Chapter-6

6. Magnetic measurements

Magnetic measurements of the as fabricated samples were carried out by utilizing magnetic force microscopy (MFM) and super conducting interference device (SQUID). For MFM measurements, Mn and Cr doped ZnS samples were coated on glass substrate with area 1cm x 1cm. For MFM characterizations samples were sent to Centre for Microscopy Microanalysis & Image Processing, University “Politehnica” of Bucharest, Romania. For SQUID measurements, pallets were prepared from the powdered transition metal (TM) doped ZnS and ZnO samples (TM: Co, Mn, Cr, Ni). All SQUID measurements were carried out at UGC, DAE consortium Indore. The samples were characterized within 1-2 weeks from their synthesis.

6.1 Magnetic measurement of bare ZnO

The magnetic characterization of undoped ZnO was carried out by using SQUID. To explore magnetic properties of bare ZnO and TM(Mn,Co,Ni) doped ZnO nanostructures we have performed SQUID measurements in two ways:

(a) M~T response: Magnetic moment (M) of the samples was recorded by varying temperature (T) within the range 4K to 300K. During M~T study, investigation was done for both zero field cooling (ZFC) and field cooling (FC). ZFC and FC was measured for two different fields, 100 Oe and 0.1 T.

(b) M~H response: By varying magnetic field magnetic moment exhibited by the samples were recorded. The magnetic field was varied from zero to several Tesla in both directions.
The M~H curve of bare ZnO exhibited typical diamagnetic nature. The M~H response of bare ZnO is presented in figure: 6.1. The diamagnetic behaviour of ZnO arises due to the paired electrons of its \(d\) orbital, which is responsible for the absence of a permanent net magnetic moment per atom. Then, when electrons are paired together, their opposite spins cause the magnetic fields to cancel with each other. Accordingly, when an applied magnetic field is acting on this atom slightly unbalances their orbiting electron and creates small magnetic dipoles within the atoms which oppose the applied field. This action is responsible to produce a negative magnetic effect.

*Figure 6.1:* Dependence of magnetization with applied magnetic field, M~H response of bare ZnO at 300K.

### 6.2 Magnetic measurement of TM doped ZnO

**(i) Mn doped ZnO DMS**

Magnetic characterization of the Mn:ZnO samples were carried out by utilizing SQUID within a temperature range of 4-300 K. Initially, we have investigated the change of magnetic moment (M) of the sample with respect to the temperature (T). The magnetic moment of the samples was recorded by varying temperature within the range 4K-300K for both at zero field cooling (ZFC) and field cooling (FC). ZFC and FC curves give the first hand signature of
magnetic response of the specimen. The results of Mn:ZnO samples are being presented in figure: 6.2. $M^\sim T$ response for Mn-1 and Mn-5 samples are presented in Figure: 6.2A and 6.2C. For these two samples the sharp magnetic moment below 50 K was recorded beyond 0.0014 emu while for the sample Mn-3 the magnetic moment was recorded beyond 0.006 emu (figure: 6.2B). The $M^\sim T$ response of Mn-3 sample in a narrow range of temperature is presented in figure: 6.2D. The significant difference between FC and ZFC curve as indicated in the figure: 6.2D, which indicates the existence of ferromagnetism in the sample where Curie temperature is above 300 K. The overall $M^\sim H$ for Mn-1 sample in a wide range of magnetic field at 10K is shown in figure: 6.3A. The saturation magnetisation ($M_s$) exhibited by Mn-1 at 10K was recorded as 0.1029 emu. The $M^\sim H$ response at 10K for the sample within -4000 Oe to +4000 Oe is shown in figure: 6.3B. The remanence magnetisation ($M_r$) and coercive field ($H_c$) for Mn-3 at 10K were recorded as 0.00418 emu and 1200 Oe respectively.

For practical applications, room temperature ferromagnetism is a vital point to be considered. This is one of the major objectives of our investigations. We have studied variations of magnetic moments ($M$) of Mn:ZnO system with respect to the change of magnetic field ($H$) at room temperature. The $M^\sim H$ response for all samples (Mn-1, Mn-3 and Mn-5) at 300K are presented in figure: 6.4. All samples exhibited hysteresis loop indicating ferromagnetic nature of the Mn:ZnO system at room temperature.

It can be noted that Mn concentration plays an important role to influence magnetic moment in the specimen. As we have observed from ZFC and FC responses for the samples (figure: 6.2), Mn-3 sample exhibited highest magnetic moment compared to other two samples. Since, Mn-3 sample contains intermediate Mn concentration, so control over concentration of transition metal at the time of doping is a vital point in having considerable magnetic response.
Figure 6.2: M~T response (ZFC and FC at 0.1T) of Mn doped ZnO (A) Mn-1, (B) Mn-3 and (C) Mn-5 within temperature range 4K to 300k, (D) ZFC and FC for Mn-3 sample within narrow temperature range (75K to 300K) showing significant difference between ZFC and FC curves.

Figure 6.3: M~H response of Mn-3 sample at 10K (A) M~H response at wide range of magnetic field, (B) M~H loop from -4000 Oe to +4000 Oe.doped ZnO (A) Mn-1, (B) Mn-3 and (C) Mn-5 within temperature range 4K to 300k.
In case of M~H response for all samples we have observed that the Mn-3 sample exhibited maximum magnetic moment, while the Mn-1 exhibited lowest magnetic response. The recorded values of magnetic moments exhibited by the samples at 1T magnetic field are given in the table: 6.1.

