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Study of Ferromagnetism in Mn Doped ZnO Dilute Semiconductor System

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Abstract
The wide band gap semiconductor ZnO when doped with a very low percent of some transition metal ions can exhibit above room temperature ferromagnetism, transforming it into a unique compound for spin-electronic applications. In the present work we have compared the electronic structure of two polycrystalline Zn₁₋ₓMnₓO pellets (for x=0.02 and 0.04), prepared by low temperature processing, and carefully characterized. The Rietveld refinement of the XRD patterns established that the samples have the ZnO lattice with ZnS type Wurtzite hexagonal symmetry and no detectable impurities. The samples exhibit distinctly different magnetic properties. The pure ZnO pellet shows a diamagnetic behaviour, the 2% sample displayed a clear FM ordering at 300 K while the 4% sample did not show any ordering even upon cooling. Their electronic structure has been investigated using x-ray absorption and x-ray photoemission spectroscopy with an aim to find out how the changes in the electronic structure can correlate to the magnetic properties in such diluted magnetic semiconductor materials. The results show that most of the Mn ions of the ferromagnetic sample are in the divalent state. For the higher Mn percent nonmagnetic sample, a larger contribution of higher oxidation Mn states are dominant and the oxygen content also increases. The two factors can be correlated to the suppressed ferromagnetism, though it is hard to exactly predict that which of these two factors weighs more.

1. Introduction
Dietl’s prediction, that the ferromagnetism at high temperature can be obtained in many wide band gap semiconductors such as ZnO, GaAs, GaN when doped with diluted transition metals can show...
ferromagnetism above room temperature, has attracted considerable research interest [2-14]. Following it, there has been intense searching for ferromagnetic ordering in doped dilute magnetic semiconductors (DMS’s) focusing on possible spin-transport properties, which has many potentially interesting device applications. Spintronic devices such as spin-valve transistors spin light-emitting diodes, non-volatile memory, logic devices, optical isolators and ultra-fast optical switches are some of the areas of interest for introducing the ferromagnetic properties at room temperature in a semiconductor [15-18].While the DMS’s based on III–V semiconductors show ferromagnetism only at very low temperatures, the oxide-based DMSs may be ferromagnetic at room temperature or at even higher temperatures.

The occurrence of ferromagnetism in DMS’s has been long debated due to confronting reports. Considerable doubts and fears have been expressed that even though the Mn clusters are expected to give an antiferromagnetic state, rather than a ferromagnetic (FM) order, very small clusters can be ferromagnetic [2]. The first reports of room temperature FM ordering in Mn-doped ZnO powder, bulk pellets as well as thin films with Curie temperatures far above 300K came from Sharma et al [19,20]. This was confirmed by Blythe et al [21] who made a detailed study of dependence of the FM ordering on the processing temperature. On contrary, Kane et al [22] claimed no evidence of an FM ordering in Zn$_x$Mn$_{1-x}$O, Zn$_x$Co$_{1-x}$O bulk single crystals. Instead, they claimed a paramagnetic behaviour in case of the former and hysteresis in the latter owing to super-paramagnetic Co clusters embedded in a diamagnetic ZnO matrix. Kittilstved et al [23] have, on the other hand, not only observed high- $T_c$ ferromagnetism in ZnMnO and ZnCoO systems but also show how their $T_c$ can be manipulated through in situ as well as ex situ chemical manipulation. Long et al [24] studied the effects of annealing atmosphere on FM behaviour for the ZnCoO bulk samples. They show that the air-annealed samples has weak FM ordering, but the samples annealed in vacuum or Ar/H$_2$ show a strong FM behaviour, indicating that the strong ferromagnetism is associated with high oxygen vacancies density. The enhanced room-temperature FM behaviour is also found in the samples with high carrier concentration controlled by doping interstitials Zn.

