Room temperature ferromagnetism with high magnetic moment and optical properties of Co doped ZnO nanorods synthesized by a solvothermal route

Bappaditya Pal a, Soumen Dhara b,1, P.K. Giri b,⇑, D. Sarkar a

a Department of Physics, Gauhati University, Guwahati 781014, India
b Department of Physics, Indian Institute of Technology Guwahati, Guwahati 781039, India

A R T I C L E   I N F O
Article history:
Received 30 March 2014
Received in revised form 27 May 2014
Accepted 16 June 2014
Available online 24 June 2014

Keywords:
ZnO nanorods
Co doping
Ferromagnetism
Defects
Photoluminescence

A B S T R A C T
Zn1−xCoxO (x = 0, 0.05, and 0.07) nanorods (NRs) exhibiting ferromagnetism above room temperature and with high magnetic moment have been synthesized by a solvothermal route. XRD, FESEM, TEM, EDS and XPS measurements reveal the growth of single phase wurtzite structure Zn1−xCoxO NRs with the successful incorporation of Co ions inside the ZnO matrix. TEM micrograph reveals clearly the formation of long ZnO NRs with diameter of 50–90 nm and length of 0.3–0.6 μm. High resolution TEM lattice images and the electron diffraction patterns show that all the NRs are single crystalline. Room temperature magnetic measurements exhibit ferromagnetic behavior with high magnetic moment of 1.83 emu/g for 2 T field, coercivity of 53 G. Temperature dependent magnetization measurement shows a Curie temperature of the order of 398 K. Photoluminescence (PL) spectra exhibit near band edge UV emission and defect related visible emission, which is expected to play a significant role in the FM ordering. PL and UV–VIS spectra reveal slight modification of band edge due to doping effect. Systemic structural, magnetic, and optical studies reveal that both the nature of the defects as well as Co2+ ions are significant ingredients to attain high moment as well as high ordering temperature in the 1-dimensional ZnO NRs. Magnetic interaction is quantitatively analyzed and explained using a bound magnetic polaron model and expected to arise from the intrinsic exchange interaction of Co ions and VZn, O i related defects. These findings provides a better insight into the underlying mechanisms of high temperature ferromagnetism in Zn1−xCoxO NRs.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Transition metal (TM) doped ZnO is being highly explored, for the attainment of ferromagnetic ground state with a Curie temperature (Tc) greatly exceeding room temperature, leading to a novel behavior for the use of both charge and spin of electrons for their promising applications in spintronic devices [1–6]. The coexistence of magnetic, electric, optical properties and other heterojunction applications increase the potential of TM-doped ZnO (ZnO:TM) to be a multifunctional material [2,5,7,8]. ZnO-based DMSs have been studied intensively following the theoretical prediction of room-temperature ferromagnetism (RTFM) by Mn-doping in p-type ZnO or by Co doping in n-type ZnO [3,9]. A considerable amount of experimental data and corresponding mechanisms of ZnO-based DMSs, especially on Co-doped ZnO, have been published during last decade [2,10–12]. Correspondingly, several theoretical models have been developed to explain the coupling mechanism. So far, the most popular mechanisms suggested for magnetic ordering are carrier mediated exchange interaction [3], and the bound magnetic polaron (BMP) model with respect to the intrinsic defects related to vacancy or interstitials [13,14]. However, the conclusive origin of RTFM has yet to be uncovered, and the mechanism behind the magnetic ordering is still under debate. Descending to nanoscale dimensions, additional effects related to the high surface-to-volume ratio, surface defect contributions appear, making the whole issue on Co-doped ZnO DMSs more complex, but also more interesting.

Furthermore, in the literature there exists controversy whether the FM observed in oxide DMSs could be solely related to intrinsic defects [15,16]. In addition, some startling reports on the RTFM in nonmagnetic doped [17,18], and undoped oxide (ZnO,TiO2, MgO, CeO2, etc.) [19,20] systems indicate that in specific cases the
magnetic properties may be not exclusively related to the presence of the magnetic ions but strongly mediated by the point defects, such as (Ov, Zn, and Zn0). These point defects related FM is termed as ‘d0 ferromagnetism’ which is often observed only in thin film and nanostructures having the high surface–volume ratio, exhibiting notable surface effects, as most of the defects must exist near the surface [20,21]. This implies that the size and morphology of nanostructure can strongly affect the observed FM and is expected to be an excellent model by itself for studying the defect-related FM. The objective to clarify the clear defect origin and definite coupling mechanism behind RTFM in undoped ZnO has inspired extensive experimental as well as theoretical interests [16,17,21]. However, it is very difficult to establish a direct link between the magnetization and defects due to complexity of defect states in ZnO and to have its suitable handling for the device application purpose. As a result, the nature of the d0 FM for the undoped systems needs more delicate investigations.

