Investigation of the insulator to half-metal transition in Cr-doped ZnO at low temperature (19 K) wurtzite structure

Sarajit Biswas*
Dept. of Physics, Taki Government College, P.O.-Taki, Dist., North 24 Parganas, 743429, West Bengal, India
*Corresponding: srisabuj.phys@gmail.com

Abstract

The structural, electronic and magnetic properties of pure and Cr-doped ZnO with a low temperature (19 K) wurtzite structure were studied by employing density functional theory (DFT) as implemented in the tight-binding linearized-muffin-tin orbital (TB-LMTO) method. Pure ZnO is observed as a nonmagnetic insulator in which all the Zn-3d orbitals are found occupied and electrons are perfectly paired in each orbital causing nonmagnetic nature of pure ZnO. But Cr-doping in ZnO significantly changes its electronic and magnetic properties. This material encounters nonmagnetic insulator to a ferromagnetic half-metal with minute structural distortions at 50% Cr substitution for Zn. This study revealed that the doped material Zn$_{0.5}$Cr$_{0.5}$O is metallic for the majority spin species and insulating for the minority spin species with a semiconducting gap of 3.5 eV. Due to the influence of the strong electron correlation effect, three Cr-$t_{2g}$ orbitals become fully occupied by three Cr-3d electrons, while remaining single electron is shared by two e$_{g}$ orbitals in the close vicinity of the Fermi level. This sharing of the single electron by two e$_{g}$ orbitals is responsible for the metallic behavior of Zn$_{0.5}$Cr$_{0.5}$O for the spin majority channel. The parallel alignment of unpaired electrons in the Cr-3d orbitals is responsible for the ferromagnetism of this material.

Keywords: Density functional theory (DFT); Ferromagnetism, Half-metal; Local spin density approximation (LSDA); Wurtzite structure

1. Introduction

Recently, research studies have investigated the area of wide band gap semiconductor materials due to their wide range of applications. Among them, zinc oxide (ZnO) as a II-VI compound semiconductor material has many unique features. These include its wide band gap (3.32 eV), large excitation energy (~ 60 meV), high melting point, high-temperature resistance, etc. ZnO is a promising semiconductor materials for its widespread industrial and scientific applications, such as in piezoelectric nanogenerators, transparent electrodes, ultraviolet (UV) detectors, gas sensors, optoelectronic devices, photocatalytic activity (Gao et al., 2005; Battaglia et al., 2011; Chai et al., 2009; Yi et al., 2011; Djurisi et al., 2010). Many experiments have demonstrated that doping in ZnO nanoparticles influences their physical, chemical, and structural properties (Rasouli & Moecn, 2011). In order to achieve expected properties, different kinds of elements have been doped into the ZnO lattice, including rare earth elements and metals (Chen et al., 2010; Gao et al., 2006; Zheng et al., 2011). The prime object of doping elements into ZnO nanocrystals is to increase or decrease the band gap energy of this system through the doping of exact doping elements. When doping with transition metals such as V, Cr, Fe, Co or Ni, ZnO nanoparticles turn into a promising host semiconductor material. Dietl et al., (2000) theoretically demonstrated that Mn-doped ZnO would be ferromagnetic at room temperature and could be applied to spintronic devices. In addition, another research has been carried out to improve the structural, optical and magnetic properties of Cr-doped ZnO thin films (Yilmaz et al., 2011; Lin et al., 2012; Iqbal et al., 2013; Shah et al., 2014).

