization, there can be multiple metastable states [although, for convenience, only one is shown in Fig. 5(b)] for surface spin configurations, separated by rotational barriers, which can be crossed with increasing thermal energy. For a ZFC sample, at very low temperature, as a small field is applied [e.g., 100 Oe, as seen in Fig. 4(a)], due to canting of the surface spins in a disordered configuration, the system remains in a spin-glass state, as depicted in Fig. 5(b), where there is no long-range order. With the increase of temperature, the thermal energy helps the disordered surface spins to get themselves oriented (by providing the required energy to cross the barrier) along the resultant core magnetization direction and thus to drive the whole system to a
In Fig. 6(a), for the field values 1000 and 1500 Oe, we have calculated the dc susceptibility $\chi_0$ from the magnetization data and plotted it in a Curie-Weiss-like plot. It appears from the curves in Fig. 6(a) that above the temperature corresponding to the meeting point of the FC and ZFC curves (as can be seen from Fig. 4), both curves can be fitted with the Curie-Weiss-type linear behavior resulting in high negative Weiss temperatures. This may apparently indicate an antiferromagnetic ground state for the system. For an accurate determination of the exact nature of intrinsic magnetism for the system, we have plotted the inverse differential susceptibility $1/\chi_{\text{diff}}$ (taking the difference of the $M$ vs $T$ plots for 1500 and 1000 Oe) as a function of temperature in Fig. 6(b), since the differential susceptibility plots can more certainly decide about the exact ground state.\(^{33}\) From this plot, it is very obvious that there are two kinds of magnetic phases coexisting in the system. The dotted line in the figure corresponds to the paramagnetic Curie behavior ($C/T$ type) and the dashed line corresponds to a fit for ferromagnetic Curie-Weiss behavior [$C/(T−θ)$] with a positive $θ$ of 59.5 K. This situation implies that some randomized surface spins are always present in the system, giving rise to a paramagnetic contribution superimposed on the core-dominated ferromagnetism. This is indeed supported by the hysteresis loop measurements. The Curie-Weiss fit results in an effective magnetic moment of 0.334 $μ_B$ from the relation $μ_{\text{eff}} = (3k_B C/N_A)^{-1/2}$ ($N_A$ is the Avogadro number), which is much less than the theoretically calculated value. The moment per magnetic cation can be less due to several factors. Since the concentration of Fe is very close to the cationic percolation threshold, nearest-neighbor antiferromagnetic interaction (superexchange) between the Fe ions can lower the magnetic moment. Also, the presence of uncoupled Fe$^{3+}$ spins on the surface of the nanoparticles may lower the magnetic moment. The presence of any small randomly distributed cluster (consisting of Fe free spins or due to iron oxides) undetected by XRD can also be the cause for the same. Moreover, due to the nanostructured nature of the material, weaker interparticle exchange is also responsible for the low magnetic moment.