![Figure 6.4](image)

**Figure 6.4**: M~H response of Mn-1, Mn-3 and Mn-5 at 300K, showing hysteresis loop for all samples.

**Table 6.1**: Magnetic moment exhibited by Mn doped ZnO samples at magnetic field 1T.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Magnetic moment (emu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-1</td>
<td>7.62 X 10^{-4}</td>
</tr>
<tr>
<td>Mn-3</td>
<td>2.35 X 10^{-3}</td>
</tr>
<tr>
<td>Mn-5</td>
<td>2.30 X 10^{-3}</td>
</tr>
</tbody>
</table>
For better understanding of the magnetic response exhibited by the Mn-3, the M~H loop at 300K is presented in figure: 6.5. The selective response of M~H curve at the origin for the sample Mn-3 at 300K is presented in figure: 6.6. Though weak ferromagnetism has been exhibited by the sample, its remanence magnetization (Mr) and coercive field can be realised within small magnetic field. Although, all three Mn doped ZnO samples showed similar
features, but, Mn-3 exhibited highest coercive field of $H_c = 96.41$ Oe at 300 K, while Mn-1 showed negligible amount of remanence magnetization and coercive field at 300K. The values of remanence magnetization and coercive field at 300K exhibited by Mn-3 and Mn-5 are shown in the table: 6.2.

**Table 6.2:** Remanence magnetization($M_r$) and coercive field ($H_c$) exhibited by Mn-3 and Mn-5 at 300K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_r$ (emu)</th>
<th>$H_c$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-3</td>
<td>9.5x10^{-5}</td>
<td>96</td>
</tr>
<tr>
<td>Mn-5</td>
<td>5.6x10^{-5}</td>
<td>69</td>
</tr>
</tbody>
</table>

The inverse of susceptibility vs. temperature of ZFC and FC curves is being depicted in figure: 6.7. A least squares fit of the linear portion of the curves (figure: 6.7) above 100 K gave a negative Weiss temperature ($\theta_w$) for the sample. The value of $\theta_w$ is obtained as $-225$ K. The high negative values of $\theta_w$
indicate either strong antiferromagnetic or ferromagnetic interactions in these Mn-doped samples. It is to be noted that there is a sharp increase in the long magnetic moment below 50 K for all Mn doped ZnO samples. A typical Curie–Weiss behaviour is observed above 100 K. Very large negative values of θ, along with a deviation from linearity below 50 K are in consistency with other reports [310-313]. The type (ferro-antiferro) of the magnetic interaction will depend on the Mn-Mn distances. In a random mixture of Zn and Mn ions, some Mn ions could be at a shorter distances than other, resulting in antiferromagnetic coupling; thus, increasing the Mn content will reduce Mn-Mn distances and reinforce antiferromagnetic interaction, consistent with the theory of superexchange [314].

(ii) Co doped ZnO DMS

The magnetic measurements of the Co doped ZnO samples are done by using SQUID within temperature 4K to 300K. Zero field cooling (ZFC) and field cooling (FC) of Co-3 sample at two magnetic field 0.1 T and 100 Oe was performed to investigate the influence of magnetic moment of our specimen with variation of temperature when the specimen was exposed to two different magnetic fields. The M~T response for ZFC and FC at two different magnetic field (0.1 T and 100 Oe) is presented in figure: 6.8. From the figure it was observed that at two magnetic fields, a considerable change in the magnetic moment of the specimen occurred. For higher magnetic field (0.1 T) the magnetic moment was recorded as 14.7x10^{-4}, while at low magnetic field (100 Oe) the magnetic moment went down to 1.522x10^{-4} emu. On the other hand the inset of figure: 6.8 presents the ZFC and FC plot at 100 Oe in a close view, showing a significant difference between ZFC and FC curves. From this we can infer that as synthesised sample has a good signature of existence of ferromagnetism at room temperature. In the next step we have performed M~H response with the same sample to confirm room temperature ferromagnetism in the Co-3 sample.
To have a better understanding regarding ZFC and FC exhibited by Co-3 at 100 Oe, the M~T curve is presented in the figure: 6.9a in a wide view. The significant difference between ZFC and FC curve indicates ferromagnetic nature of the sample with Curie temperature above 300K. The figure: 6.9(b) and figure: 6.9(c) show the M~H curve for Co-3 doped ZnO sample at 10K and 300K respectively.

**Figure 6.8:** ZFC and FC response of Co-3 at 0.1 T and 100 Oe. **Inset:** exhibiting considerable difference between ZFC and FC for the sample at 100 Oe.

The Hysteresis loop exhibits ferromagnetic nature of the sample at room temperature. At 10K, the measured saturation magnetization ($M_s$), remanence ($M_r$) and coercive field ($H_c$) are 0.61 emu/g, 0.003 emu/g, and 104 Oe respectively. At room temperature the corresponding values of saturation magnetisation and remanence decrease to 0.0024 emu/g and 4.7E-4 emu/g respectively but the coercive field increases upto 136 Oe. An increase in coercive field at room temperature by ~ 31% was recorded for Co-3 sample. The inset in figure: 6.9b and figure: 6.9c show selective response of M~H curves at 10K and 300K respectively.

The corresponding values of remanence magnetization ($M_r$), saturation magnetization ($M_s$) and coercive field ($H_c$) for the sample Co-3 at 10K and 300K is presented in the table: 6.3.
Figure 6.9: (a) M\textsuperscript{T} response (ZFC and FC at 100 Oe) of Co-3 sample, M\textsuperscript{H} response of the sample at (b) 10K and (c) 300K; inset: (b) selective M\textsuperscript{H} response at the origin at 10K, (c) at 300K.
Table 6.3: Values for remanence magnetization ($M_r$), saturation magnetization ($M_s$) and coercive field ($H_c$) for Co-3 corresponding to 10K and 300K.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>$M_r$ (emu)</th>
<th>$M_s$ (emu)</th>
<th>$H_c$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10K</td>
<td>0.003</td>
<td>0.61</td>
<td>104</td>
</tr>
<tr>
<td>300K</td>
<td>4.7x10^{-4}</td>
<td>0.0024</td>
<td>136</td>
</tr>
</tbody>
</table>

In a similar work, ZHOU Shao-Min et al. [315] considered three possibilities for the origin of ferromagnetism in Co doped ZnO nanostructures. The first one is the carrier-induced ferromagnetism (RKKY or double exchange mechanism) that is often reported for the III-V semiconductors [316-318]. The second possibility is the presence of weak ferromagnetism due to CoO phase, whereas CoO is well known for its antiferromagnetic nature [319-321]. The third possible origin is the existence of micro Co clusters [322] in the sample. In our XRD, HRTEM, SAED and EDX study no secondary phases of Co or CoOs were detected. These observations indicate that the Co ion systematically substitute for Zn sites without changing the wurtzite structure of the samples. Thus we conclude that the observed ferromagnetism is due the presence of free carriers and localised spins. The defects produced due to Zn interstitials and O vacancies usually induce n-type characteristics.