In their ab initio calculations, Sato et al., (2002) reported that V, Fe, Cr, Co and Ni doping in ZnO shows ferromagnetic ordering above room temperature. However, experimental studies of Cr-doping in ZnO show conflicting results. In some studies, the magnetic behavior of Cr-doped ZnO appears to be very sensitive to the deposition method. For example, Ueda et al., (2001) did not detect ferromagnetism in Cr-doped ZnO films synthesized by the pulse laser deposition method. However, Roberts et al., (2005) detected ferromagnetic ordering at a doping concentration of 9.5% in the magnetron sputtering method. Additionally, Jin et al., (2001) confirmed no ferromagnetic behavior for a Cr-doped ZnO thin film at low temperature (LT) even down to 3 K. In some studies (Thota et al., 2006; Bhargava et al., 2011; Gad et al., 2015), it was observed that for a low Cr-concentration (up to x=0.10), Zn$_{1-x}$Cr$_{x}$O has a single phase, but a higher Cr-concentration (x>0.15) confirms a secondary phase of ZnCr$_2$O$_4$, which gives the oxidation state of Cr as +3. Coexistence of these
two phases results in a crystal defect due to the non-homogeneous distribution of Cr into ZnO. However, Xu et al., (2008) and Zhuge et al., (2009) incorporated Cr in the ZnO materials uniformly and observed no secondary phase. For doping in the compound Zn$_{1-x}$M$_x$O (0.05-0.25): M=Cr, Mn, Co, Ni, the doping level was as high as 25%, but no additional secondary phase was observed (Ueda et al., 2001). It’s important to note that all the cited works were carried out in the room temperature phase.

Current research is limited considering the Cr-doping effect in ZnO at low temperature (LT) structure. (Jin et al., 2001; Kim et al., 2014). In a study by Ueda et al. (2001), a doping level in the compound Zn$_{1-x}$M$_x$O (M=Cr, Mn, Co, Ni) reached 25%. S. Thota et al., (2006) reported the highest doping of 30% in ZnO by Ni, Co, Mn. Zhuge et al., (2010) increased the Co-doping in ZnO up to 37.7%. Furthermore, in materials such as CrO$_2$, high doping of Ru (~50%) was carried out by West et al., (2015). This research showed significant changes in the electrical and magnetic properties. In addition, a higher concentration of Cr in ZnO (as much as 50%) has interestingly exhibited an insulator to half-metal transition concomitantly with a magnetic phase transition (from nonmagnetic to ferromagnetic). These results and issues have led to more investigations on the electronic, magnetic and structural properties of Zn$_{0.5}$Cr$_{0.5}$O.

In this paper, the electronic, magnetic and structural properties of pure and Cr-doped ZnO have been extensively investigated in LT (19 K) hexagonal wurtzite structure. It is revealed for the first time that this material encounters a nonmagnetic insulator to ferromagnetic half-metal transition for 50% Cr-doping (Zn$_{0.5}$Cr$_{0.5}$O). This transition is very interesting because the half-metallic ferromagnetic behavior of Zn$_{0.5}$Cr$_{0.5}$O can be utilized for spintronic devices, thermochromic devices, optical and holographic devices, sensors, actuators and power meters, or thermometers. This research investigates the origin of the insulator to half-metal transition for Cr-doping in ZnO, and likewise, the origin of ferromagnetism of Zn$_{0.5}$Cr$_{0.5}$O.

2. Method of calculations

Self-consistent spin-polarized electronic structure calculations of pure and Cr-doped ZnO were carried out using density functional theory (DFT) (Hohenberg & Kohn, 1964; Kohn & Sham, 1965) as implemented in the tight-binding linearized-muffin-tin-orbitals (TB-LMTO) method in its atomic sphere approximations (ASA) (Anderson, 1975; Perdew & Wang, 1992). The local spin density approximations (LSDA) (Perdew & Wang, 1992; Anderson & Jepsen, 1984) were employed in the first-principles electronic structure calculations.

The ideal ZnO has a hexagonal wurtzite structure with the space group P6$_3$mc (space group number 186). The primitive unit cell contains two Zn and O atoms each. The Zn atom is located at the center of a tetrahedron made up of four O atoms, i.e. at the center of a ZnO$_4$ tetrahedron. The lattice parameters used were: $a = b = 3.2465$ Å and $c = 5.2030$ Å, $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$. Each Zn atom is located at (0.3333, 0.6667, 0.3812), whereas the O atom is located at (0.3333, 0.6667, 0) (Yoshio et al., 2001). A Cr concentration of $x = 0.5$ in Zn$_{1-x}$Cr$_x$ was employed to investigate the substitution effect of Cr in the LT ZnO.