The $M$ vs $H$ hysteresis loops are presented in Figs. 7(a)–7(c). Figure 7(a) shows a comparison of the low- and high-temperature hysteresis loops. As expected, in low-temperature loops (2, 5, and 20 K), as seen in Fig. 7(b), the paramagnetic contribution is high (may be due to disordered Fe$^{3+}$ spins on the nanoparticle surface) and at 300 K that contribution is lowered. As is seen in Fig. 7(a), the sample has a well-defined hysteresis at room temperature with a coercive field of 94.4 Oe and a remnant magnetization of 0.0788 emu/g. The corresponding values at 5 K are 177.8 Oe and 0.177 emu/g. The saturation in magnetization at low temperature (2 K) is achieved at a very high field, as shown in Fig. 7(c). The magnetic moment per Fe as calculated from the 2 K magnetization data is $\sim 1.13 μ_B$ and at room temperature that value decreases down to $\sim 0.05 μ_B$. The obtained hysteresis at room temperature supports the fact that the magnetic behavior is weakly ferromagnetic and not superparamagnetic. To verify this in a different way, we have also plotted the $M/M_s$ ($M_s$ is the saturation magnetization) versus $H/T$ for the $M$ vs $H$ data at different temperatures, and all the curves remain distinct. For superparamagnetic systems, as is well known, the curves merge into a single one.\(^{43,55}\) This rules out the possibility of thermal-energy-induced spontaneous magnetization reversal as happens in the case of an assembly of single-domain particles leading to superparamagnetic behavior. More convincingly, the
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superparamagnetic limit for Fe-doped systems can be calculated by the expression for the relaxation time $\tau = \tau_0 \exp(E_A/V/k_B T)$, where the anisotropy energy density $E_A$ has a value of $5 \times 10^4$ J/m$^3$ for Fe, and $V$ and $k_B$ are the particle volume and Boltzmann constant, respectively. For superparamagnetic systems, taking $\tau_0 \sim 10^{-9}$ s and the typical measurement time to be $\sim 10^3$ s, at 5 and 300 K, the critical nanoparticle diameters for superparamagnetic behavior are 4 and 8 nm, respectively. Hence in the presently studied system, at 5 K, as there are very few particles of 4 nm diameter, there is no chance of obtaining superparamagnetism. At 300 K, although some of the particles are within the critical limit, as there is a wide size distribution, the system behaves as a ferromagnetic one. Moreover, unlike manganite$^{56}$ or ferrite$^{45}$ nanoparticles, the irreversibility obtained in this study is not an outcome of only surface spin disorders, an obvious signature of which is very high field irreversibility and shifted hysteresis loops as seen in Refs. 56 and 45. None of these signatures are seen in the present study. Hence, the ferromagnetism obtained might be an outcome of some intrinsic magnetic nature of the material studied. In addition to this, although we have obtained room-temperature ferromagnetism for our sample, the magnetic moment per Fe ion is much lower than the spin-only calculated limits. To investigate the actual reason for the observed ferromagnetism and low value of magnetic moment per Fe, we have carried two more magnetic studies, viz., EPR and FM resonance measurements, and also Mössbauer studies.

IV. EPR MEASUREMENTS

To probe the exact electronic configuration and oxidation state of the dopant TM ion more critically and also to understand the ferromagnetic mechanism of the sample at a microscopic level, electron paramagnetic resonance measurements were carried out for the present sample. The EPR experiments were carried out using a Bruker spectrometer at the X band ($\nu=9.60$ GHz) equipped with 100 kHz frequency modulation. The temperature was varied in the range 100–450 K using the variable temperature accessory Eurotherm B-VT 2000. Diphenyl-picrylhydrazyl (DPPH) was used as a reference for calibration of $g$ factors. The shape and the area of the EPR spectra were analyzed by standard numerical methods.

Electron paramagnetic resonance is an effective tool to investigate the origin and nature of observed ferromagnetism in a material. The temperature-dependent changes in the line position, integrated intensity, and linewidth in the EPR spectra can be used to obtain information about the range of magnetic ordering, spin fluctuations, spin-glass behavior, etc. In addition to this, the technique is used to extract information about the oxidation state of the dopant cation involved in the spin coupling.$^{44,57-59}$ Figures 8(a) and 8(b) show the EPR spectra of Zn$_{0.9}$Fe$_{0.1}$O recorded at room temperature and at 100 K. Both of the EPR spectra of Zn$_{0.9}$Fe$_{0.1}$O can be considered as a superposition of two overlapping signals, an intense and broad Gaussian signal and at 100 K. Both of the EPR spectra of Zn$_{0.9}$Fe$_{0.1}$O can be considered as a superposition of two overlapping signals, an intense and broad Gaussian signal and a narrow Lorentzian signal with $g_{\text{eff}}=2.005$. For the sake of convenience, the broad and narrow signals are designated as signal A ($g_{\text{eff}}=2.126$) and signal B ($g_{\text{eff}}=2.005$), respectively. In the temperature range of the investigations, the effective $g$ factor ($g_{\text{eff}}$) for the broad signal (signal A) was observed to be greater than 2, a clear signature of ferromagnetism in this material. At the highest temperature of investigation (450 K), the linewidth of signal A decreased to $\Delta H_{pp} \sim 1350$ G and $g_{\text{eff}}=2.0846$. Signal A is attributed to ferromagnetic resonance arising from exchange interactions between the Fe ions. It may be mentioned in passing that such temperature-dependent changes in the linewidth and line position of the resonance signal would not occur in the paramagnetic state. The observed broadening of the signal and a shift of the center of resonance to the lower fields is due to the presence of a nonhomogeneous local magnetic field, which modifies both the resonance field and the line shape of the signal. This effect is greater at lower temperatures.$^{60}$ The inset of Fig. 8 depicts a measure of the total number of spins participating in producing signals A and B. It is evident from the figure that, with increasing temperature, the number of spins taking part in ferromagnetic interaction (signal A) increases at the cost of decrease in the number of spins participating in paramagnetic signal B.
On lowering the temperature from 450 to 100 K, the line shape and the resonance field of signal $B$ remained practically unchanged; however, an increase in the signal intensity was observed. Whereas signal $A$ showed a gradual increase in the linewidth $\Delta H_{pp}=2000$ G at 100 K with lowering of temperature, signal $B$ does not show any such signature thus indicating its nonferromagnetic origin. Figure 9 depicts the temperature dependence of EPR spectra recorded in the range of 100–450 K. With the increase of the temperature, the line shape becomes more symmetric and the resonance field increases to higher fields. Due to the smaller value of the spin lattice relaxation time, the EPR of the Fe$^{2+}$ signal cannot be resolved within the experimental temperature range. The signal $B$ is attributed to the presence of an uncoupled Fe$^{3+}$ ion ($^6S_{5/2}$, $S=5/2$), the linewidth and position matching with those of Refs. 61 and 62, giving rise to an additional paramagnetic contribution. For more critical investigation of the ferromagnetic (signal $A$) and paramagnetic (signal $B$) contributions, the peak-to-peak linewidth $\Delta H_{pp}$, peak area, intensity, and resonance field or line position $H_r$ is plotted as a function of temperature for signal $A$ in Fig. 10(a). As expected for the FMR signal, the linewidth, area, and intensity decrease as a function of temperature, whereas the line position increases with temperature. However, below 300 K, as the signal is a combination of two spectra, determination of the line position may become erroneous. Hence, the line position is plotted only for temperatures greater than 300 K. It is evident from the EPR spectra, the system remains ferromagnetic up to 450 K. As there is almost no change in the linewidth and line position for signal $B$, we have plotted only the area and intensity for signal $B$ as a function of temperature in Fig. 10(b). Both of these quantities decrease with increase of temperature.