All Co doped ZnO samples show ferromagnetic behaviour at room temperature. The Co-3 doped sample shows maximum saturation magnetization 0.0024 emu/g and coercive field 136 Oe. at room temperature. The origin of the ferromagnetism is still a source of active research and may involve a carrier-induced magnetism. We have adopted a simple fabrication method which can be applied to fabricate other TM doped ZnO nanostructures for future spintronic applications.
(iii) Ni doped ZnO DMS

Till date, fewer studies have been focused on the Ni-doped ZnO system, in which diverse magnetic properties have been observed. Superparamagnetic behaviour has been observed above 30 K [323], while, Paramagnetism has been reported by Yin et al [276], which may be an indication of the occurrence of NiO or Ni precipitates. Besides, RT FM has also been realized recently in Ni-doped ZnO samples. Liu et al [324] have observed RT FM in Ni-doped ZnO thin films prepared by pulsed-laser deposition, which is related to the n-type carriers that ultimately arise from oxygen vacancies in the films according to the carrier-mediated mechanism. In addition, the RTFM observed in the bulk polycrystalline Ni doped ZnO samples prepared with the sol–gel technique has been explained on the basis of the impurity d-band splitting model [325]. Moreover, Mao et al [326] have also obtained RT ferromagnetic Ni-doped ZnO samples prepared by solid state reaction, but FM originates from the nanosized Ni clusters formed from the decomposition of NiO during calcination.

As fabricated Ni doped ZnO sample (Ni-3) was characterized by using SQUID, initial FC and ZFC measurements indicated ferromagnetic nature of the sample at both low and room temperature which is shown in the figure: 6.10. The magnetic field during FC and ZFC measurement was kept constant at 0.1 T. It was observed that above 250 K, a slight difference exist in between the ZFC and FC curves which can be realised in a close view.

- The $M^\sim H$ response of Ni-3 at 10K and 300K are presented in figure: 6.11 and 6.12. The clear hysteresis loop at 10K indicates strong ferromagnetic nature of the sample at low temperature with saturation magnetization 0.1237 emu. Compared to this, $M^\sim H$ response at 300K exhibits weak ferromagnetism which can be visualized from the comparative curve as presented in figure: 6.13. It has been observed that the saturation magnetisation exhibited by the Ni-3 sample at room temperature cannot be realised at higher fields. It exhibits hysteresis nature below 1 T, but $M^\sim H$ curve is straight above 1 T.
As observed from the figure that the paramagnetism was predominant at higher magnetic fields. The establishment of the paramagnetism at higher magnetic fields also explains the no-saturation of the M-H curves at low fields.

![Figure 6.10](image1.png)

**Figure 6.10:** (A) $M$~$T$ response (ZFC and FC at 0.1 T) of Ni-3 sample

![Figure 6.11](image2.png)

**Figure 6.11:** $M$~$H$ response of the sample (Mn-3) at 10K.
Figure 6.12: $M^\sim H$ response of Mn-3 at 300K.

Figure 6.13: Comparative $M^\sim H$ response for Ni-3 at both 10K and 300K.

The strong paramagnetic behaviour at high fields can be attributed to the presence of magnetic dipoles located on the surface of nanocrystals that
exhibited a minimum interaction with their neighbours inside of the crystal. Consequently, the interchange energy in those magnetic dipoles would be reduced increasing their freedom to get re-oriented. Therefore, since diminishing the crystal size will increase the crystal surface to crystal volume ratio, the population of dipoles ordered in the same direction will decrease. Thus, the sum of the total amount of dipoles oriented along the same direction will also decrease. In short, and from a magnetic ordering viewpoint, the crystal surface will usually be less magnetically ordered than the centre of the nanocrystal [327].

Table 6.4: Values for remanence magnetization ($M_r$), saturation magnetization ($M_s$) and coercive field ($H_c$) for Mn-3, Co-3 and Ni-3 at 300K.

<table>
<thead>
<tr>
<th></th>
<th>$M_r$ (emu/gm)</th>
<th>$M_s$ (emu/gm)</th>
<th>$H_c$ (oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn:ZnO</td>
<td>2.99x10^{-4}</td>
<td>0.0024</td>
<td>69</td>
</tr>
<tr>
<td>Co:ZnO</td>
<td>4.5x10^{-4}</td>
<td>0.0035</td>
<td>136</td>
</tr>
<tr>
<td>Ni:ZnO</td>
<td>2.23x10^{-4}</td>
<td>8.53x10^{-4}</td>
<td>192</td>
</tr>
</tbody>
</table>

The dependence of magnetic moment with variation of magnetic field at room temperature for transition metal (Mn, Co, Ni) doped ZnO is presented in a single $M$–$H$ plot as shown in figure: 6.14. All three TM:ZnO sample exhibited clear hysteresis loop indicating existence of ferromagnetism at room temperature.

The ferromagnetic behaviour of the samples had been observed within small range of magnetic field, it was about -0.1 T to +0.1 T. So, it can be revealed that very small amount of magnetic field is required to align all
magnetic moments within the nanocrystals. This opens wide possibility to use the as-prepared samples for future applications at room temperature. The data coercive field ($H_c$), remanence magnetization ($M_r$) and saturation magnetization ($M_s$) for the above TM doped ZnO sample shows values which are consistent with typical diluted magnetic semiconductor nanostructures. The corresponding values of $M_r$, $M_s$ and $H_c$ data are shown in the table: 6.4.