Since 1D nanostructures are ideal for their diverse optoelectronic and nanoelectronic properties, arising due to quantum confinement effects in the radial direction, systematic electrical, optical and magnetic studies of undoped and Co doped ZnO 1D nanostructure are of high interest. It is important to synthesize one-dimensional (1D) nanostructures to utilize the semiconductor nanostructures as building blocks in functional nanoscale devices [22,23]. Many researchers have tried to synthesize ZnO based 1D DMS nanostructure [17,23,24]. Liang et al. has reported chemically synthesized Co doped ZnO NRs with RTFM for nanoelectronic application [23]. Tao et al. have observed enhanced FM in the Zn0.98Co0.02O thin film, due to the combined effect of 1D size and homogenous doping of Co in ZnO nanowires [24]. In but many reports, the magnetic moment found was of the order of m e m u / g. Only a few studies have reported on doped 1D single-crystalline NW/NR that showed FM above room temperature with high magnetic moment value. Moreover, synthesis of doped ZnO nanorods showing FM above room temperature with a high moment and high crystallinity still remains a significant challenge for future spintronic devices. Hence, it is essential to have a careful control over the synthesis conditions to obtain such DMS nanostructures with specific morphology. ZnO NRs have been obtained earlier using physical and chemical methods such as facile two-step solution route [25], thermal decomposition [24], VLS growth [26] and chemical vapor deposition (CVD) [27] etc. However, compared to these methods, synthesis by solvothermal route using autoclave offers great advantages, such as easy and effective control of synthesis parameters, like low synthesis temperature and absorption spectra, the kind of defects present and their changes with doping.

2. Experimental details

2.1. Synthesis of ZnO nanorods

Zn1-xCoxO (x = 0, 0.05, 0.07, molar percentage) NRs are synthesized by a facile two-step solvothermal route. Zinc acetate dihydrate (Zn(Ac)2, 2H2O) and cobalt acetate tetra hydrate (Co(Ac)2·4H2O) of analytic grade and sodium hydroxide (NaOH) pellets (Merck) are used for the synthesis of undoped and doped ZnO NRs. Distilled deionized (DI) water is used during all the experiments. In a typical synthesis, (Zn(Ac)2, 2H2O) and (Co(Ac)2·4H2O) of different molar percentages are mixed with 50 ml DI water with continuous stirring for 1 h. In the two-step synthesis process, the pre-stirring step is essential for the growth of ZnO nanorods, as it yields an intermediate product of Zn(OH)2, which serves as a reservoir and slowly releases Zn2+ ions to allow the nucleation and growth for ZnO. Next the solution mixture is transferred into Teflon-lined autoclave (Berghof, BR-100) of 100 ml capacity. Then 25 ml NaOH solution (1 M) is drop wise added with increasing temperature up to 90 °C in few steps, under continuous stirring. We carefully observe that this kind of slow reaction with drop caste addition of NaOH have tendency for the Co ions to insert inside the ZnO matrix and distribute quite well. While just mixing the precipitates all together and heating have chances to produce TM related secondary phases also it might lead to irregular shaped nanocrystals. Next the chamber was closed and the mixture was heated at different temperatures (140–150) °C for 18 h. and then cooled down to RT naturally. The precipitates were collected, alternately washed with deionized water several times till the pH ~ 7 is reached and finally dried in room temperature. The final products with colors from light green to deep green are obtained with the increasing doping concentration of Co.

