Chapter 4

OPTICAL, HYPERFINE AND MAGNETIC BEHAVIOUR OF Fe-DOPED ZnO NANOCRYSTALS
4.1 Introduction

Wide band gap semiconductors sparsely doped with magnetic elements (diluted magnetic semiconductors; DMSs) are in the focus of intense research due to the possibility of using such materials for spintronic applications [1]. In recent decades considerable research attention has been paid to diluted oxide based magnetic semiconductors with high Curie temperature. Among all the oxide DMSs, zinc oxide (ZnO) having high excitonic binding energy has received enormous research interest due to its widespread applications [2] as has been mentioned in the previous chapter.

Based on the early experimental results and theoretical predictions, ZnO has been doped with transition group elements to exploit the spin of an electron associated with its charge for potential applications in spintronics and the observation of room temperature ferromagnetism in transition metal (TM) doped samples had initiated a surge of intense research activities [3, 4]. Thereafter, several groups have supported the observation of room temperature ferromagnetism in transition metal ion doped ZnO samples [5-8]. But quite a few controversial results have also been reported. Jin et al. did not observe any signature of ferromagnetism in their transition metal doped ZnO thin film prepared by the laser molecular beam epitaxy method [9]. Sati et al. however have shown intrinsic ferromagnetism in Zn_{1-x}Co_xO epitaxial thin films [10]. Kim et al. have found room temperature ferromagnetism in Zn_{1-x}Co_xO thin film and suggested that it results from impurity present in the sample in the form of Co clusters [11]. Kolesnik et al. did not find ferromagnetism in transition metal ion doped polycrystalline single phase ZnO sample but the observed ferromagnetic order in cobalt and iron doped ZnO samples prepared under selected synthesis conditions was assigned to the secondary phases present in the samples [12]. An experimental and theoretical study on Zn_{1-x}Co_xO (x = 0.05, 0.1 and 0.15) polycrystalline samples by Risbud et al. has shown that the nearest-neighbour interaction in the system is antiferromagnetic and
ferromagnetic order can occur only in the presence of additional hole doping [13]. A thorough computational study by Spalidin on Co and Mn doped ZnO system also showed that ferromagnetism is not possible without additional carrier doping; doping ZnO simultaneously with Co and Cu was shown to be necessary to achieve ferromagnetism [14]. Later, an experimental work by Jayakumar et al. had shown existence of room temperature ferromagnetism in ZnO samples doped simultaneously with Co and Cu whereas the sample doped with only Co was paramagnetic [15]. However Shim et al. reported that room temperature ferromagnetism in ZnO co-doped with Fe and Cu was due to a secondary ZnFe$_2$O$_4$ phase [16]. Experimental work by Hong et al. indicated that the presence of defects such as vacancies might be responsible in getting magnetic order in ZnO [17]. Similar conclusion was made by Sundaresan et al. where the presence of vacancies at the surface of the nanomaterials was argued to be the reason for getting room temperature ferromagnetism [RTFM] in nonmagnetic oxides [18]. A theoretical study by Wang et al. on ZnO thin film and nanowire has shown that presence of Zn vacancy is essential to obtain magnetism in ZnO that has not been doped with any transition metal impurity [19]. Karmakar et al. had reported weak ferromagnetism at room temperature in Fe-doped ZnO nanocrystals; the presence of Fe$^{3+}$ in such system was argued to be due to hole doping in the system by Zn vacancies that can favour stable ferromagnetic ordering in the Fe-doped samples [20]. Straumal et al. claimed that room temperature ferromagnetism in pure and Mn doped ZnO thin film is associated with vacancies at grain boundaries [21]. Tamura et al. found RTFM in Fe doped ZnO thin film while Mn and Co doped ZnO did not show any ferromagnetic behavior and suggested that half filled 3D band in the mid-gap of ZnO is responsible for RTFM in the case of Fe doped ZnO [22]. Singhal et al. have reported weak ferromagnetism at room temperature in colloidal Fe-doped ZnO nanocrystals and described this as its intrinsic property [23]. A
recent report on polycrystalline Fe-doped ZnO nanorod by Kumar et al. has shown weak ferromagnetic behavior at room temperature [24].