3. Results and discussion

3.1 Structural properties

The structure of both pure ZnO and Zn$_{0.5}$Cr$_{0.5}$O in the LT phase are illustrated in Figure 1. The primitive unit cell of pure ZnO consists of two Zn and O atoms each. The Zn atoms have a four-fold coordination with O atoms. These four O atoms form a regular ZnO$_4$ tetrahedron with Zn at the center of such a tetrahedron (see Figure 1(a)).

![Fig. 1. Crystal structures of pure ZnO (a) and Zn$_{0.5}$Cr$_{0.5}$O (b). Zn, O and Cr atoms are represented by the yellow, red and violet solid spheres.](image)

In each ZnO$_4$ tetrahedron, there is a single apical O atom (in the c-direction) and three basal O atoms (in the ab plane). The measured apical and basal Zn-O bond lengths are 1.9834 and 1.9737 Å, respectively. The Zn-Zn bond distances are 3.2064 and 3.2465 Å for apical and basal planes, respectively. The $\angle$Zn-O-Zn angles in these two planes are 108.251$^\circ$ and 110.663$^\circ$, respectively.

The crystal structure of Zn$_{0.5}$Cr$_{0.5}$O was a point of focus. In this structure, two types of oxygen coordination are alternatively observed in the c-direction that results in the formation of alternating ZnO$_4$ and CrO$_4$ tetrahedrons running in the c-direction (Figure 1(b)). All the Zn-O, Cr-O, Zn-Zn and Cr-Cr bond lengths and $\angle$Zn-O-Zn, $\angle$Cr-O-Cr and $\angle$Zn-O-Cr bond angles are reported in Table 1. The apical and basal Zn-O bond lengths are shortened by 0.0023 Å and 0.0016 Å, respectively.
While both Zn-Zn apical and basal bond distances are reduced by 0.0029 Å, more interestingly all the Zn-O-Zn and Cr-O-Cr bond angles in the basal planes are equal (110.650°) in Zn_{0.5}Cr_{0.5}O. It is also noticeable from Table 1 that Zn-O-Zn bond angle is reduced by 0.013°. Nevertheless, the shortening of Zn-O, Zn-Zn bond distances and Zn-O-Zn bond angles is so small that the structural distortions of the crystal are insignificant and thus are very hard to detect experimentally.

**Table 1.** Calculated bond lengths and angles in ZnO and Zn_{0.5}Cr_{0.5}O in hexagonal wurtzite structure at 19 K.

<table>
<thead>
<tr>
<th></th>
<th>ZnO</th>
<th>Zn_{0.5}Cr_{0.5}O</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bond lengths (Å)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn-O</td>
<td>1.9834</td>
<td>1.9737×3</td>
</tr>
<tr>
<td>Cr-O</td>
<td>-</td>
<td>1.9811</td>
</tr>
<tr>
<td>Zn-Zn</td>
<td>3.2064</td>
<td>3.2465</td>
</tr>
<tr>
<td>Cr-Cr</td>
<td>-</td>
<td>3.2035</td>
</tr>
<tr>
<td>Bond angles (°)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;Zn-O-Zn</td>
<td>108.251</td>
<td>110.663×3</td>
</tr>
<tr>
<td>&lt;Cr-O-Cr</td>
<td>-</td>
<td>110.650</td>
</tr>
<tr>
<td>&lt;Zn-O-Cr</td>
<td>-</td>
<td>110.265</td>
</tr>
</tbody>
</table>

3.2 Electronic structure of pure ZnO

The formal valence of Zn in ZnO is +2 (Zn²⁺), i.e. the number of Zn-3d electron is ten (3d¹⁰). The hexagonal crystal field splits Zn-3d bands into triply degenerate t₂g and doubly degenerate e₉ states. The t₂g states further split into dₓ²-ᵧ², dₓz and dᵧz orbitals, while the e₉ states split into dₓ²-ᵧ² and dᵧz orbitals. All the t₂g and e₉ states are fully occupied by the available ten Zn-3d electrons. Hence, they are shifted well below E₉, resulting in the insulating behavior of ZnO. Electrons are perfectly paired in these orbitals. This result causes zero net magnetic moments. The densities of states (DOS) calculated in the LSDA method are illustrated in Figure 2. It is obvious from this figure that the DOS for both spin channels are exactly the same. The valence band is found in the energy spectrum ~6.77 to 0 eV, and the conduction band is observed above 1.6 eV. Thus, the band gap detected is E₉ ≈ 1.6 eV, which is a worthy improvement over other theoretically determined values (E₉ ≈ 0.73-0.76 eV) calculated in the high-temperature structure (Osuch et al., 2006; Li et al., 2009).