2.2. Characterization

The phase purity and crystal structure of the Zn1-xCoxO samples are characterized by X-ray diffraction (XRD) (Rigaku RINT 2500 TTRAX-III, Cu K radiation). The morphology of the samples are identified using a field emission scanning electron microscopy (FESEM) (Sigma, Zeiss). The high magnification surface morphologies are studied by transmission electron microscopy (TEM), high-resolution TEM (HRTEM), selected area electron diffraction (SAED) pattern and energy dispersive X-ray spectrum (EDS) (JEOL-JEM 2010 operated at 200 kV). The optical absorption spectra are recorded using a commercial UV–VIS spectrophotometer (Perkin Elmer UV Win Lab). The room temperature PL spectra of all the samples were recorded with a 325 nm He–Cd laser excitation using a commercial PL spectrometer (Flurolog-3, Horiba) equipped with a PMT (photo multiplier tube) detector. The magnetic properties of the samples are examined by using a Lakeshore vibrating sample magnetometer (VSM) (Model no. 7410). XPS measurement was carried out with a fully automated XPS microprobe (PHI X-tool, ULVAC-PHI) using Al Kα X-ray beam (1486.7 eV) with beam current of 5 mA. Carbon 1s spectrum is used for the calibration of the XPS spectra recorded for various samples.

3. Results and discussion

3.1. Microstructure and morphology

Fig. 1(a) shows a typical XRD pattern for the Zn1-xCoxO (x = 0, 0.05, 0.07) samples. All the diffraction peaks like (100), (002) and (011) correspond well to the hexagonal wurtzite ZnO crystal structure, hence it shows that Zn1-xCoxO samples have single-phase hexagonal wurtzite structure, indicating good quality doping of Co ions throughout the ZnO lattice. It should be noted that no other secondary peaks related to Co clusters or other oxides of Co ions are observed in the XRD pattern. Also it shows clear shifting of the diffraction peaks towards the higher angle for the three most intense peaks of the XRD pattern. The lattice parameters a, c and the cell volume V are calculated from the XRD peak positions.

Fig. 1. XRD pattern of Zn1-xCoxO (x = 0, 0.05, 0.07) samples, the corresponding diffraction peaks for ZnO are marked in the pattern.
and we find that lattice parameters decrease with doping; as a consequence, the lattice volume decreases with increasing doping concentration (details: in Table 1). This is consistent with the fact that the ionic radius of Co$^{2+}$ is 0.58 Å, whereas that of Zn$^{2+}$ is 0.60 Å [28]. The shifting of XRD pattern and corresponding decrease of the lattice parameters suggest that Co$^{2+}$ ions are successfully incorporated into the ZnO lattice at the Zn$^{2+}$ sites.

The general morphologies of Zn$_{1-x}$Co$_x$O samples are shown in Fig. 2. Nearly spherical nanoparticles (NPs) are formed for the undoped ZnO (see inset of Fig. 2(a)) and NRs are formed for the high concentration of Co doped ZnO samples (Fig. 2(b)). Note that low concentration of Co doped sample shows spherical shaped NPs. The difference of the crystal growth velocities in different directions is expected to cause the change of morphologies. The surface energies are different for different crystal faces for ZnO nanocrystals. C-axis exhibits the highest growth rate due to the structure and surface anisotropy [29]. Further, the presence of Co ions in the precursor solution induces a thermodynamical barrier, which retards the formation of the nucleation, as well as the growth rate of the primary nuclei (Zn$^{2+}$). Effectively Co$^{2+}$ ions have more time to deposit uniformly on the nuclei along the c-axis, as a result c-axis growth has a faster rate than that along other directions. Meanwhile, for pure ZnO and lower doping concentrations the intermediate Zn(OH)$_2$ dissolves rapidly due to the relatively low energy barrier, giving a high concentration of Zn$^{2+}$ ions in the precursor, resulting irregular crystal formation. As the doping concentration increases, the aspect ratio of length to diameter increases due to C-axis growth and it leads to the long length of the NRs. Similar findings of increasing NR/NW length with doping concentration increases, the aspect ratio of length to diameter increases due to C-axis growth and it leads to the long length of the NRs. Similar findings of increasing NR/NW length with doping concentration increases, the aspect ratio of length to diameter increases due to C-axis growth and it leads to the long length of the NRs.