Such controversial results clearly indicate that the cause of room temperature ferromagnetism in diluted magnetic semiconductor is still debated and further experimental and theoretical studies are needed to arrive at a definite conclusion. Since nanostructured materials contain a large concentration of defects in the form of vacancies at the grain boundaries they are ideal materials to study the role of vacancy in getting room temperature ferromagnetism in different oxide systems.

In the present work, a comprehensive study was carried out on Fe-doped ZnO nanostructures prepared by a chemical route. Different techniques were used to confirm the existence of room temperature ferromagnetism in the samples and ascertain the presence of vacancies in them as reported by many workers. The structural characterization of the samples was carried out by x-ray diffraction (XRD) and transmission electron microscopy (TEM). The optical characterization of the samples was done by Fourier transform infrared (FTIR) spectroscopy, photoluminescence (PL) and UV-visible spectroscopy. Magnetic properties of the Fe-doped samples were carried out by a vibrating sample magnetometer and a Faraday balance magnetometer. Local structure around the doped Fe atoms was investigated using $^{57}$Fe Mössbauer spectroscopy. The samples were also studied by positron annihilation lifetime spectroscopy (PALS) technique to ascertain the presence of cation vacancy in the system. Room temperature ferromagnetism has been observed in the Fe doped samples. The presence of cation vacancy in ZnO structure as detected by positron annihilation technique has been shown to be a possible reason for getting room temperature ferromagnetism in the Fe-doped samples.

4.2 Experimental details
Zn$_{1-x}$Fe$_x$O (x = 0.03, 0.05 and 0.07) nanocrystalline samples with different atomic fraction of iron were prepared by the chemical coprecipitation method. Required amount of Zn(NO)$_3$.6H$_2$O and Fe(SO$_4$)$_2$.7H$_2$O were dissolved in Milli-Q water. The solution was stirred vigorously at 60 °C and then it was cooled down to room temperature. After that, sodium dodecyl sulphate (SDS) was added to the solution and the whole solution was hydrolyzed by dropwise addition of NaOH under vigorous stirring. The obtained precipitate was washed several times and was heat treated in air at 200 °C for eight hrs. The percentages of Fe and Zn in the samples were checked by a Perkin Elmer make inductively coupled plasma atomic emission spectrometer (ICP- AES). The phase purity of the prepared samples was established by x-ray diffractometry (Bruker D8 Advance diffractometer using a Cu K$_{\alpha}$ source, λ = 1.54056 Å) and their morphological characterizations were made by transmission electron microscopy (JEOL 2010, operated at 200 kV). The selected area electron diffraction (SAED) measurements and energy dispersive x-ray analysis (EDX) of the samples were also carried out.

Fourier transform infrared (FTIR) spectra of all samples were taken with a Perkin Elmer spectrum GX spectrometer in the frequency range of 2500 – 400 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. Photoluminescence (PL) spectra were recorded in a Perkin-Elmer LS-55 luminescence spectrometer. UV–visible absorption spectra were taken on a Shimadzu UV – 1601 PC spectrophotometer. Dc magnetic susceptibility measurements of the samples were carried out in the temperature range 300 to 14 K with a sensitive Faraday balance magnetometer. The low temperature environment was created with the help of a closed cycle helium cryo-cooler of APD, USA. Magnetization measurements were taken by a vibrating sample magnetometer (VSM) of Cryogenics, UK. Mössbauer measurements were carried out in a standard PC-based multichannel analyzer with 1024 channels working in the constant acceleration mode. A 10 mCi $^{57}$Co in Rh matrix was used as the radioactive source. The
system was calibrated with a high purity iron foil of thickness 12 μm. The low temperature measurements were recorded by using a Janis, USA make closed cycle refrigerator fitted with a special anti-vibration stand. The spectra thus obtained were fitted using a least squares fitting programme assuming Lorentzian line shapes [25]. Positron annihilation lifetime measurements were carried out using a fast - fast coincidence system consisting of two 1 inch tapered off BaF$_2$ scintillators coupled to XP 2020Q photo multiplier tubes. The prompt time resolution of the system using a $^{60}$Co source with $^{22}$Na gate was 260 ps. The lifetime spectra were deconvoluted using the code PATFIT 88 after incorporating necessary source corrections [26].