However, these results did not affect the accuracy for comparison of the related properties (e.g., band structure, DOS properties, etc.). The total DOS (TDOS), projected DOS of Zn-3d and O-2p bands are represented in Figure 2. Clearly, TDOS is predominantly due to the Zn-3d character, which is found in the energy range -6.77 to -5.09 eV, while the energy range -4.52 eV to 0 eV is O-2p dominated. The calculated DOS of Zn-3p, Zn-4s, and O-2s are also shown in Figure 3. The contributions from these levels to the TDOS are insignificant compared to the Zn-3d or O-2p levels. Therefore, the electronic properties of ZnO depend entirely on the Zn-3d or O-2p orbitals.

![Fig. 2.](image1.png) Calculated total (green), Zn-3d (red) and O-2p (blue) DOS of pure ZnO at 19 K. All the Zn-3d states are fully occupied and shifted below E₉.

![Fig. 3.](image2.png) Calculated DOS of Zn-3p (dotted maroon), Zn-4s (red) and O-2s (blue). The contributions to total DOS from these states are insignificant.

3.3 Electronic properties of Zn_{0.5}Cr_{0.5}O

Let us now concentrate on the DOS calculations of Zn_{0.5}Cr_{0.5}O. The primitive unit cell of Zn_{0.5}Cr_{0.5}O contains one atom each of Zn and Cr and two O...
atoms. Total, Zn-3d, Cr-3d and O-2p DOS are depicted in Figure 4.

For both spin channels, three groups of energy bands corresponding to Zn-3d, O-2p and Cr-3d bands are detected. In the spin-up channel, the Zn-3dt_{2g} and e_{g} bands are found around -9.5 to -8.58 eV and -8.58 to -8.15 eV, respectively. Therefore, no spin gap is observed between t_{2g} and e_{g} bands. Five peaks corresponding to d_{x^2-r^2}, d_{xy} and d_{xy} states are observed at -9.4, -9.0, -8.8, -8.5 and -8.4 eV, respectively.

In the spin minority channel, Zn-3dt_{2g} and e_{g} bands are found in the energy spectrum -9.4 to 8.56 eV and -8.56 to -8.15 eV, respectively. Five peaks corresponding to d_{x^2-r^2}, d_{xz} and d_{yz} states are respectively found at -9.36, -8.95, -8.7, -8.52 and -8.38 eV. From the calculation of the number of Zn-3d electrons and Zn-3d DOS (Table 2), it is evident that all the Zn-3d states are occupied for both spin channels. The electrons in each orbital are perfectly paired, as shown in Figure 7(a).

![Fig. 5. Calculated Zn-3p, Zn-4s, Cr-3p, Cr-3s and O-2s DOS. Contributions to total DOS from these states are insignificant.](image)

The formal valence of Cr in Zn_{0.5}Cr_{0.5}O is +2 (Cr^{2+}). That is to say, it has four electrons in its 3d (d^4) bands. Due to strong Hund’s coupling, these four electrons would occupy Cr-3d bands of majority spin channel. Out of these four electrons, three occupy t_{2g} states and the remaining single electron is shared by the e_{g} states. This sharing of an electron by the e_{g} orbital is responsible for the metallic character of Zn_{0.5}Cr_{0.5}O. The spin minority channel remains insulating with a semiconducting gap of 3.5 eV.