To rule out the possibility of formation of impurity phases during the synthesis, which may be responsible for the observation of the room-temperature ferromagnetism, EPR spectra were also recorded for high-purity Fe$_3$O$_4$ (identified with the secondary phase) and Fe$_2$O$_3$ samples at room tem-
perature (figure not shown). The EPR spectra of these compounds were much different than those observed under the present investigations.

Since EPR measurements have shown some signature of the presence of doped iron in two valence states Fe$^{2+}$ and Fe$^{3+}$, we wanted to resolve that issue by Mössbauer spectroscopic measurements.

V. MÖSSBAUER SPECTROSCOPY

To probe the local magnetic environment prevailing around the Fe sites and also to determine the oxidation state of Fe in the ZnO matrix, Mössbauer spectra were recorded for the sample as a function of temperature.

The $^{57}$Fe Mössbauer spectra were recorded using a conventional constant acceleration velocity drive and the temperature was varied in the range 4 – 300 K using a continuous flow cryostat. The spectra were recorded in transmission geometry with a $^{57}$Co(Rh) source.

Figure 11 depicts the Mössbauer spectra recorded at three different temperatures, viz., at 300 (room temperature), 12, and 4 K, along with the least-squares fitting. From all three spectra, the presence of uncoupled Fe$^{3+}$ is evident, since all of them indicate the presence of a paramagnetic doublet.$^{62-65}$ The doublet becomes more and more asymmetric with lowering temperature due to the change in the magnetic environment within the sample. The isomer shifts for the 300, 12, and 4 K spectra are 0.56, 0.62, and 0.55 mm/s, respectively. The initial increase and subsequent decrease of the isomer shift may happen due to the transition of the sample to the spin-glass state with lowering of temperature. This transition due to the freezing of the surface spins changes the local environment of the Fe$^{3+}$ ions and thus affects the $s$-electron density. More critical observation of the low-temperature Mössbauer data for 12 K in Fig. 12 indicates the presence of quadrupole splitting for both Fe$^{3+}$ and Fe$^{2+}$. In the same figure, we have also indicated the position of sextets. The observation of a distinct Fe$^{2+}$ signal is difficult due to its very short spin-lattice relaxation time. The values for the quadrupole splitting for both Fe$^{3+}$ and Fe$^{2+}$, as obtained from Fig. 12, are 0.73 and 1.4 mm/s, respectively.$^{65,66}$

Hence from both EPR and Mössbauer measurements we
have obtained evidence of the existence of both Fe\(^{3+}\) and Fe\(^{2+}\) within the sample. Our next aim is to qualitatively explore various possibilities to understand the current experimental scenario.