Various theoretical attempts have been put forward to explain the ferromagnetism in these DMS systems. In ZnO system it has been proposed that the ferromagnetism can be obtained by the mediation of the shallow donors or acceptors [23] or the holes in the valence band [1]. Garcia etal [6] suggested that the ferromagnetism in this system should be associated with the co-existence of Mn$^{3+}$ and Mn$^{4+}$ via a double-exchange mechanism. Based on x-ray-magnetic-circular dichroism studies of diluted Zn$_{1-x}$Co$_x$O films, it is shown that Co ions substituted to Zn in the ZnO matrix are not responsible for the origin of FM ordering [6-8] but the anion sublattice may be instead responsible of the ferromagnetism [8]. Occurrence of ferromagnetism in undoped HfO$_2$ thin films have urged the researchers to re-judge the real role that doping may play in tailoring the magnetic properties of these oxides [25]. Some reports [25-28] on ferromagnetism in various undoped oxides claimed that magnetism is certainly possible in undoped semiconducting and insulating oxide thin films, that originates due to oxygen vacancies. But despite a lot of theoretical and experimental attempts, the origin of ferromagnetism in semiconductors remains an issue of debate. When assigning the origin of ferromagnetism in Mn-doped ZnO DMS, it is important to distinguish the contributions of the transition metal with different valence bonds, providing evidence to explore whether the magnetization originates from the magnetic precipitates or not.

In this paper we have studied the electronic structure of two single phase polycrystalline ZnMnO samples with 2% and 4% Mn concentration. The two samples exhibit entirely different magnetic behaviour as shown by SQUID. The 2% sample displayed clear FM ordering at 300 K, the 4% sample did not show any ordering even upon cooling. The electronic structure of these two samples has been investigated using x-ray absorption and photoemission spectroscopy to find out how the changes in the electronic structure can correlate to the observed magnetic properties.
2. Experimental techniques

High purity (99.999%) ZnO and MnO$_2$ powders from Johnson Matthey Company (JMC) were mixed and ground for long time to get a homogeneous mixture. The ground mixture was calcined at (450±5)$^\circ$C for nearly 14 hrs raising the temperature very slowly above 100$^\circ$C in a microprocessor controlled furnace and similarly cooling it very slowly after completion of the calcinations. The resulting lumps were ground for ~5 hrs and pellets of 10 mm diameter using a hydraulic pressure of nearly 7 tons. The pellets were then sintered at (500±5)$^\circ$C for 18 hrs. The important feature of our sample preparation was the low-temperature processing. When high-temperature ($T > 700^\circ$C) methods were used, samples were found to exhibit no ferromagnetic ordering at room temperature.

The hysteresis loops were measured at different temperatures by a dc-SQUID magnetometer (MPMS-XL, Quantum Design) at CBPF, Brazil. The x-ray diffraction (XRD) patterns of the samples were collected on a Rigaku x-ray diffractometer equipped with CuK$_\alpha$ radiation. The 2$\theta$ scan was from 10$^\circ$ to 90$^\circ$ with a step size of 0.05$^\circ$. Rietveld profile refinements of the XRD patterns were carried out using the FULLPROF Program [29].

The Mn $L_{2,3}$ edge x-ray absorption spectra in total electron yield mode were recorded at the BACH beamline of Elettra in Trieste, Italy. The spectra were recorded at 300 K at pressure better than 5x10$^{-10}$ mbar. The measurements were performed on Zn$_{0.98}$Mn$_{0.02}$O and Zn$_{0.96}$Mn$_{0.04}$O pellets (referred to as the 2% sample and 4% sample, respectively, in the following) and on some reference samples, i.e. MnO, La$_{1.2}$Sr$_{1.65}$Ca$_{0.15}$Mn$_2$O$_7$ bilayer manganite, all scraped in UHV before each measurement. The core level x-ray photoemission spectra were measured using an x-ray photoelectron spectrometer at IUC, Indore, India using the Al K$_\alpha$ radiation. The samples were scraped uniformly with diamond files before carrying out the measurements. Final spectra were taken after minimizing the feature coming from carbon contamination of the surface (C 1s peak). The vacuum in the chamber was ~4.4 x 10$^{-10}$ Torr. We kept scraping the samples in situ to get uncontaminated surface throughout the measurements. No shift was observed due to charging of the samples.