3.2. Phase identification

Identification of chemical state is made by determining the binding energies of each element in the XPS spectra. XPS measurements provide further evidence for the inclusion of Co ions into the host lattice. Fig. 3 shows the XPS spectra of (a) Zn 2p, (b) Co 2p and (c) O 1s states of pure and 7% Co-doped ZnO NRs. Two strong peaks centered on 1021.54 eV and 1044.61 eV (Fig. 3(a)), which are in agreement with the binding energies of Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ respectively, with a spin-orbital splitting of 23.07 eV, confirm that Zn is present as Zn$^{2+}$. The Co 2p$_{3/2}$ and Co 2p$_{1/2}$ core levels are observed at 780.10 eV and 795.55 eV (Fig. 3b) respectively, with a spin–orbital splitting of 15.45 eV, indicating that Co ions have a valence of 2+ in the Co-doped ZnO NRs. Moreover, the presence of Co as metal cluster in the Co-doped NRs can be ruled out because the differences of the 2p$_{3/2}$ and 2p$_{1/2}$ for the metallic state should be 15.05 eV [10,31]. These results demonstrate that a proper substitution of Co$^{2+}$ ions in the host ZnO lattice can be achieved via the present route without any impurity oxide phase. The O 1s peak in the surface is coherently fitted by three Gaussian components, centered at 530.6, 531.3 and 532.6 eV, respectively, as shown in

![Fig. 2. (a) FESEM image of the 5% Co doped ZnO NPs, inset shows the undoped ZnO NPs. (b) TEM image of the 7% Co doped ZnO NRs, (c) SAED pattern and (d) HRTEM lattice image for a single 7% Co doped ZnO NR showing c-axis growth. (e) EDS spectra of a single Co doped ZnO NRs, showing presence of Co inside the ZnO lattice.](image)

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Crystal structure from XRD</th>
<th>Lattice constants</th>
<th>Elemental composition from XPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped ZnO</td>
<td>31.73 36.23</td>
<td>3.253 5.211</td>
<td>Zn (at.%) O (at.%) Co (at.%)</td>
</tr>
<tr>
<td>5% Co doped</td>
<td>31.78 36.29</td>
<td>3.249 5.201</td>
<td>38 62 0</td>
</tr>
<tr>
<td>7% Co doped</td>
<td>31.95 36.44</td>
<td>3.232 5.179</td>
<td>28.8 64.9 2.8</td>
</tr>
</tbody>
</table>

![Table 1: Lattice parameters and elemental composition of ZnCo$_{1-x}$O$_x$, extracted from the XRD pattern and XPS spectra, respectively.](table)
and OH group is very less in all the samples. This is shown in Table 2. It shows the presence of Vo from optical absorption measurement. The observed changes in the absorption edges indicate a change in the band structure due to doping and resulting defect. Since the dimensions of the synthesized nanostructures are larger than excitonic Bohr radius in ZnO, size effect is unlikely to cause the observed blue shift. The sp–d exchange interaction between the ZnO band electrons and localized d-electrons associated with the doped Co ions may cause the change in such band structure. The interaction leads to a modification in the energy bands.

PL studies for the pure ZnO and Co doped ZnO samples at room temperature reveal strong UV emission peak and a broad green–yellow emission band ranging from 450 nm to 730 nm, as shown in Fig. 5(b–d). Observed broad PL peaks in the UV as well as in the visible region indicate existence of multicomponents which are extracted after fitting with multiple Gaussian functions. The obtained individual peak positions are tabulated in Table 2. Undoped ZnO NPs exhibit an excitonic emission band centered on 3.25 eV (Peak I). Co-doped ZnO NRs show a systematic blue shift in the above mentioned UV emission with increase of Co doping concentration. The near band-edge transition is generally attributed to the recombination of free excitons. The blue shift of the UV emission peak has been attributed to the strong exchange interaction between the d-electrons of Co ions and the s, p electrons of the host band. Along with the free excitonic UV emission, one additional peak (Pak II) centered at 3.15 eV is observed from all of the samples near the tail region of the above UV emission. This emission may be due to the recombination of free carriers at band tail states of ZnO. Band tail states are caused by the presence of lattice disorder/defects on the surface of nanostructures and in the present case, Co doping induced lattice disorder is expected.

Next, PL peak is the green emission peak (Peak III) centered on ~2.38 eV, which is commonly observed in the ZnO nanostructures. The origin of this peak is considered as the presence of V$_{Zn}$ or antisite oxygen (O$_{Zn}$) related defects. Other sources, such as singly ionized oxygen vacancy states (V$_{O}$) on the surface of ZnO nanostructures might also be possible. In a recent review, Janotti et al. presented strong arguments in favor of the Zn vacancies (V$_{Zn}$) instead of the oxygen vacancies (V$_{O}$) being the origin of the green luminescence. Also, as our samples are O rich, as found from XPS and EDS analysis, the presence of V$_{O}$ is very less. The intense yellow emission (Peak IV) is observed from all of the samples, centered on ~1.81 eV. This emission peak may be attributed to the recombination process associated with the oxygen interstitials (O$_{i}$). Other sources, such as contributions from hydroxyl groups, as presence of small intensity V$_{O}$ and hydroxyl group are seen by XPS measurements. Most of the theoretical calculations agree that V$_{Zn}$ and V$_{O}$ are the lowest energy defects, while the zinc and oxygen interstitials to be high in energy. Generally the defects which are favored under Zn-rich conditions (V$_{Zn}$, Zn$_{i}$) act as donors, while those favored under O-rich conditions (V$_{O}$, O$_{i}$) act as acceptors.