VI. DISCUSSION ABOUT THE PRESENCE OF Fe\(^{3+}\)

Usually, if Fe is present in the substitutional site in a defect-free ZnO crystal, the valence state of Fe will be +2. However, both EPR and Mössbauer results confirm the presence of uncoupled Fe\(^{3+}\) within the sample, giving rise to the associated paramagnetic behavior. In this section, we discuss the various possibilities for the presence of iron in both valence states for the Fe-doped ZnO system.

The uncoupled Fe\(^{3+}\) ions may be due to the presence of nearest-neighbor cationic vacancies and thus effectively doping holes in the system. In other words, if cationic vacancies (Zn for the present case) are present in the nearest-neighborhood of Fe\(^{2+}\) in the substitutional cationic site, to neutralize the charge imbalance, the valence state of Fe can be converted to +3. This can happen mostly on the surface of the nanoparticles, where the probability of the presence of vacancies is higher.

The increase in the intensity of the EPR signal with lowering of the temperature may be due to freezing of these Fe\(^{3+}\) spins. This observation is consistent with the increase in the paramagnetic contribution as seen in the low-temperature hysteresis loops. For Mn-doped ZnO nanoparticles, as seen in Ref. 44, the FMR signal was observed at room temperature for nominal 2 at. % Mn\(^{2+}\) in a ZnO matrix. Though the origin of ferromagnetism in these compounds is not totally understood, it was proposed that the exchange interaction between the Mn\(^{2+}\) ions was responsible for the ferromagnetism in these compounds. Recently, in Ref. 67, surface-vacancy-induced ferromagnetism was obtained for a series of oxide materials including ZnO. In the present situation also, defects may play important roles in obtaining ferromagnetism. A cation vacancy near Fe can promote Fe\(^{2+}\) into Fe\(^{3+}\) and also mediate the Fe\(^{2+}\)-Fe\(^{3+}\) exchange interaction. Since the TM doping percentage is slightly on the higher side toward the cationic percolation threshold, Fe\(^{2+}\)-Fe\(^{3+}\) exchange, although being less in number in comparison to the Fe\(^{2+}\)-Fe\(^{2+}\) interaction, may also be possible.

Another possible source of Fe\(^{3+}\) can be the presence of minute segregated impurity phases like spinel ferrites, remaining undetected by XRD. At room temperature, the well-known spinel ferrite ZnFe\(_2\)O\(_4\) is paramagnetic (with an anti-ferromagnetic ordering below 10 K) in a bulk sample with all the Fe\(^{3+}\) in the octahedral interstitial site in a close-packed lattice of oxygen. On the other hand, nanocrystalline nonstoichiometric ZnFe\(_2\)O\(_4\) can have Fe\(^{3+}\) in both tetrahedral and octahedral sites and can result in a ferrimagnet with high magnetic moments. However, for the present case, the EPR and Mössbauer studies reveal some more details. The line position, signal shape, and nature of evolution of the signal shape with temperature are different from those in the ferrimagnetic ferrite phase. Moreover, the EPR signal for Fe\(^{3+}\) is of paramagnetic nature with g = 2 and there is a possibility that EPR spectra may not resolve the signals for Fe\(^{3+}\) from the tetrahedral and octahedral sites, as can be obtained from NMR studies. Also, the isomer shift obtained for the paramagnetic doublet matches neither the tetrahedral nor the octahedral Fe\(^{3+}\) isomer shift values in nanocrystalline ferrimagnetic zinc ferrites. In the Fe-doped ZnO system, Fe ions are present in the tetrahedral site. If, due to the presence of the cation vacancy, the valence state changes to +3,
the crystal field no longer possesses tetrahedral symmetry and hence the isomer shift may not match the value corresponding to tetrahedral sites. Also, in Ref. 48 the associated secondary phase was Fe$_2$O$_3$, the formation of which reduced the value of magnetic moment of the sample. The presence of Fe$_3$O$_4$ and Fe$_2$O$_3$ in the present sample is already nullified by verification of EPR spectra of those compounds.

Hence, in the present studies, the ferromagnetism obtained may be defect induced. In the following section, we try to understand the present experimental situation with the help of ab initio electronic structure calculations.