3. Results and discussion

3.1. Characterization results

The XRD patterns of pure ZnO with Wurtzite hexagonal structure and no impurity peaks are displayed in figure 1a. The cell parameters were refined with the help of a least square refinement program that are in good agreement with the reported values. Figures 1 b,c show the fitted XRD patterns of the 2% and 4% Mn doped ZnO sample, respectively, recorded at 300 K. The patterns show the single phase ZnS type Wurtzite hexagonal symmetry with no signature of any peak from any other phase. We used the FULLPROF Program [29] for Rietveld profile refinements of the XRD patterns. The Rietveld refinement were carried out using the P6$_3$mc space group (No.186, Z=3), with each atom in the Wurtzite hexagonal structure residing on the 2b Wyckoff position with the Zn atoms at (1/3,2/3,0) and the O atoms at (1/3,2/3,z) co-ordinates. In the refinement process the Mn occupancy was varied for the two Zn and O sites to locate the exact site of Mn. The best fit was obtained when Mn atoms occupy the Zn site with total preference while the Mn atoms occupying the O site gave very poor fits. In fact, the atomic scattering lengths of the three atoms i.e. Zn (Z= 30), Mn (Z= 25) and O (Z= 8) are quite different as these are far away in the periodic table, hence all the three atoms can be easily distinguished in the profile refinement. Our Rietveld analysis shows that Mn atoms occupy the Zn site with total preference. The cell parameters are shown in Table 1. The refined parameters shown in the table further confirm the stoichiometry and the single phase nature of the samples.
The XRD pattern of ZnO powder at 300K. b. the fitted XRD pattern of Zn$_{0.98}$Mn$_{0.02}$O sample. c. the fitted XRD pattern of Zn$_{0.96}$Mn$_{0.04}$O at 300K. Observed (calculated) profiles are shown by dotted (solid) curves in case of fig. b and c. The short vertical marks represent Bragg reflections. The lower curves are the difference plot.

**Table-1.** Crystallographic data for Zn$_{1-x}$Mn$_x$O samples at 300K obtained using the Rietveld refinement of the powder XRD patterns. Space group is P6$_3$mc (No. 186, Z = 2). Each atom in the Wurtzite hexagonal structure resides on the 2b Wyckoff position with Zn atoms at (1/3,2/3,0) and O atoms at (1/3,2/3,z).

| Sample          | Cell parameters | Discrepancy factors |
|-----------------|-----------------|---------------------|
|                 | a [Å] c [Å] V [Å$^3$] O [positional parameter z] $\chi^2$ R$_p$ [%] R$_wp$ [%] |
| ZnO             | 3.249 5.207 47.69 0.612 |
| Zn$_{0.98}$Mn$_{0.02}$O | 3.252(3) 5.212(5) 47.73 0.628 1.76 6.15 7.92 |
| Zn$_{0.96}$Mn$_{0.04}$O | 3.253(2) 5.213(4) 47.76 0.637 1.76 6.34 8.63 |
3.2. Magnetization measurements

The magnetization versus field (hysteresis) curves at 300 K for Zn$_{0.98}$Mn$_{0.02}$O and Zn$_{0.96}$Mn$_{0.04}$O samples are shown in figure 2a. All the measurements were repeated several times with the time interval of several weeks to minimize the experimental error. The curves clearly reveal a room temperature FM ordering of the 2% sample but no such signature for the 4% sample. In fact, the 4% sample shows a purely a paramagnetic state (see inset). The shape of the loop does not rule out the presence of some para-magnetic (PM) contribution even for the 2% sample. Figure 2b displays the separated PM and the FM contributions along with the experimental curve and the fit made to it. The saturation magnetization and coercivity estimated come out to be ~ 0.0019 emu/g and ~ 19.8 Oe respectively. Figure 3 displays the comparison of the curves at 300K and 50K for the FM sample. The sample shows an appreciable enhancement in saturation magnetization as well as the coercivity upon cooling (~0.0029 emu/g and ~ 27.9 Oe respectively at 50K). The sample with 4% Mn did not show any FM ordering even upon cooling down to 5K (not shown here). Pure ZnO pellet prepared in same conditions was also measured at room temperature and 50 K but it showed a diamagnetic behaviour at both these temperatures (not shown).