4.3 Results and discussion

4.3.1. Structural studies

Figure 4.1: XRD patterns of Zn$_{1-x}$Fe$_x$O ($x = 0.03, 0.05, 0.07$) samples. The mark (*) shows impurity phase.

*Figure 4.1: XRD patterns of Zn$_{1-x}$Fe$_x$O ($x = 0.03, 0.05, 0.07$) samples. The mark (*) shows impurity phase.*
The XRD patterns of Fe-doped ZnO nanocrystalline samples with different atomic fraction of
dopant ion (x = 0.03, 0.05 and 0.07 which are denoted hence onwards as ZF3, ZF5 and ZF7
respectively) are shown in Figure 4.1. The observed diffraction peaks have been compared
with the standard JCPDS files of ZnO, which indicates formation of wurtzite phase in all the
samples. In the sample ZF3, no additional peak apart from that corresponding to ZnO is
detected. In the samples ZF5 and ZF7 a peak of small intensity is seen at 32.7° (d = 0.1753
Å) which could not be identified. In the sample ZF 7, the additional peak at 35.25° (d =
0.1873 Å) has been identified as due to a small fraction of ZnFe$_2$O$_4$ secondary phase. No
peak corresponding to α-Fe, α-Fe$_2$O$_3$, γ-Fe$_2$O$_3$ or Fe$_3$O$_4$ could be detected in any of the
samples. A shift towards lower angle has been observed for all strong peaks with increase in
Fe concentration in the ZnO structure. Similar observation has been reported by other
workers also and has been interpreted as due to incorporation of dopant ions into the lattice of
the host material [27]. Apart from shifting, the peaks were also found to be broadened with
increase in concentration of iron in ZnO. This has been explained as due to reduction of grain
size and development of strain in the ZnO lattice with incorporation of Fe atoms. The average
grain sizes of the samples were estimated from the broadening of the diffraction peaks using
the Debye-Scherrer equation

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

(4.1)

where $\lambda$ is the wavelength of the x-ray radiation, β is the FWHM of the peak and $\theta$ being the
Bragg angle at the peak position. The estimated particle sizes were 28 nm, 24 nm and 18 nm
for the samples ZF3, ZF5 and ZF7 respectively. It appears that incorporation of Fe in the ZnO
structure reduces the grain growth that causes reduction of average grain size as reported by
others also [28, 29].
Transmission electron micrographs of the sample ZF 5 is presented in Figure 4.2. As can be seen (Figure 4.2 (a)) the particles are more or less spherical having a distribution of size between 15 to 35 nm. The average particle size obtained matches well with the size estimated from the XRD line broadening. The selected area electron diffraction (SAED) pattern (Figure 4.2 (b)) shows the crystal structure of the sample.

Figure 4.2 (a) TEM image of ZF5, and (b) SAED pattern of the same sample.
4.2(b)) shows the crystalline nature of the prepared sample. Figure 4.3(a) shows the high resolution TEM image of a selected zone of the sample.

Figure 4.3: (a) HR-TEM image, and (b) EDX spectrum of ZF5 sample.
The clear fringe pattern indicates that the particles are single crystalline in nature and are free from major lattice defects. The elemental composition of the sample was checked by energy dispersive x-ray analysis (Figure 4.3(b)), which confirms the presence of only Zn, Fe and oxygen in the sample. The concentration of Fe as measured by ICP-AES technique in the samples ZF 3, ZF 5 and ZF 7 was found to be 2.96, 5.18 and 6.81 atomic percentage respectively. This confirms that the prepared samples are having the intended stoichiometry.