VII. THEORETICAL INVESTIGATION

A. Structure and computational details

Pure ZnO crystallizes in the wurtzite structure, a hexagonal analog of the zinc-blende lattice, with a space group $P6_{3}mc$ (no. 186) with two formula units per unit cell, where each Zn atom is tetrahedrally coordinated with four other O atoms. The lattice constants are $a=b=3.2495$ Å and $c=5.2069$ Å and the atomic positions for Zn are $(0,0,0)$ and $(1/3,2/3,0.5)$ and for O are $(0,0,0.3408)$ and $(1/3,2/3,0.8408)$. The analysis of electronic structure and magnetic properties is carried out in the framework of the tight-binding linear muffin-tin orbital method in the atomic sphere approximation within the LSDA. The space filling in the ASA is achieved by inserting empty spheres at the interstitials and by inflating the atom-centered nonoverlapping spheres. The atomic radii are chosen such that the charges on the empty spheres are negligible and the mutual overlap between all kinds of combinations of interstitial and atomic spheres is within the permissible limit of the ASA. In order to study the effects of TM doping in this system, we have constructed a supercell with the size being dependent on the percentage of TM doping. In the present case, we have performed a $(2 \times 2 \times 2)$ supercell calculation with 64 atoms (including empty spheres) and 16 formula units of ZnO. To simulate a TM-doped system, we have replaced the appropriate number of Zn atoms with TM atoms. The size of the supercell is chosen to achieve the doping percentage comparable to our experimental data. For all these self-consistent calculations, the $k$-point mesh size is $(12,12,8)$. The calculations have also been carried out and verified with a smaller supercell with 32 atoms and with eight formula units of ZnO.

B. Results and discussion

In this section, we shall discuss the electronic structure of Fe-doped ZnO both with and without defects (i.e., Zn and O vacancies) in order to understand the origin of ferromagnetism in these systems. Although our calculations are for the bulk system, they will provide important insights about the origin of intrinsic ferromagnetism in the Fe-doped ZnO nanocrystals considered in this work.

In Fig. 13 we have displayed the paramagnetic density of states (DOS) for 12.5%-Fe-doped ZnO without any defects. The characteristic feature of the DOS is the deep Fe-derived states in the semiconducting gap of ZnO. These states are broadened due to hybridization with O $p$ states. The expected valence state of the substitutional Fe atom will be $+2$ it will be in the $d^5$ configuration. The Fe $d$ states in the tetrahedral coordination gets split into twofold-degenerate $e$ levels and threefold-degenerate $t_2$ levels with the $e$ levels being lower in energy. So, out of the available six electrons per Fe, four electrons are accommodated in the low-lying $e$ level and the rest into the $t_2$ levels in the non-spin-polarized calculation as can be seen in Fig. 13(a).

The resulting partially filled $t_2$ levels have an appreciable density of states at the Fermi energy, $D(E_F) \sim 12.84$ states/eV/Fe making the paramagnetic state unstable and susceptible to the Stoner instability. Stability, however, can be achieved by incorporating magnetic order into the system with spin polarization and thereby resulting in a difference between the population of the majority and minority spin channels due to electronic rearrangement. The results of the spin-polarized calculations are displayed in Fig. 13(b). We find that the majority spin channel (spin down) is fully occupied, while the minority spin channel is only partly occu-
pied resulting in a half-metallic ferromagnet with 100% spin polarization. We note from the figure that the exchange splitting is much larger in comparison to the crystal field splitting and the system therefore favors a high spin configuration with the various levels serially filled up as $e\downarrow (2), t_2\downarrow (3), e\uparrow (1)$ (where the numbers in parentheses indicate the number of electrons). Hence, the spin-down channel completely filled while the spin-up $e\uparrow$ level is half filled resulting in a net integral magnetic moment of $4\mu_B$. However, such a situation cannot stabilize ferromagnetism in the presence of Coulomb correlations. If the Coulomb correlations are included, as in the LSDA+ $U$ method, the half-filled $e\uparrow$ band will split and the system will be an insulator. In fact, a recent LSDA+$U$ calculation\textsuperscript{73} indicated an insulating antiferromagnetic state to be more stable in comparison to the ferromagnetic state. Hence, from the preceding discussion we conclude that Fe-doped ZnO is unlikely to stabilize in a ferromagnetic state. In view of our experimental results, as discussed in the previous section, supporting the presence of defects in the system, it is very likely that the defects play a crucial role to stabilize ferromagnetism in this system. In the following section we have, therefore, analyzed the electronic structure of Fe-doped ZnO in the presence of defects, viz., (i) O and (ii) Zn vacancies.