**Fig. 2a** Magnetization vs. Field curve for Zn$_{0.98}$Mn$_{0.02}$O at 300K. The inset shows the curve for Zn$_{0.96}$Mn$_{0.04}$O at 300K **Fig. 2b** Magnetization vs. Field curve for Zn$_{0.98}$Mn$_{0.02}$O at 300K alongwith the paramagnetic and FM contributions.
Fig. 3. Comparison of hysteresis curves for Zn$_{0.98}$Mn$_{0.02}$O sample at 50K and 300K.

3.3. XAS m,earurements

The Mn $L_{2,3}$ edge x-ray absorption spectrum measured for the 2% sample is shown in figure 4a. Spectra for MnO (Mn$^{2+}$ reference system) and the La$_{1.2}$Sr$_{1.65}$Ca$_{0.15}$Mn$_2$O$_7$ bilayer manganite (reference system of a mixed valent Mn$^{3+}$/Mn$^{4+}$ compound) are also shown for a comparison. The spectrum of the 2% FM sample is very different from that of the bilayer manganite, which has the main peak at nearly 2.5 eV higher energy than the main peak of the 2% sample (at 640 eV). This indicates a significant change in the charge state and crystal field of Mn in the two systems. The spectrum of the 2% sample is also different from the spectrum of Mn metal [our ref. 10], which does not display multiplet structures. This rules out the possibility of Mn impurities getting segregated in metallic clusters form. In fact, the spectrum from of the 2% sample shows multiplet structures qualitatively similar to those of MnO, suggesting that Mn ions in the sample Zn$_{0.98}$Mn$_{0.02}$O are nearly divalent. However, the Mn $L_1$ edge reveals several differences between the two spectra, if we look at figure 4b carefully. Firstly, the lower energy multiplet lines at 639 eV do not appear for Zn$_{0.98}$Mn$_{0.02}$O. Secondly, there is an increased spectral weight around 642 eV in Zn$_{0.98}$Mn$_{0.02}$O. These differences indicate that the local environments of Mn in Zn$_{0.98}$Mn$_{0.02}$O and MnO are different. The absence of the multiplet lines at 639 eV can be assigned to a lower absolute value of the crystal field parameter $10Dq$ for Zn$_{0.98}$Mn$_{0.02}$O with respect to the corresponding value for MnO. In fact the difference spectrum between the Zn$_{0.98}$Mn$_{0.02}$O and MnO spectra (figure 4b) does show similarities with the Mn $L_3$ spectra of the bilayer manganite.
Fig. 4 (a) Mn $L_{23}$ XAS spectra of La$_{1.2}$Sr$_{1.65}$Ca$_{0.15}$Mn$_2$O$_7$ bilayer manganite, Zn$_{0.98}$Mn$_{0.02}$O, MnO systems
(b) Mn $L_3$ XAS of the Zn$_{0.98}$Mn$_{0.02}$O compared to Mn $L_3$ XAS of MnO, difference spectrum between the Mn $L_3$ XAS of MnO and the Mn $L_3$ XAS of Zn$_{0.98}$Mn$_{0.02}$O, Mn $L_3$ XAS of the bilayer manganite shown for comparison.

3.4. XPS measurements
Zn 2p, 3p, Mn 2p and O1s core level XPS spectra were measured for pure ZnO and the two doped samples to study the electronic structure in each case. The results are presented for each in the following subsections.