![Figure 6.14: Comparative M~H response for Ni-3 at both 10K and 300K.](image)

Apparently, the magnetic properties observed so far in Ni:ZnO strongly depend on the methods and conditions used in the preparation. The origin of RT FM observed in such a system remains a controversial subject. It is not yet clear whether the observed phenomenon is truly intrinsic or related to secondary phases such as Ni clusters [328]. However, we believe that, the weak ferromagnetic interaction as observed at room temperature may be due to intrinsic property of the nanocrystal and also ‘O’ vacancy in the system. It is to be noted that, we have not observed any evidence of the existence of
secondary phases during EDX, XRD and TEM studies. In fact, existence of small amount of secondary phases in the sample cannot be ruled out because our characterization tools may not go beyond to detect them.

6.3 Magnetic measurement of TM doped ZnS

(i) Mn doped ZnS nanostructure

(a) MFM studies

Figure 6.15: Magnetic force microscopy (MFM) image of Mn doped ZnS nanostructures exposed to the sample-C embedded in PVA. Two images with magnification surface area (a) 2500 nm X 2500 nm and (b) 5µm X 5µm are shown.

Magnetic force microscopy is a well established method to probe the micro-magnetic properties of samples with lateral resolution down to ~50 nm. The advantage of MFM is that less sample is needed, thinning or polishing of the sample is not necessary. Moreover, the technique yields information on both the structural (AFM mode) as well as the magnetic (MFM mode) aspects with regard to sample’s surface. Therefore, the topology and magnetic domain structure of a sample may be correlated efficiently at the nanometer scale.
Figure: 6.15a and 6.15b show MFM image of ZnS:Mn (sample C) at two different magnifications. In figure: 6.15b, nanoparticles with their clear response to magnetic field has been visualized. The average size of the magnetic cores (black spot) in figure: 6.15a is measured as ~60 nm (actual particle size) and white regions spreading over the cores are ascribed to the region of influence by the respective particles. Sharp contrast of the magnetic cores, encircling white bands is seen for many isolated particles. Therefore, it is evident that ZnS:Mn nanoparticles can respond appreciably to magnetic force and fields and MFM in this regard, can be a very good tool to exploit magnetic domains and particle-particle interactions.

With MFM studies, one could obtain visual information with regard to magnetic cores and influence zone. Investigation of Mn-incorporated diluted semiconductor nanosystems would be promising in the area of spintronics and other miniaturized magnetic & optoelectronic devices.

(b) SQUID measurements

We have investigated the magnetic properties of Mn doped ZnS samples using a SQUID magnetometer in the temperature range 4–300 K. The temperature dependence of magnetization is shown in figure: 6.16 for 3 at.% Mn doped ZnS. The figure shows a plot of zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements performed on the materials by applying 100 Oe. magnetic field.

From the M~T response of the Mn:ZnS nanostructure it has been observed FC curves which give indicates absence of ferromagnetism in the sample. Since, a distinct splitting between ZFC and FC measurement reveals the presence of a magnetic transition temperature. The difference between ZFC and FC gives the net magnetization value (ΔM = FC − ZFC) in the sample by eliminating the para-and diamagnetic contributions, leaving only the contributions from the ferromagnetic regime [329]. We have performed SQUID measurements for 1at.% Mn doped ZnS sample, but observed same nature that
exhibited by the 2 at.% Mn doped sample. Inset of figure: 6.16 represents the inverse susceptibility curve of ZFC plot for Mn:ZnS sample at 100 Oe. The inverse susceptibility curve is almost linear which exhibit curie Weiss behaviour and indicates that the as-synthesised sample is paramagnetic in nature.

Figure 6.16: Temperature dependence of magnetization (ZFC and FC) for Mn doped ZnS at 100 Oe. , inset: Inverse susceptibility curve for ZFC curve of Mn:ZnS sample.

(ii) Cr doped ZnS nanostructures

(a) MFM studies

To exploit magnetic properties, we have carried out MFM studies on the Cr doped ZnS samples. A typical MFM micrographs on a section of the ZnS:Cr sample in PVP is shown in figure: 7.17. The micrograph yields information regarding magnetic (MFM mode) aspects with regard to sample’s surface. The topology and magnetic domain structure of the sample are correlated efficiently at the nanometer scale. Moreover, the technique yields information on both the structural (AFM mode) as well as the magnetic (MFM mode)
aspects with regard to sample’s surface. Therefore, the topology and magnetic domain structure of a sample can efficiently be correlated at the nanometer scale. Figure: 6.17(a) depicts uniform distribution of magnetically influenced nanoparticles.

![Figure 6.17: (a) Magnetic force microscopy (MFM), showing coloured image of magnetically influenced Cr:ZnS nanostructures in PVP. and (b) Isolated MFM image for Cr doped ZnS in PVA matrix.](image)

The figure: 6.17(b) is basically a phase image of the Cr:ZnS sample embedded in PVA matrix; it shows clear response to the magnetic field. The average size of the magnetic cores (black spot) is measured as ~ 165 nm and white regions spreading over the cores are ascribed to region of influence by the respective particles. Thus, it is evident that ZnS:Cr nanoparticles can respond appreciably to magnetic force and fields and MFM in this regard, can be a very good tool to exploit magnetic domains and particle-particle interactions.
(b) SQUID measurements

For magnetic characterization by using SQUID magnetometer, we have prepared Cr:ZnS samples for two different Cr concentration, 1at.%Cr and 2at.%Cr. ZFC and FC measurements were carried out for both the samples. The dependence of magnetic moment with variation of time (ZFC plot) for 1 at%Cr at 100 Oe. magnetic field is presented in figure: 6.18. At low temperature, below 100 K, the magnetic moment increases above 30x10^{-6} emu, which is very small compared to other typical diluted magnetic semiconductors. This indicates paramagnetic nature of the sample.