The peak at around 1.81 eV in Co-doped ZnO NRs signify the characteristic transition of the high-spin Co$^{2+}$ impurity level, namely 4T$_{1}(P) \rightarrow 4A_{2}(F)$ d–d internal transition. Generally, the orange–red emission (~1.81 eV) is considered as the evidence of the incorporation of Co$^{2+}$ ions in ZnO crystal lattice. Here doped cations might provide competitive pathways for recombination, nonradiative process or charge transfer process which results in quenching of the overall green–yellow emission. Also participation of the defects in FM interaction as bound states might be the reason for decrease of defect related emission in the doped NR.

![Fig. 3. XPS spectra of the (a) Zn 2p$_{3/2}$ and 2p$_{1/2}$ states and (b) Co 2p$_{3/2}$ and 2p$_{1/2}$ states of 7% Co doped ZnO NRs, (c) O 1s spectrum of undoped ZnO NPs and, (d) O 1s spectrum of 7% Co doped ZnO NRs.](image-url)
samples. Similar reduction effects of luminescence have been observed previously in nanocrystals [12]. Thus doping of Co$^{2+}$ ions also can be used to tune the visible PL properties of the ZnO nanostructures and this intern affects the magnetic properties of the doped ZnO NRs.

3.4. Magnetic properties

We observe distinct ferromagnetic behavior at and above RT in the doped Zn$_{1-x}$Co$_x$O samples measured by VSM. Fig. 5(a) shows the magnetic hysteresis ($M$–$H$) loop with magnetic moment of 1.83 emu/g for 2 T field, coercivity of 53 G and retentivity of 160 m emu/g for the 7% Co doped ZnO NRs, measured at RT. Its low coercive field indicates the soft ferromagnetic nature of the NRs. We have measured the $M$–$H$ loop several times to check the reproducibility and we have found no alteration of moment with time, implying the intrinsic nature of the FM in the ZnCoO NRs. Further we find symmetric nature in the coercivity and hysteresis loop for the low temperature $M$–$T$ measurement. Note, that the magnetic moment value for the Co doped ZnO NRs, as observed here, is relatively high as compared to the other findings for the ZnO based DMS NRs/NWs [25,43]. Fig. 4(b) shows the temperature dependent magnetization for the same sample in the temperature range 300–573 K for 1500 G field. From the differential plot of the $M$–$T$ curve we obtain the $T_c$ as 398 K. A tiny hump around 380 K can be seen, indicating some secondary phase might be present but its contribution is negligible, since it vanishes with slight increase in temperature. Also all other characterizations have shown absence of any secondary phases. $T_c$ value for Co metal is 1300 K which implies that the observed FM cannot be due to the Co clusters or its other phases. As seen from the $M$–$T$ curve, at higher temperature the magnetization shows a rapid decrease with temperature, indicating continuous transition from FM ordered state to paramagnetic (PM) disordered state, supporting single phase nature of the NRs. Note that, we observe relative low moment value (70 m emu/g) and coercivity as 185 G for the 5% Co doped ZnO samples with the presence of the hysteresis loop. As its growth and the morphology are entirely different, with spherical shaped NPs, the low moment occurs may be due to specific morphology and associated defect structures. In our earlier work of Co doped (low concentration) ZnO NWs synthesized by vapor deposition, we found very low magnetic moment and its nature as PM [26]. Also, despite the presence of intrinsic defects no measurable magnetic moment is observed in the undoped samples. This confirms that defects alone are not sufficient to account for the observed strong FM in case of our samples. Probably the particular slow reaction synthesis promotes the insertion of Co ions inside the ZnO matrix helping long range FM interaction. We believe that the C-axis growth of the NRs with the axial accommodation of Co ions and the presence of $\nu_{Zn}$, $O_{Zn,V}^-$, hydroxyl groups $Co^{2+}$ d–d internal transition.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak I (eV)</th>
<th>Peak II (eV)</th>
<th>Peak III (eV)</th>
<th>Peak IV (eV)</th>
<th>Peak V (eV)</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped ZnO</td>
<td>3.25</td>
<td>3.15</td>
<td>2.38</td>
<td>2.11</td>
<td>–</td>
<td>3.26</td>
</tr>
<tr>
<td>5% Co doped</td>
<td>3.28</td>
<td>3.15</td>
<td>2.40</td>
<td>2.11</td>
<td>1.81</td>
<td>3.28</td>
</tr>
<tr>
<td>7% Co doped</td>
<td>3.29</td>
<td>3.15</td>
<td>2.38</td>
<td>2.14</td>
<td>1.81</td>
<td>3.30</td>
</tr>
<tr>
<td>Identity</td>
<td>NBE</td>
<td>Band tail states</td>
<td>$\nu_{Zn}$, $O_{Zn,V}^-$</td>
<td>$O_\alpha$, hydroxyl groups</td>
<td>$Co^{2+}$ d–d internal transition</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4. (a) UV–Vis absorption spectra for the undoped and Co doped ZnO samples. (b–d) PL spectra of undoped, 5%, 7% Co doped ZnO samples, respectively. Different PL peaks (I–V) are fitted with Gaussian functions. Note the scaling factors in respective data to enable comparison of intensity.
interaction to attain such a high moment value in Zn$_{1-x}$Co$_x$O NRs. Other groups have reported about the role of axial accommodation of Co ions and size dependence due to axial growth of Co doped ZnO NRs for the enhancement of RTFM [12,44].