3.4.1. Zn 2p and 3p XPS data.
The Zn 2p$_{3/2}$ XPS spectra for the pure ZnO and the Mn doped samples are displayed in figure 5a. All the three spectra show a symmetric featured single peak at ~1023 eV. A single Gaussian was nicely fit to all the spectra and no change in the peak positions was noticed upon Mn doping. The single Gaussian rules out the possibility of multiple components of Zn in any of these samples. Figure 5b shows the Zn 3p core level XPS spectra. The spectra show the 3p$_{3/2}$ and 3p$_{1/2}$ bands located at ~88.6 and 91.6 eV, respectively. The two Gaussians were fit to the Zn 3p spectra but again no shift observed in the positions of two bands (3p$_{3/2}$, 3p$_{1/2}$), that reconfirms the absence of any other multiple Zn components in these samples. The area under the peaks of 2p$_{3/2}$, 3p$_{3/2}$ and 3p$_{1/2}$ progressively decreases as the concentration of Mn at Zn site increases that was natural. Thus no electronic structural change is observed at the Zn site by Mn doping.
The Zn 2p$_{3/2}$ XPS spectra for the Zn$_{1-x}$Mn$_x$O [x=0, 0.02, 0.04] samples along with the Gaussian fits. The Zn 3p XPS spectra along with the Gaussian fits.

3.4.2. Mn 2p$_{3/2}$ XPS data.
The Mn 2p$_{3/2}$ XPS spectra are shown in figure 6. The three Gaussian peaks located at 640.0, 642.6 and 645.0 eV, can be attributed to Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$ valence states, respectively. To make a quantitative estimation of atomic percent of Mn$^{2+}$ and the other valence states, the area of the different valence bonds of Mn were calculated and the results are summarized in the table 2. It has been found that the largest Mn$^{2+}$ atomic concentration appeared in the FM 2% sample. In the non-FM 4% sample the Mn$^{2+}$ percent declines and the higher valence states Mn$^{3+}$ and Mn$^{4+}$ dominate.

3.4.3. Oxygen 1s data.
Asymmetric Oxygen 1s spectra, shown in figure 7 indicate that multi-component oxygen species are present in the near-surface region of these samples. The high energy peaks located at 532.7 and 533.5 eV are due to the chemisorbed oxygen of the surface hydroxyl, -CO$_3$, absorbed H$_2$O, absorbed O$_2$ or the surface contamination. But the most intense first peak at ~ 531.2 eV is due to the actual O1s contribution from the samples. Area under the peak O 1s progressively increases by the doping of Mn. The first Gaussian peak that is corresponding to Oxygen 1s feature has been highlighted in the inset of figure 7. This enhancement of oxygen and the increase of Mn valence state with increase in Mn concentration can be attributed to the charge neutrality of the samples similar to the reports of magnetic ordering in ZnO thin films [30] and may be causing the suppression of ferromagnetism. This is in agreement to reports [24] that have shown that the air-annealed sample has weak FM ordering, but the sample annealed in vacuum or Ar/H$_2$ show a strong FM behaviour, indicating that the strong magnetic ordering might be associated with high oxygen vacancies density.
Fig. 6. Gaussian fits in the Mn 2p$_{3/2}$ XPS for the Zn$_{1-x}$Mn$_x$O [x=0.02, 0.04] samples. Fig. 7. The O 1s XPS spectra for the two samples along with the Gaussian fits. The Gaussian corresponding to Oxygen 1s feature is shown in the inset for clarity.

Table-2. Area of the peaks under the Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$ Gaussians and the absolute quantity of Mn$^{2+}$ in the 2 and 4% doped samples.

| Sample       | Area of peaks [in arb.units] | Quantity [%] of Mn$^{2+}$ in all Mn valence bonds | Quantity [%] of Mn$^{2+}$ in Zn$_{1-x}$Mn$_x$O sample |
|--------------|------------------------------|-----------------------------------------------|-----------------------------------------------|
| Zn$_{0.98}$Mn$_{0.02}$O | 3672.1  2521.3  1681.3  | 46.63  | 0.93 |
| Zn$_{0.96}$Mn$_{0.04}$O | 1011.8  4073.9  3494.2  | 11.79  | 0.47 |