Figure 6.18: Temperature dependence of magnetization (ZFC) for 1at.%Cr doped ZnS at 100 Oe..

Figure 6.19: Temperature dependence of magnetization (ZFC and FC) for 3at.%Cr doped ZnS at 100 Oe.
Figure 6.20: Inverse susceptibility Vs Temperature plot for ZFC of 3at.%Cr doped ZnS at 100 Oe.. The dotted line cuts negative Curie-Weiss temperature ($\omega_0$) 125K.

The ZFC and FC measurements for 3at.%Cr doped ZnS sample is shown in figure: 6.19. It has been observed that no significant different persists in between ZFC and FC curves. This in turn, indicates that the net ferromagnetic contribution in the sample is negligible. The inverse susceptibility Vs temperature variation plot for this sample is presented in the figure: 6.20, which exhibits Curie-Weiss behaviour with negative Curie-Weiss temperature ($\omega_0 = -125K$). A sharp increase in magnetic moment below 50K along large negative value of Curie-Weiss temperature suggests that the dominant spin-spin interaction were of strong antiferromagnetic type.

From the above investigation on Cr:ZnS system, though 3at.%Cr doped sample exhibited noticeable magnetic moment compared to 1at.% Cr sample, yet it was far away from exhibiting room temperature ferromagnetism. It can be inferred that Cr concentration in ZnS plays an important role influence magnetic moment in the specimen. From the study, it can be speculated that due to the absence of ferromagnetism in the sample, there is a less possibility
to apply them in practical applications. Since, spintronics or any other electronic appliances room temperature ferromagnetism is the most important factor.

### 6.4 Significant observations

- M~H responses of bare ZnO exhibited typical diamagnetic nature.
- In the M~T measurements at 300K, all TM (Co,Mn,Ni) doped ZnO nanostructures displayed significant difference between FC and ZFC curves, which indicated the existence of ferromagnetism in the samples where Curie temperature is above 300K.
- M~H responses of TM: ZnO samples were carried out at room temperature for all TM doped ZnO samples exhibited typical hysteresis loop, which evidenced the existence of ferromagnetic coupling in the samples.
- We have investigated the influence of Mn content in the magnetic properties of Mn:ZnO system. As per observation, at low Mn$^{2+}$ ion concentration (Mn-1) magnetic responses ($H_c$, $M_r$, $M_s$) were minimum, at medium Mn$^{2+}$ ion content (Mn-3) these became maximum, again at increased Mn$^{2+}$ ion content (Mn-5) these responses were lowered. For example, in the M~H response at room temperature, Mn-1 showed negligible but evident coercive field, in turn, the respective values for Mn-3 and Mn-5 were recorded as 96 Oe. and 69 Oe. respectively. Thus, it can be reasonably inferred that TM ion concentration in diluted magnetic semiconductors plays a vital to influence magnetic properties in the specimen.
- In the susceptibility curve of Mn-3, a typical Curie–Weiss behaviour was observed above 100 K along with large negative values of Curie–Weiss temperature ($\theta_w$= - 225K) along with a deviation from linearity below 50 K, which suggests that there exist either ferromagnetic or antiferromagnetic couplings in the specimen.
• All Co doped ZnO samples show ferromagnetic behaviour at room temperature. Compared to Mn:ZnO and Ni:ZnO systems, a significantly large difference between ZFC and FC curves has been observed in Co:ZnO system, which indicated existence of strong ferromagnetic coupling in Co:ZnO system. A linear increase in magnetic moment with increasing magnetic field was displayed by Co:ZnO system. The M~H response for Co-3 studied at 10K as well as 300K exhibited clear hysteresis loops indicating ferromagnetic nature of the sample at both temperatures. Compared to 10K measurements, the corresponding values of saturation magnetisation and remanence at room temperature have lowered, but the coercive field has increased by ~31%.

• The M~H responses of Ni:ZnO system showed strong ferromagnetic coupling at 10k, but comparatively weak ferromagnetism at room temperature. For Ni-3, saturation magnetisation at room temperature was obtained at low magnetic field, but at higher field, no saturation was obtained. The strong paramagnetic behaviour at high fields can be attributed to the presence of magnetic dipoles located on the surface of nanocrystals that exhibited a minimum interaction with their neighbours inside of the crystal.

• In the MFM study, uniform distribution of magnetic domains for TM(Cr,Mn) doped ZnS system were detected.

• In contrast to TM:ZnO system, all TM(Mn,Cr) doped ZnS sample exhibited paramagnetic behaviour. M~T response in case of Mn:ZnS system is more significant than Cr:ZnS. In the M~T response of Cr:ZnS system, 2at.% Cr doped sample displayed slight higher magnetic moment compared to 1at.% Cr from which we can infer that TM ion content in ZnS can play a role to influence magnetic moment in the specimen.

• The origin of the ferromagnetism is still a source of active research and may involve a carrier-induced magnetism. In our XRD, HRTEM, SAED and EDX study no secondary phases due to TM incorporation were detected. These observations indicate that the TM ion systematically substitute for Zn sites.
without changing the wurtzite structure of the samples. It suggests that the observed ferromagnetism in TM:ZnO may be purely intrinsic and due to the presence of free carriers and localised spins. The defects produced due to Zn interstitials and O vacancies usually induce n-type characteristics.

- Finally, we conclude that all TM(Mn,Co,Ni) doped ZnO nanostructures exhibited room temperature ferromagnetism. From the comparative M~H response of all TM doped sample it was found that Co:ZnO system exhibited largest value of remanence magnetization (4.5x10^{-4} emu/gm), saturation magnetization (3.5x10^{-3} emu/gm) along with coercive field 136 Oe. From this we can reasonably infer that Co-3 can be good candidate for device making purpose. This significant result can be applied to luminescence / spintronic applications.