4.3.2. Optical studies

Fourier transform infrared spectroscopy (FTIR) gives information about functional groups present in a compound along with the molecular geometry and inter or intra molecular interactions. Figure 4.4 shows the FTIR spectrum of Zn$_{1-x}$Fe$_x$O samples. The most prominent band at 460 cm$^{-1}$ is assigned to stretching vibration of Zn-O, which also confirms ZnO
wurtzite structure formation [30]. The two absorption peaks at 1125 cm\(^{-1}\) (C-O) and 1385 cm\(^{-1}\) (-SO\(_2\)-O-) confirm the presence of SDS at the surface of nanoparticles.

Photoluminescence (PL) spectroscopy is an important tool to characterize the optical properties of a semiconductor. PL intensity may be directly correlated with the defect density in a fluorescent material. The room temperature PL spectra of Fe-doped ZnO nanocrystalline samples are shown in Figure 4.5(a). As can be seen from the figure, all the samples have shown a dominant peak around 380 nm. This peak in the UV region is typically observed in ZnO nanocrystalline materials and has been assigned to the near band edge emission (NBE) since the energy corresponding to this peak is almost equal to the band gap energy of bulk ZnO [31]. A close look at Figure 4.5(a) reveals a blue shift of the UV peak position in the Fe-doped samples, which confirms incorporation of Fe in the ZnO structure. The other weak luminescence band at 422 nm is attributed to defect related deep level emission.
corresponding to radiative transition of electron from the zinc interstitial defect level to the valence band [32]. Similar luminescence band was observed in our earlier work on nanocrystalline pristine ZnO [33]. A clear reduction in intensity of this band is seen in the sample ZF3 in comparison with the pristine ZnO sample indicating a reduction of defect density. The intensity corresponding to this emission again increases in the samples ZF5 and ZF7. The reason for such increase could be due to formation of some kind of additional defects as the dopant concentration increases.

The UV-visible spectra of the samples have been shown in Figure 4.5(b). From the figure, blue shift in absorption edges can be seen in the Fe-doped samples. Since the particle sizes of the present samples are much bigger than the sizes for which quantum confinement is prominent, the observed blue shift can not be assigned to the size effects. This shift most
probably occurs due to band structure deformation caused by the incorporation of Fe$^{3+}$ ions in the lattice [34-36].

Figure 4.6: Variation of (a) susceptibility ($\chi$) and (b) $\chi T$, with temperature.
4.3.3 Magnetization studies

Figure 4.6 (a) shows the temperature dependent dc susceptibility behavior of Zn$_{1-x}$Fe$_x$O nanocrystalline samples. As can be seen from the figure, the value of susceptibility for the sample ZF5 is more than that for the sample ZF3 (particularly below 150 K) which is expected as the sample ZF5 contains higher concentration of Fe. The lower value of susceptibility for the sample ZF7 in comparison with that for the sample ZF5 at lower temperature (~ 20 K) has been assigned to the presence of small fraction of secondary phase (zinc ferrite) in the sample ZF7 that is essentially antiferromagnetic having a Neel temperature of the order of 10 K. However the presence of ferromagnetic interaction is evident from the non-linear nature of the $\chi T$ vs T graph that has been discerned in Figure 4.6 (b) [37].

![Figure 4.7: Room temperature M-H loop of ZF3 and inset shows the enlarged central part of the loop.](image-url)
Figure 4.7 shows results of M-H measurement of the sample ZF3 at room temperature. A clear hysteresis loop has been observed indicating ferromagnetic nature of the sample. From the loop, the remanant magnetization and coercive field were estimated to be $5.15 \times 10^3$ emu g$^{-1}$ and 1.984 kOe respectively. It may be noted the magnetization value did not show saturation even after applying a magnetic field of 7 T. This indicates presence of magnetic relaxation in the sample. The very fine particles present in the sample undergoing superparamagnetic relaxation at room temperature could be the reason for not getting a saturated value of magnetization.