Table 2. Calculated total densities of states (TDOS) and DOS (states/eV/f.u./spin) in 19 K

<table>
<thead>
<tr>
<th></th>
<th>ZnO</th>
<th>Zn_{0.5}Cr_{0.5}O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of electrons</td>
<td>up spin (↑) / down spin (↓)</td>
<td>up spin (↑) / down spin (↓)</td>
</tr>
<tr>
<td>Zn-3d</td>
<td>4.95 / 4.97</td>
<td>4.97 / 4.96</td>
</tr>
<tr>
<td>Cr-3d</td>
<td>- / -</td>
<td>3.98 / 0.02</td>
</tr>
<tr>
<td>DOS (states/eV/f.u./spin)</td>
<td>Zn-3d 4.94 / 4.96</td>
<td>Cr-3d 3.97 / 0.03</td>
</tr>
</tbody>
</table>

Considering these two spin channels, the system is thereby a half-metal. It is also unambiguous from Figure 4 that Cr-3d_{t_{2g}} and e_{g} bands are found in the energy windows -2.36 to -0.87 eV and -0.87 to 1.0 eV, respectively, for the spin-up channel. The number of Cr-3d electrons calculated for the up and down spin channels is four and zero, respectively. This is consistent with the total DOS calculation at E_F (see Table 2). Furthermore, Zn-3p, 4s, Cr-3p, 3s and O-2s DOS are also calculated (Figure 5), but their contributions to the total DOS are insignificant.

To understand the electronic structure accurately, total (Figure 6(a)) and partial band structures (PBS) of all the 3d orbitals are also optimized. The PBS of d_{x^2-r^2}, d_{xy}, d_{xy} and d_{xy} orbitals are demonstrated in Figures 6(b) to 6(e). It is emerged out from Figures 6(b) to 6(d) that all the three t_{2g} orbitals (d_{x^2-r^2}, d_{xy} and d_{xy}) are occupied by three electrons, and they are shifted below E_F. Nevertheless, the d_{xy} orbit is almost occupied, while the d_{xy} is found almost empty.

Eventually, they are still touching E_F. Therefore, the fourth electron is shared by the e_{g} orbital. This sharing of the single electron by the e_{g} orbital is responsible for the metallic nature of Zn_{0.5}Cr_{0.5}O in the LT phase. The ground state magnetic moment calculated is -3.85 μ_B/Cr (Table 3) for all Cr –ions. This result confirms that only one kind of Cr (Cr^{2+}) is present in the crystal and consequently the Cr^{3+}-ions are absent. Therefore, any secondary phase, such as ZnCr_{2}O_{4}, is not observed in the structural study upon 50% Cr-doping, and there exist only CrO_{4} and ZnO_{4} tetrahedrons.

3.4 Magnetic properties
The undoped ZnO is found nonmagnetic, while Zn_{0.5}Cr_{0.5}O is found ferromagnetic. The available ten 3d electrons are equally distributed in five Zn-3d orbitals. These are perfectly paired in the opposite direction that results in zero net magnetic moments. This is consistent with the calculated magnetic moments (see Table 3). The distribution of electrons in the t_{2g} and e_{g} orbitals are schematically depicted in Figure 7(a). Next, the magnetic properties of Zn_{0.5}Cr_{0.5}O should be considered. The available ten Zn-3d electrons are almost equally distributed in all Zn-3d orbitals such that the effective magnetic moment of Zn is almost zero (-0.01μ_B). The effective and Cr-magnetic moments calculated are -3.9μ_B and -3.85μ_B respectively. This indicates that the effective magnetic moment is almost fully contributed by the Zn ions.
Fig. 6. Calculated partial band structures of Cr- dε
t2 (b), dε/2 (c), dxz (d), dε/2 (e) and dε (f) states of
Zn0.5Cr0.5O for majority spin species. All the Cr- dε/2, dyz, dxz states are occupied. The dx2-y2 state is almost
occupied and dε state is almost empty but both touch
the Fermi level.