The observed FM ordering in these materials has been speculated to be due to presence of some secondary phases or clustering effect. In the present samples the possible secondary phases could be manganese oxide phases, such as MnO, MnO$_2$ and Mn$_3$O$_4$. Here, first of all, we should mention that we had followed the low-temperature processing to avoid any secondary phases which are reported to be evolved only when high-temperature (T > 700 °C) methods were used. However, of the manganese oxides stated above, the MnO and the MnO$_2$ may be safely ruled out as they are anti-ferromagnetic. Ferromagnetic Mn$_3$O$_4$ has a Curie temperature at 43K that is far below all these samples [31]. In addition, another possible phase ZnMnO$_3$ is established to show a spin-glass behaviour [32,33]. If the formation of a
secondary Mn-related phase were responsible for the FM behaviour, an increase in Mn concentration would presumably increase the secondary phase volume fraction and related magnetization signature, instead, the opposite behaviour is observed that by increasing the Mn content from 2 to 4 at% caused a complete destruction of FM order. This rules out the magnetization due to any precipitating secondary phase in our samples.

Many theoretical attempts have been put forward to explain the observed magnetic ordering in these materials. Some are based upon mediation of the charge carriers [23] or the holes in the valence band [1], others are based upon the co-existence of Mn$^{3+}$ and Mn$^{4+}$ via a double-exchange mechanism. Also it has been argued, on the basis of experimental data, that the FM ordering in the ZnO system should not originate from oxygen vacancies as in the case of TiO$_2$ and HfO$_2$ films, but from defects on Zn sites [30,34]. A theoretical work stating that for ZnO, oxygen vacancies or Zn interstitials should result in antiferromagnetism, while ZnO with Zn vacancies has more chance to be ferromagnetic [34], supports this argument. It was also reported that magnetization of films of 10-50 nm-thick is much larger than that of the thicker films. This reveals that defects must be located mostly at the surface and/or the interface between the film and the substrate, or possibly nanometer-size layers at the interface/surface. According to Ruderman-Kittel-Kasuya-Yoshida theory [35,36] the ferromagnetism is a carrier-induced mechanism. This arises due to the exchange interaction between local spin-polarized electrons like the electrons of Mn$^{2+}$ ions, and conductive electrons. This interaction leads to the spin polarization of conductive electrons. Subsequently, the spin-polarized conductive electrons perform an exchange interaction with local spin-polarized electrons of other Mn$^{2+}$ ions. Thus, after the long-range exchange interaction, almost all Mn$^{2+}$ ions exhibit the same spin direction. The conductive electrons are regarded as a media to contact all Mn$^{2+}$ ions. As a result, the material exhibits FM ordering. More local spin-polarized electrons are produced with increasing Mn$^{2+}$ concentration. Hence the best FM properties should be occurred for the low percent Mn sample as seen in our case, a plausible and explanation of the ferromagnetic ordering in the Mn-ZnO system.

4. Summary

We have studied the electronic structure of two polycrystalline ZnMnO pellets doped with diluted Mn concentration (2% and 4%). The important feature of our sample preparation was the low-temperature processing to avoid the secondary phases. When high-temperature (T > 700 °C) methods were used, samples were found to exhibit no ferromagnetic ordering at room temperature. The samples were characterized by SQUID and XRD. The XRD patterns and the Rietveld refinement confirmed that the samples are single phase with no detectable impurities having the ZnO lattice with Wurtzite hexagonal symmetry. The SQUID measurements show that the samples exhibit different magnetic properties. The 2% sample shows a clear room temperature FM ordering, the 4% sample did not show any ordering down to 5K. Pure ZnO pellet prepared in same conditions showed rather a diamagnetic behaviour from 300 to 50K. The electronic structure of these samples was investigated using x-ray absorption and x-ray photoemission spectroscopy. The XPS, XAS results show that most of the Mn ions of the ferromagnetic sample are in the divalent state. For the nonmagnetic sample, a larger contribution of higher oxidation Mn states (3+, 4+) is present and the oxygen content also shows an increment, which can be correlated to the suppressed ferromagnetism. Our studies reveal that the suppression of ferromagnetism can be associated with higher oxidation Mn state and the higher oxygen vacancies density. However, these studies are not enough to conclude which of these two factors weighs more in the suppression mechanism or some more factors are important.
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