### 6.5 Possible applications in spintronic devices

Spintronc has a vast area for research. A good number of people are engaged to explore spintronic devices for next generation technology. Along with modern sophisticated tools adequate requirements are needed to achieve the goal towards practical spintronic devices. Our noble approach was to fabricate good quality DMS sample so that it could be utilized for future spintronic applications.

In 1999, Y. Ohno [330] and his group performed an experiment on electrical spin injection in a ferromagnetic semiconductor heterostructure. They have reported the fabrication of all-semiconductor, light-emitting spintronic devices using III-V heterostructures based on gallium arsenide. Electrical spin injection into a nonmagnetic semiconductor was achieved (in zero magnetic field) using a p-type ferromagnetic semiconductor as the spin polarizer. Spin polarization of the injected holes was determined directly from the polarization of the emitted electroluminescence following the
recombination of the holes with the injected (unpolarized) electrons. They performed their experiment below room temperature, since Curie temperature of III-V semiconductor was within $40^\circ$-$90^\circ$ C. In their Spin-injection set up, the experiment was performed under 0.1 T magnetic field with 20 nm spacer. This work encouraged other researchers to develop Spin-LED.

The most promising candidates for high-temperature semiconductor spin aligners appear to be the diluted magnetic alloys Ga–$M$–N and Zn–$M$–O (where, $M = V$, Cr, Mn, Fe, Co and Ni). Mean-field calculations performed by Dietl et al [335] predicted that these materials could exhibit ferromagnetism at and above room temperature upon doping with transition metal elements on the order of 5 at.% material. High-temperature ferromagnetism in these materials stems partly from their strong p–d hybridization owing to their small interatomic spacing and small spin–orbit coupling.

Another promising approach for efficient electrical spin injection is through the use of a diluted magnetic semiconductor (DMS) spin aligner in which the conductivity mismatch can be greatly reduced. In II–Mn–VI paramagnetic semiconductors such as CdMnTe and ZnMnSe, the sp–d exchange interaction between itinerant electron spins and localized Mn$^{2+}$ ions results in a large Zeeman splitting of the conduction band states under the presence of an applied magnetic field. The Zeeman splitting is given by $E = g_\ast \mu_B H$ where $g_\ast$ is the effective electron $g$-factor. With no external magnetic field, the exchange fields due to the Mn$^{2+}$ ions are randomly oriented and cancel one another. Application of a magnetic field creates a net magnetization of the Mn spins and a non-zero Zeeman splitting. When an unpolarized current supplied from a non-magnetic metal contact is driven through the DMS layer, the injected electrons quickly scatter into the energetically lower spin sub-band and become spin-polarized within a picosecond along the magnetic field direction. These spin-polarized carriers may then travel by drift or diffusion into an adjacent non-magnetic semiconductor.
These and similar predications encouraged intensive experimental activity aimed at developing transition metal doped ZnO for spintronic applications.

Our present study suggests that out of all TM doped ZnS and ZnO samples few of them can be considerably employed for next generation technology. Room temperature ferromagnetism in DMS was a big challenge, we have achieved this goal by fabricating TM doped ZnO samples adopting very simple inexpensive chemical method. It opens a large possibility of research in this emerging area. To fabricate nanostructures for research purpose, all laboratories cannot provide sophisticated tools like MBE, in turn; chemical approach can be available everywhere for large scale fabrication. By adopting this simple method we have fabricated al TM doped ZnO nanostructures with sizes below 20 nm, which is very much promising for low dimensional spintronic devices. As per our investigations, the saturation magnetization for all TM doped ZnO samples were obtained at low magnetic field (below 1 T). This is encouraging, because our samples could be controlled by applying adequate magnetic field.

There are a number of requirement for achieving practical spintronics devices. The most fundamental requirements are:

- The capability to transport the carriers with high transmission efficiency within the host semiconductor or conducting oxide;
- The capability to detect or collect the spin-polarized carriers and to be capable of controlling transport through external means such as biasing of a gate contact on a transistor structure. These type aspects of spin injection, spin-dependent transport, manipulation and detection form the basis of current research and future technology.
6.5.1 Proposed Scheme for spin aligner in Spin LED

The optical polarization state may be characterized through many techniques, but most rely on a quarter-wave retarder and linear polarizer to decompose the electroluminescence into its right- and left-circularly polarized components. A typical experimental setup is shown in figure: 6.21. A lens is used to collimate the emission from the spin-polarized light sources, which then passes through the retarder–polarizer optics. Calcite polarizers transmit satisfactorily from 0.3 to 2.3μm, which is more than adequate for all spin-polarized light sources considered to date. Quarter-wave retarders, on the other hand, are designed for a particular wavelength and must be matched to the wavelength of the light source. This is particularly troublesome for analysis of spin-polarized light sources containing wide band gap materials in the active region due to the lack of suitable retarders. For incoherent light sources emitting over a broad spectra range, an achromatic quarter-wave plate centred at the peak emission wavelength may be desirable. After passing through the retarder–polarizer combination, a collection lens is used to focus the light onto a spectrometer or photodetector. From the Mueller matrices for a rotating quarter-wave plate and linear polarizer, it may be shown that the intensity of the emission emerging from the retarder-polarizer combination is given by

\[ I(\theta,\phi) = \frac{1}{2} [S_0 + S_1 + S_3 \sin(2\theta) + (S_2/2)\cos(4\theta) + (S_2/2)\sin(4\theta)] \]  

where \( S_0, S_1, S_2 \) and \( S_3 \) are the familiar Stokes parameters.

Degree of Circular polarization will be measured as

\[ \pi_{CP} = \frac{S_3}{S_0} \]  

It is the ratio of two stokes parameters.

and \( \theta = \omega t \), is the angle of rotation of the quarter-wave plate fast axis.
Figure 6.21. Typical experimental setup for characterization of spin-polarized light sources [Ref: 331].