Table 3: Calculated total ground state energy (eV), magnetic moments (µ), band
gap (eV) for ZnO and Zn0.5Cr0.5O in 19 K

<table>
<thead>
<tr>
<th></th>
<th>ZnO</th>
<th>Zn0.5Cr0.5O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground state energy (E₀)</td>
<td>-7475.68</td>
<td>-5986.40</td>
</tr>
<tr>
<td>Effective mag. mom. (µeff)</td>
<td>0</td>
<td>-3.90</td>
</tr>
<tr>
<td>Zn - mag. mom. (µZn)</td>
<td>0</td>
<td>-0.01</td>
</tr>
<tr>
<td>Cr - mag. mom. (µCr)</td>
<td>-3.85</td>
<td>-3.85</td>
</tr>
<tr>
<td>O - mag. mom. (µO)</td>
<td>-0.04</td>
<td>-0.01</td>
</tr>
<tr>
<td>Band gap (Eₐ)</td>
<td>1.65</td>
<td>0</td>
</tr>
</tbody>
</table>

magnetic moments arise entirely from the Cr-magnetic
moments. The distributions of electrons in different
orbitals are schematically depicted in Figure 7(b).
All the Cr-3d electrons are aligned parallel due to the
strong Hund’s rule coupling. The ground state energies
calculated for undoped and doped ZnO are also reported
in Table 3. The ground state energy increases markedly
by 1489.28 eV upon Cr-doping in ZnO. This result
indicates that the repulsive force increases due to Cr-
doping, meaning electron correlation predominates in
the doped material Zn0.5Cr0.5O. Therefore, electron
correlation together with the strong Hund’s rule
channel is responsible for the ferromagnetic behavior of
Zn0.5Cr0.5O.

4. Conclusions

In this work, the structural, electronic and magnetic
properties are extensively studied for both pure and Cr-
doped ZnO in an LT (19 K) wurtzite structure. Pure ZnO
is found to be a nonmagnetic insulator. The insulating
behavior of ZnO is ascribed by the complete filling of each
Zn-3d orbital and its shifting below the Fermi level. In each
orbital, two electrons are perfectly paired in the opposite
direction, which is responsible for the nonmagnetic
behavior of pure ZnO. Interestingly, the scenario changes
dramatically at 50% Cr-doping for which the material
encounters an insulator to half-metal transition. This
preserves ferromagnetism that is accompanied by strong
electron correlations of Cr-3d electrons. In the spin-up
channel, the system Zn0.5Cr0.5O is found to be metallic
due to the sharing of the single electron by the Cr-e_g
orbitals. The electrons in the Cr-3d orbitals are identified
as unpaired and aligned parallel to each other due to the
strong Hund’s rule coupling causing ferromagnetism.
Finally, shortening of Zn-O or Zn-Zn bond distances
and ζZn-O-Zn bond angles caused by Cr-doping is
insignificant for structural distortions in Zn0.5Cr0.5O.

References


first-principles tight-binding theory.

Battaglia, C., Escarre, J., So derstro m, K., Charriere,

Bhargava, R., Sharma, P.K., Chawla, A. K., Kumar, S., Chandra, R., Pandey, A.C. & Kumar, N. (2011). Variation in structural, optical and magnetic properties of Zn$_{1-x}$Cr$_x$O (x = 0.0, 0.10, 0.15, and 0.20) nanoparticles: Role of dopant concentration on non-saturation of magnetization. Materials Chemistry and Physics, 125(3): 664-671.


Zheng, B.J., Lian, J.S. & Jiang, Q. (2011). Highly transparent and conductive Zn$_{0.86}$Cd$_{0.11}$In$_{0.03}$O thin film prepared by pulsed laser deposition. Journal of Superconductivity and Novel Magnetism, 24(5): 1627–1632.


Dr. Sarajit Biswas

Section of Physics, College of Technology, West Bengal, India

Abstract

A study was conducted on the atomic, electronic, and magnetic properties of pure zinc oxide and zinc oxide enriched with chromium using a Fortsätt cold-cathode technique. The zinc oxide was pure 

(TB-LMTO) and was also conducted using the DFT method. We found that the pure zinc oxide was non-magnetic, whereas the zinc oxide enriched with chromium was magnetic. When chromium was added to zinc oxide, the material became magnetic. This study showed that the enriched material was 50% enriched with zinc oxide. As a result of strong electron interactions, 

3.5 eV of the main spin types, the material was classified as non-conductive for the minority spin types, and the Fermi level was close to the Fermi level. The parallel alignment of non-magnetic channels in different spin sets was 

Cr-3d states, this sharing of the electron at the Fermi level was responsible for the magnetic properties of this material.