4.3.4 Mössbauer studies

To explore the local environment and ionic state of iron in the doped ZnO samples they were characterized by $^{57}$Fe Mössbauer spectroscopy. The sample ZF3 did not show appreciable absorption. Figure 4.8 (b, & a) shows typical spectra recorded for the sample ZF5 at room temperature and at 20 K. The sample ZF7 showed similar doublets corresponding to the paramagnetic phase. The value of isomer shifts (IS) at room temperature obtained for ZF5 and ZF 7 are 0.32 mm/s and 0.54 mm/s respectively. The higher value of isomer shift of the sample ZF7 compared to that of the sample ZF5 indicates lower s-electron density in the sample. The observed isomer shifts indicate that the valence state of iron in the samples is Fe$^{3+}$. This could be due to the presence of nearby cationic vacancies at the substitutional sites, which trigger conversion of Fe$^{2+}$ to Fe$^{3+}$ to neutralize the charge imbalance [20]. The quadrupole splittings (QS) obtained for the samples ZF5 and ZF7 are 0.67 mm/s and 0.75 mm/s respectively. The higher quadrupole splitting for ZF7 indicates enhancement of electric field gradient around Fe probe atoms as more Fe atoms are introduced in the ZnO lattice. The IS and QS for the sample ZF5 at 20K were 0.39 mm/s and 0.94 mm/s respectively. The small increase in isomer shift respect to that at the room temperature is due to second order Doppler shift. It may be noted that though magnetization studies indicated the ferromagnetic nature of
the samples, the samples ZF5 and ZF7 showed clear doublets instead of a sextet pattern usually obtained for a ferromagnetic material.

The persistence of a doublet pattern even at 20 K for the sample ZF5 (Figure 4.8 (a)) ruled out the presence of superparamagnetic (SPM) relaxation in the sample. A sextet pattern was expected to develop at the cost of the doublet intensity if SPM particles were present. It may also be noted that M-H measurement of the sample ZF3 at room temperature indicated presence of SPM particles in the sample as the magnetization value did not saturate even at 7 T field. This apparent discrepancy between the results obtained from Mössbauer and magnetization measurements could be explained as due to the huge difference between the measurement time scales of the two techniques (~ 100 sec for VSM and ~ 10^{-8} sec for Mössbauer spectroscopy).
4.3.5 Positron annihilation studies

To confirm the presence of Zn vacancy in the samples and how the overall defect concentration varies with the concentration of the dopant atoms, the samples were examined by positron annihilation lifetime spectroscopy. The lifetime of positrons in a material depends on the average electron density at annihilation sites. If defect in the form of vacancy or void is present in a sample the electron density at the defect site will be less resulting in a longer positron lifetime. In nanocrystalline materials grain boundaries act as sink and source for such kind of defects and are strong trapping center for positron. Therefore in nanocrystalline materials having grain size smaller than the diffusion length of positrons (~ 52 nm in ZnO), positrons generally traverse through the grain and annihilate at the grain boundaries [38]. So
positron annihilation lifetime study can give vital information regarding defects present at the grain boundaries in nanomaterials.

Table 4.1 Positron annihilation lifetime and intensity values of the prepared samples.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
<th>$\tau_3$ (ns)</th>
<th>$I_1$ (%)</th>
<th>$I_2$ (%)</th>
<th>$I_3$ (%)</th>
<th>$\tau_m$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>0.186 ± 0.005</td>
<td>0.394 ± 0.0105</td>
<td>3.47 ± 0.096</td>
<td>60.25 ± 2.8</td>
<td>37.49 ± 2.7</td>
<td>2.2 ± 0.33</td>
<td>0.005 0.0105 0.096 60.25 ± 2.8 37.49 ± 2.7 2.2 ± 0.33 0.338</td>
</tr>
<tr>
<td>ZF 3</td>
<td>0.171 ± 0.005</td>
<td>0.376 ± 0.0077</td>
<td>3.44 ± 0.091</td>
<td>51.28 ± 2.54</td>
<td>46.43 ± 2.51</td>
<td>2.28 ± 0.34</td>
<td>0.004 0.0077 0.091 51.28 ± 2.54 46.43 ± 2.51 2.28 ± 0.34 0.340</td>
</tr>
<tr>
<td>ZF 5</td>
<td>0.177 ± 0.004</td>
<td>0.385 ± 0.0094</td>
<td>3.34 ± 0.10</td>
<td>58.61±2.6</td>
<td>39.47 ± 2.6</td>
<td>1.91 ± 0.32</td>
<td>0.004 0.0094 0.10 58.61±2.6 39.47 ± 2.6 1.91 ± 0.32 0.320</td>
</tr>
<tr>
<td>ZF 7</td>
<td>0.185 ± 0.004</td>
<td>0.396 ± 0.011</td>
<td>3.82 ± 0.12</td>
<td>65.12 ± 2.6</td>
<td>33.07 ± 2.6</td>
<td>1.7 ± 0.31</td>
<td>0.004 0.011 0.12 65.12 ± 2.6 33.07 ± 2.6 1.7 ± 0.31 0.316</td>
</tr>
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</table>