Figure 6.22. Schematic representation of a spin-LED under the (a) Faraday, (b) quasi-Voigt and (c) oblique Hanle effect geometries. [Ref: 331]

The goal of most experiments involving spin-polarized light sources is to relate the device’s optical polarization to the spin polarization of carriers injected from a magnetic spin-aligner layer into a non-magnetic semiconductor. Three measurement geometries are typically employed for the characterization of spin-polarized light sources [331]: (a) Faraday, (b) Quasi-Voigt and (c) Oblique Hanle effect geometries [figure: 6.22].

Spin-LED measurements are most commonly performed in the Faraday geometry since the selection rules are best understood in this configuration, allowing a fairly direct conversion between spin and optical
polarizations. A typical experimental setup under the Faraday geometry as from Ref: 331 is shown in figure: 6.2.

![Proposed Scheme of Prototype Spin-LED.](image)

After merging our idea to develop a spintronic device along with the discussion above we find maximum possibility to utilise our as-fabricated Co:ZnO sample as a spin aligner in Spin-LED model. In most of the Spin-LED sources, GaMnAs, InGaAs and ZnMnS DMSs were utilized as spin aligners. As per our present investigations on II-VI based transition metal doped diluted magnetic semiconductors, we have observed that TM(Co,Mn,Ni) doped ZnO exhibited few desirable basic properties as predicted by Dietl et al. [332]. These samples with low dimensional size (less than 20 nm) displayed room temperature ferromagnetism and showed the possibility to operate within 0.1T magnetic field. Out of all samples, Co:ZnO system, doping with 3at.%Co exhibited significant magnetic properties which are similar to the typical diluted magnetic semiconductors. From these observations, we can reasonably infer that Co-3 sample could be promising candidate as a spin aligner for efficient spin injection.
A typical prototype Spin-LED utilizing $\text{Co}_{0.03}\text{Zn}_{0.97}\text{O}$ as spin-aligner as proposed by us is shown in figure: 6.23. As we have discussed in chapter-1 that the most straightforward approach to design a Spin-LED would be to implant Mn into the top contact p-GaN layer of the standard GaN/InGaN LED. Here, we propose to use $\text{Co}_{0.03}\text{Zn}_{0.97}\text{O}$ as spin aligner, since this particular sample have achieved few basic requirements as discussed earlier. In the figure: 6.22 ‘H’ is the external magnetic field (~ 1T). The LED source is set in the quasi-Voigt geometry. In presence of the external magnetic field the spin of the spin aligner will be align parallel to the magnetic field. This could be possible for the material $\text{Co}_{0.03}\text{Zn}_{0.97}\text{O}$, since it exhibited RTFM during investigations. In turn, randomly oriented spins of the spacer will be antiparallel to the magnetic moment of the spin aligner which will make it possible to inject spin polarised light. The source can be used in the set up as shown in figure: 6.21 for measuring degree of circular polarization.

Though we have suggested a scheme, we do not claim that these are the sufficient requirements to get circularly polarized light at the collector end. For practical visualisation of the complete experimental set up more parameters have to be explored along with adequate measuring tools.

In fact, we believe that to design a ‘spintronic device’ is not an easy task.

### 6.6 Possible applications in Luminescent devices

ZnO and ZnS are the most studied wide band gap semiconductor, they have tremendous potential in luminescent device applications due to their properties like: Size dependant emission, broad excitation range, high quantum yield, etc..

(a) In our study it has been observed that both undoped and organic host (PVA/PVP) coated ZnS exhibited intense blue emission. Usually, the blue emission exhibited by ZnS is due to ‘S’ vacancy which can quinch out the
band-edge and other defect related emissions. There is a possibility to tune the luminescence response to its requirement by controlling the amount of sulphur at the time of synthesis.

(b) Colour tuneable application: Typical PL spectra were observed for TM doped ZnS. The Mn doped ZnS exhibited orange-yellow emission at \(~580\) nm which opens wide possibility to control the luminescence intensity by controlling the doping concentration of the transition metal by controlling the aspect ratio of ZnO:TM nanorods the luminescence can be tuned,

(c) It was predicted that nanorods with smaller length is useful for Oxygen gas sensor, while nanorods with larger dimension is more useful in UV optical sensor. Thus, by controlling the synthesis protocol the length of the nanorods can be controlled which in turn will give the opportunity to apply them in desired Luminescent device applications.

### 6.6.1 Possible application in design of biological marker

Nanostructured zinc oxide (ZnO) thin films are showing an increasing potential as sensing components in electronic nose instruments. As described in [333–335], these materials have been successfully applied in the detections of volatile organic compounds particularly associated to markers of meat spoilage. With certain markers such as ethanol, the nanostructured ZnO thin films have shown detection levels in the ppb levels, thus outperforming traditional metal oxide semiconductors based on \(\text{SnO}_2\).

In a recent paper Martin Längkvist et al. [336] proposed a fast sensor based on ZnO nanostructured thin film which can be used as fast classification of meat spoilage marker. The application area that they have considering is
food safety and in particular they aimed at developing an instrument that can be used in situ for rapid identification of meat spoilage.

Mn-doped ZnO is an n-type semiconducting material. When it is exposed to the atmosphere, the oxygen molecules react with its surface and capture electrons from its conduction band. This in turn leads to a decrease in the electron concentration and, hence, increases the surface resistance until equilibrium. The stabilized surface resistance forms the baseline for the sensing studies. When the reducing vapours like ethanol or TMA are presented to the sensing element, the vapour reacts with surface-adsorbed oxygen species and increases the electrons concentration on the surface. As a result, the surface resistance decreases from the stabilized baseline and attains saturation. This change in surface resistance has a strong correlation with the concentration of ethanol/TMA in dry air atmospheric conditions [335].