4. Origin of the FM interaction

Actually incorporation of the TM ions into the ZnO host lattice involves either the replacement of TM ions on regular Zn sites, or positioning on nonregular (i.e., interstitial) sites. The magnetic properties of the final system depend on many more parameters including the concentration and distribution of the TM ions, type and concentration of defects, n-type doping, p-type doping, morphology of the host lattice, etc. Also on account of the nanostructure nature, the surface effects are very pronounced for the high surface-to-volume ratio. There are two interacting subsystems in DMS materials: the delocalized conduction band electrons, valance band holes and the diluted system of localized magnetic moments associated with the TM ions. Ferromagnetic interaction couples the spins of s-like electrons or p-like holes near the band edges to the d-shell spins of the TM ions. The first proposed model was the Zener model driven by the exchange interactions between carriers and localized spins (s–d interaction) [45]. Later Dietl et al. have used the Zener description to realize possible origin of RT FM as hole-mediated exchange interactions and theoretically predicted a curie temperature above room temperature in p-type ZnO with 5% Mn atoms as dopants and a carrier concentration of $3.5 \times 10^{19}$ holes cm$^{-3}$ [3]. Later different groups have demonstrated that the FM state is stabilized by additional electron or hole doping in case of TM doped ZnO [46,47]. Lee and Chang have investigated the variation of magnetic interactions for different geometries of Co ion accommodation on Zn regular sites and found that the FM state is more stable than the antiferromagnetic one when Co ions are continuously aligned along the c-axis, instead of that along the a-axis and FM enhances with additional electron doping [44].

The presence of intrinsic defects (V$_{Zn}$, Zn$_i$, O$_{Zn}$, O$_i$, etc.) play an important role in FM interaction for Co doped ZnO systems [37,38,48]. The long-range interaction is necessary to obtain HT FM in dilute concentration of Co doped ZnO DMS systems and it can be mediated by defect induced states [4]. According to the bound magnetic polaron (BMP) model, bound electrons (holes) in the defect states can couple with TM ions and cause the ferromagnetic regions to overlap, giving rise to long range FM ordering [13,14]. When donors or acceptors are present, the sp–d interaction often leads to the formation of BMPs. A BMP is a particular type of complex near an occupied donor or an acceptor. It consists of the bound electron (hole) together with the spins of the TM ions within a hydrogenic Bohr orbit of radius $r_B$ (for ZnO, $r_B = 0.76$ nm). Due to the sp–d interaction the latter spins can have a significant net ferromagnetic alignment, in this case the BMP resembles a “ferromagnetic ball” embedded in the host lattice doped with TM ions that surround it [14]. Percolation of BMPs promotes high magnetic moment and high Curie temperature. In an earlier work on Co doped ZnO NPs, we have demonstrated the important role of BMPs to achieve HT FM with high moment for the ZnO based DMS system [35].