2. Fe-doped ZnO with defects

Figure 14 displays the total as well as the partial DOS for 12.5\%-Fe-doped ZnO with 12.5\% O vacancies [top, (a) and (b)] and 12.5\% Zn vacancies [bottom, (c) and (d)] with a single Fe and a single vacancy per supercell. It is evident from Figs. 14(a) and 14(b) that the oxygen vacancies produce shallow donor states while the zinc vacancies produce shallow acceptor states. These states are delocalized due to the hybridization with the Fe $d$ states. An oxygen vacancy adds electrons to the system and thereby effectively dopes $n$-type carriers into the system. These electrons are accommodated in the minority spin channel (spin up), so in comparison to the Fe-doped ZnO, the minority spin channel has fully occupied $e\uparrow$ level and singly occupied $t_2\uparrow$ level as can be seen in Fig. 14(b). On the other hand Zn vacancies dope holes into the system, resulting in a completely empty minority spin channel (spin up) and one hole in the majority spin channel (spin up) [see Fig 14(d)]. Such a situation is conducive for ferromagnetism mediated by double exchange as argued by Akaï\textsuperscript{7} where, if a $d$ orbital is partly occupied, then the electrons in that orbital are allowed to hop to the neighboring $d$ orbitals, provided the neighboring Fe atoms are in parallel spin configuration. Thus the $d$ electrons lower the kinetic energy by hopping in the ferromagnetic state. On the other hand, if the $d$ orbital is completely occupied then this reduction of energy via hopping is not possible and the system energy gets lowered by antiferromagnetic spin alignment of the neighboring Fe atoms by superexchange.\textsuperscript{74} The system can appreciably lower its energy by double exchange when it is near half filling with a sufficient (usually small) number of holes (electrons). So we expect that hole doping by Zn vacancies will be more effective to stabilize ferromagnetism in this system.

In order to explore the possibilities of ferromagnetic versus antiferromagnetic ordering in Fe-doped ZnO in the presence of O or Zn vacancies, we have performed spin-polarized density functional calculations with (i) two Fe spins parallel to each other, the ferromagnetic configuration and (ii) two Fe spins antiparallel to each other, the antiferromagnetic configuration in the presence of O and Zn vacancies. We have also calculated the energy difference $\Delta E$ as a function of Fe-Fe separation. This energy difference $\Delta E$ is also a measure of the interatomic exchange interaction and in the framework of mean-field theory is also proportional to $T_c$ for the system. The results of our calculation are displayed in Fig. 15. We note both for the O vacancy as well as the Zn vacancy that the nearest-neighbor Fe-Fe interaction is ferromagnetic; however, this exchange coupling is much stronger for the hole-doped system with Zn vacancy, according to our expectation. The further-neighbor interactions are antiferromagnetic for the electron-doped system (with oxygen vacancy), suggesting a lower probability for the electron-doped system to be a ferromagnet in agreement with the recent LDA+$U$ calculations.\textsuperscript{73} On the other hand, the further-
neighboring interactions for the hole-doped system with a Zn vacancy is ferromagnetic but are much weaker in comparison to the nearest-neighbor interactions. Such short-range exchange interaction indicates the formation of Fe clusters and the possibility of intrinsic ferromagnetism in Fe-doped ZnO to be driven by percolation.

In conclusion, our calculations indicate that hole doping, possibly by Zn vacancies, is crucial to stabilize ferromagnetism in Fe-doped ZnO. As we have argued in the experimental section also, for Fe-doped ZnO nanocrystals, cation vacancies may be present and thereby effectively dope holes into the system. A possible signature of hole doping may be the presence of Fe$^{3+}$ in our samples as confirmed by EPR measurements and Mössbauer spectroscopy.

VIII. CONCLUSIONS

We have successfully synthesized Fe-doped ZnO nanocrystals and structurally characterized them by XRD and TEM. The magnetic measurements show the presence of room-temperature ferromagnetic order within the system. The presence of spin-glass behavior at low temperature is explained by a core-shell spin structure of the individual underlying nanoparticle system. We have tried to understand the exact origin of ferromagnetism with the help of local probes like EPR and Mössbauer spectroscopy, which indicates the presence of the dopant cation in both valence states +2 and +3. The ab initio electronic structure calculations for the same material suggest that hole doping is crucial to promote ferromagnetism in this system, and the presence of Fe$^{3+}$ in our samples is a possible signature of hole doping induced by Zn vacancies.

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