In the past two decades, the awareness about food safety, particularly with respect to specific pathogenic bacteria, has increased. This is especially true in the case of meat and fish, where microbial spoilage can be dangerous for humans, and where there is a clear requirement for a rapid and accurate detection system. Traditionally, fish and meat quality is assessed by examining the structure of the food (texture, tenderness, flavor, juiciness, color), or by detecting the microorganism and its count, or by detecting the gases generated by these microorganisms. A number of techniques have been used to examine the quality of the meat, namely instrumental mechanical methods, the ultrasound technique, as well as optical spectroscopy [337,338].

In our study we have observed that the PL spectra for both bare and TM doped samples exhibited different characteristics. Intense luminescent intensities have been exhibited by both bare ZnO (figure: 6.24A) and TM doped ZnO (figure: 6.24B). Compared to doped samples, bare ZnO displayed maximum luminescence in the UV region (figure: 6.24C). In case of TM doped samples the UV intensity gets lowered along with additional peaks in the visible reason. It has already been explained in chapter-4 that the effect is attributed due to radiative recombination of d electron transfer of transition metals. This
property can be utilised for colour tunable effect for sensing purpose. We have little bit extended our study to observe PL intensity of undoped ZnO nanostructures in bacterial environment.

We have selected a particular bacteria “**staphylococcus**” which is responsible mostly for different kinds of skin diseases. Our study revealed that in bacterial environment PL intensity of ZnO nanostructures exhibited wide spectrum in the visible region.

![Figure 6.24](image)

**Figure 6.24:** Change of PL intensity of ZnO nanorods due to Mn doping, (A): PL spectra of bare ZnO nanorods, (B) PL spectra for MN:ZnO nanorods and (C) Comparative spectra for both bare and Mn doped ZnO nanorods.

![Figure 6.25](image)

**Figure 6.25:** PL spectra of bare ZnO NSs with media and staphylococcus bacteria environment.
This property is remarkable, since in the visible region we can perfectly apply this sample as a biological marker to detect these particular bacteria. Initially, we have studied the PL spectra of bare ZnO nanostructure in a medium “Mueller Hintion Agar”. It is a microbiological growth medium that is commonly used for antibiotic susceptibility testing. The PL spectra of bare ZnO nanostructures with “Mueller Hintion Agar” medium alone and with the staphylococcus bacteria cultured environment is presented in figure: 6.25.

From the PL spectra, it has been observed that for both cases a wide visible spectra appears, when bacteria is added with ZnO and media, the PL intensity gets lowered by about 50%. The sharp UV peak of ZnO changes to wide spectrum within 350 nm to 750 nm. This suggest that more different PL characteristics would be possible when TM doped ZnO NSs are utilized for the above study. The significant behaviour of PL spectra in the visible region can be utilized to design efficient biological marker. Apparently, it opens a wide possibility but for complete practical design of a biological marker extensive measures should be considered.

6.7 Limitations

a. Time-gap

Time gap between the synthesis and characterization is the most important factor in nanoscience research. Besides our own laboratory, we had to investigate our samples at three other places. For, AFM and MFM the samples were sent to Romania, SQUID investigations were done at Indore and HRTEM studies were carried out at Shillong, for which there was always a time-gap between the synthesis and analysis. Thus, investigations were performed under this limiting condition for which we may not get the expected result.

b. Reproduction of samples

For proper investigations, same sample should be exposed to all characterization tools. Scientific characterization tools at different places may demand reproduction of the same sample which may bring deviations from the
correlations among different investigations. This is another limitation which needs to be overcome. In fact, steps have already been initiated in this direction.

6.8 Future directions

a. Development of other binary semiconductor nanostructures:
   During our study we were restricted to ZnO and ZnS from II-VI groups. The study can be extended to other binary semiconductors. For example study can be extended to ZnSe, ZnTe, CdTe, CdSe etc.; since, these candidates are also promising in the nanoscale regime.

b. Development of other TM doped II-VI based DMS:
   In our study Mn, Ni and Co were considered to dope ZnO, while Cr and Mn were considered for ZnS. This study can be extended to develop other TM doped II-VI base DMS. Few reports are available on the study of RTFM with Cu, Fe doped II-VI based DMS. Along with these two TMs, one can consider other transition metals like V, Ti, Mo etc. for extensive study in this direction.

c. Possibility of developing rare earth metal doped II-VI based DMS:
   The contributions of rare earth metals in developing fluorescent lamps, lasers, fiber optics, magnetoresistive alloys, metal-halide lamps are excellent. Yttrium (Y) is used in TV red phosphor, Neodymium (Nd) and Gadolinium (Gd) are applied as rare earth magnets. There is a large possibility of extending this study by introducing rare earth metals in ZnS and ZnO semiconductor hosts to explore optical as well as magnetic properties.

d. Biological sensors:
   It has been proved that fluorescent materials are the best candidates to replace organic dyes. Thus utilizing the size dependant UV colour sensing property of nanostructures biological sensing /imaging device or marker can be developed.
e. **Post annealing:**

During the study, we have not considered post synthesis annealing. To exploit magnetic properties and also to find origin of RTFM in the TM:ZnO samples it is necessary to anneal the samples up to at least 700 °C. This is left for future study.

f. **Study of transport phenomena:**

Study of transport phenomena in the as-synthesised samples is quite necessary for practical realization of a spintronic device. The study of transport phenomena should through more light on spintronic based devices/activities.

g. **Use of more characterization tools:**

In the study, we were limited to few characterization tools due to unavailability, time factor and many other reasons. To exploit complete physical properties of the samples, this study may be extended in future by utilizing more and more modern tools.

h. **TM co-doping:**

Researchers have already investigated many interesting properties due to co-doping of TM in ZnO. We have investigated for individual TM doping cases. There is a large possibility to extend the study with co-doping of different TMs. For example, study can be extended with Mn and Co co-doping, since in our investigation both the TM have exhibited RTFM, so their co-doping in ZnO lattice host may exhibit attractive property. Similarly attempt should be taken to include other TMs for co-doping.