Intrinsic defects, such as V$_{Zn}$, O$_{Zn}$, and O$_i$ are inherently present in our Zn$_{1-x}$Co$_x$O samples due to the stabilization of structure. Zn vacancies promotes the FM ordering by affecting the occupancy of extended Co ions, also the presence of holes with zinc vacancies make Zn$_{1-x}$Co$_x$O strongly FM, as O$_i$ defects contribute holes in our samples [4]. Whereas oxygen vacancies have little effect on the magnetic couplings as the induced donor state is too deep to significantly affect the occupancy of the extended TM ions [4,37]. Further Yi have reported that Zn vacancies itself might introduce magnetic moments as well as additional holes and FM coupling of these local moments could be mediated by the high concentration of holes introduced by doping and V$_{Zn}$, resulting in RTFM [47]. Our systematic study shows that formation of defect (V$_{Zn}$, O$_{i}$) mediated BMPs and their percolation is one of the most promising candidates for the observed FM. To understand the suitability of the BMP model, we attempt to fit the $M$ versus $H$ data using the BMP model [14]. The formula used for the fitting of BMP model:

Fig. 5. (a) Room temperature $M$–$H$ plot for the 7% Co doped ZnO NRs. The inset shows the magnified $M$–$H$ loop showing clear ferromagnetic hysteresis behavior. (b) Temperature dependent magnetization ($M$–$T$) curve of the same sample, showing high transition temperature ($T_c$) and sharp ferromagnetic to paramagnetic transition.

Fig. 6. Initial curve (0–$H_{max}$) of the $M$–$H$ plot is fitted with BMP model (Eq. (1)) for the 7% Co doped ZnO NRs. Symbols are for experimental data and the solid line is a fit with the BMP model. Extracted parameters are shown in Table 3.
The first term in Eq. (1) represents the contribution of the BMP's, second term is the matrix contribution. Here $M_0 = N n m$, $N$ is number of BMPs involved, and $m_i$ is the effective spontaneous moment per BMP, $x_m$ is the susceptibility of the matrix. $L(x) = \text{coth}(x) - 1/x$, Langevin function with $x = m_{\text{eff}} H (k_B T)$, where $m_{\text{eff}}$ is the true spontaneous moment per BMP, and at higher temperature it can be approximated to $m_i = m_{\text{eff}}$. We have analyzed the $M$–$H$ curve by using Eq. (1). The parameters $M_0$, $m_{\text{eff}}$ and $x_m$ are variable in the fitting process. The experimental data along with fitted data are shown in Fig. 6 for the 7% Co doped ZnO NRs. The fitted data closely follows the experimental data and the fitted parameters are tabulated in Table 3. The spontaneous moment per BMP, $m_{\text{eff}}$ is found to be of the order of $10^{-17}$ emu. By assuming $m_i = m_{\text{eff}}$, we have estimated the concentration of BMP to be of the order of $10^{17}$ cm$^{-3}$ considering the effective Bohr radius of the BMPs as 0.76 nm (see Table 3). However, this number is relatively small compared to the necessary concentration of $10^{20}$ cm$^{-3}$ in order to have long range percolation. Thus, the calculated low concentration of BMPs cannot fully account for the observed high magnetic moment in the doped ZnO. Also, as the initial $M$–$H$ curve has not reached up to saturation value due to limitation of magnetic field, thus BMP fitting is having a limitation on the BMP parameters. It would lead to higher concentration of BMPs for the fitting up to saturation value, as observed in our earlier work [35,49]. Further, presence of $O_6$ in our samples is favorable to exhibit presence of holes due to the activation of acceptor states [41]. The activation of acceptor states for hole formation might be partly responsible for the enhancement in RTFM in the Co doped ZnO NRs, and it is consistent with the Dietl's prediction of hole mediated ferromagnetism in Mn doped ZnO system [3]. Also defect related surface spins might contribute partly for the observed FM in the Co doped ZnO NRs. Due to a large surface area, a lot of defect modes have been found in the XPS and PL spectra. Sanchez et al. have reported that the uncompensated surface spins enhance the spin polarization induced by substitute Co ions and even in the absence of magnetic ions, it might promote the formation of $p$-derived extended magnetic states [50].