The obtained positron lifetime spectra of the samples were deconvoluted with three lifetime components $\tau_1$, $\tau_2$ and $\tau_3$ with corresponding intensities $I_1$, $I_2$ and $I_3$ respectively. The obtained lifetime parameters are shown in Table 4.1. The shortest lifetime $\tau_1$ is attributed to positron annihilation at the grain boundaries. The obtained $\tau_1$ values in the present case are less than the positron lifetime in a monovacancy (~ 237 ps) but are larger than the bulk lifetime of positron (158 ps) in ZnO [39]. Therefore, $\tau_1$ corresponds to an admixture of positron lifetime in monovacancies at grain boundaries and that for annihilation with free electrons residing there. The value of $\tau_2$ in the present case varies between 376 to 396 ps which is much larger than the reported lifetime of divacancy (260 ps) in ZnO [40]. Therefore $\tau_2$ has been assigned to annihilation at the free space at the intersections of different grains such as triple junctions. The longest lifetime $\tau_3$ is assigned to pick-off annihilation of ortho-positronium formed at large voids in the intercrystalline region.

Both zinc and oxygen vacancies are present in ZnO [41]. Out of these only Zn vacancies can be detected by positron annihilation technique because they have negative charge state and act as strong trapping centers for positrons. To estimate the overall defect
(vacancy) concentration and its variation in the samples the mean positron lifetime ($\tau_m$) was calculated using the relation

$$\tau_m = \frac{\tau_1 I_1 + \tau_2 I_2 + \tau_3 I_3}{I_1 + I_2 + I_3}$$

(4.2)

A decreasing trend in $\tau_m$ can be noticed (table 4.1) with increasing dopant concentration in the sample. This clearly indicates a gradual reduction of overall defect concentration in the samples with increase in dopant concentration. However, all the $\tau_m$ values are quite high than the bulk lifetime of positron in ZnO (158 ps), which confirm the presence of large vacancies in the samples.

### 4.4 Conclusion

We have successfully synthesized Fe-doped ZnO nanocrystalline samples at low temperature by using a coprecipitation method. XRD and TEM studies confirmed the phase purity and crystallinity of the samples. PL measurements gave a blue shift of the band edge emission peak in the Fe-doped samples and showed signature of the presence of defects in the samples. UV-visible absorption spectra of the samples also showed blue shift of the absorption edges with incorporation of Fe in the ZnO structure. Magnetization measurements by VSM technique at room temperature gave typical M-H loops indicating room temperature ferromagnetism in the Fe-doped ZnO samples. Dc susceptibility measurements by a precision Faraday balance magnetometer also indicate ferromagnetic interaction in the samples. However Mössbauer spectra of the samples showed doublets at room temperature. Hyperfine parameters obtained from Mössbauer data indicate valance state of iron as Fe$^{3+}$. Positron annihilation results confirm the presence of Zn vacancies in the pristine as well as in the Fe-doped samples. Thus the present work confirms the presence of room temperature ferromagnetism in the Fe-doped ZnO nanostructure and supports the conjecture that Zn vacancy may be responsible for getting the ferromagnetic order.
References