Fig. 7 shows a schematic diagram of BMP percolation with respect to the presence of $V_{\text{Zn}}$, $O_6$ defects and distribution of Co ions in the ZnO lattice. It explains that defect mediated BMP formation within its hydrogenic radius helps to promote long range FM ordering with the increase of BMP concentration. Case 1 shows percolation of two nearby BMPs and case II is that of an isolated BMP. Whereas isolated Co ions can have rare FM interaction without the presence of defects, since they would either align antiferromagnetically in case of short-range interaction or can hardly interact through the itinerant carriers due to their dilute concentration as compared to their metallic FM phases. The doped cations provide an extra random potential, which extends the localized region as its concentration increases. Overlap between a hydrogenic electron and the cations within its orbit leads to ferromagnetic exchange coupling between them, provided the hydrogenic orbital radius is sufficiently large [51]. The number of cation sites $r_c$ within a sphere of radius $r_H$ ranges from ten to a hundred, depending on the value of $r_H$ (For ZnO, $r_H = 0.76$ nm, $r_c = 64$) [13]. Thus enhances long range FM interaction in the Co doped ZnO NRs.

Note that, we do not find any measurable magnetization in the undoped ZnO NPs. Also, defect related FM moment reported in the literature for the undoped nanostructures is of much lower magnitude (of the order of $10^{-3}$ emu/g) as compared to doped DMSs [19,52]. We observed at least three orders of higher moment in the doped ZnO NRs. Possibly, axial growth of the NRs with higher concentration of Co ion accommodation along C-axis enhances the FM interaction. Thus, it appears that both TMs as well as defects are important ingredients to attain high moment as well as high $T_c$, as observed here. More detailed experimental work like AHE [52], magnetotransport measurements [35] and optical magnetic circular dichroism [11] might provide further insights into a more precise understanding of the origin of ferromagnetism in magnetically doped oxides and the possible way to improve its quality. This 1D DMS NRs can be a good source of spin-polarized carriers and they can be used for spin injection or spin transport in spintronic devices.

### Table 3

<table>
<thead>
<tr>
<th>Sample type</th>
<th>$M$–$H$ parameters</th>
<th>Fitting parameters extracted from BMP model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_0$ (emu/g)</td>
<td>$m_{\text{eff}} \times 10^{-17}$ (emu)</td>
</tr>
<tr>
<td></td>
<td>$H_c$ (G)</td>
<td>$N \times 10^{17}$ (cm$^{-3}$)</td>
</tr>
<tr>
<td></td>
<td>$M_r$ (m emu/g)</td>
<td>$x_m$</td>
</tr>
<tr>
<td>Undoped ZnO</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>5% Co doped</td>
<td>0.07</td>
<td>8.28</td>
</tr>
<tr>
<td>7% Co doped</td>
<td>1.83</td>
<td>0.18</td>
</tr>
</tbody>
</table>

\[
M = M_0 L(x) + x_m H
\]

\[(1)\]
5. Conclusion

In summary, RTFM with high magnetic moment is reported in the Zn$_{1-x}$Co$_x$O NRs synthesized by a low temperature solvothermal route. TEM micrograph reveals the formation of long and uniform ZnO NRs with 50–90 nm diameters and 0.3–0.6 μm length. XRD, XPS, HRTEM and EDS analysis confirm the absence of Co clusters in the doped NRs. XPS spectra also confirm the presence of Co ions in 2+ states within host lattice. Magnetic measurements exhibit RTFM behavior with high moment of 1.83 emu/g at 2 T field and Curie temperature around 398 K. The structural, optical, and magnetic properties are sensitively changed by the incorporation of Co$^{2+}$ ions in the Zn$^{2+}$ lattice site. PL and XPS spectra confirm the nature of defects present in the doped and undoped samples. PL and UV–VIS measurements show doping induced modification in the band edge emission and absorption spectra. These findings suggest Co$^{2+}$ ions are successfully incorporated into the wurtzite lattice at the Zn$^{2+}$ sites. The observed FM is explained on the basis of intrinsic exchange interaction of Co ions and V$_{Zn}$, O$_x$ defects, both the Co ions as well as defects are significant ingredients to attain high moment as well as high ordering temperature.

Acknowledgments

We thank CSIR for providing senior research fellowship and financial support through project grant (03/1270/13/EMR-II) in carrying out this work. We also thank Central Instruments Facility (CIF), IIT Guwahati and Department of Electrical and Electronic Engineering, Kobe University, Japan to accomplish part of this work.

References