

Electronic Structure and Magnetic Properties of Cr-doped ZnO

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Abstract

Within the framework of Density Functional Theory (DFT) we have studied the electronic and the magnetic properties of wurtzite ZnO doped with transition-metal Cr in the presence of some defects (V_o , H, V_oH). The spectrum of band structure, density of states (DOS) and projected density of states (PDOS), and spin-density distribution in this system were investigated. The results of investigation shows that the existence of V_o in ZnO:Cr could stabilize ferromagnetic state of the system, due to the large magnetization and density of states at Fermi level. While, the existence of H introduce donor in ZnO:Cr but just polarized above Fermi level so there is no much change observed in its magnetic properties. And as for the existence of V_oH in ZnO:Cr, it turn out able to show the half-metallic properties.

Keywords: Density Functional Theory; defect related magnetism; spintronics; ZnO-based DMS

I. Introduction

Diluted magnetic semiconductor (DMS), in which some cations are replaced by transition metals can incorporate ferromagnetic properties into the semiconductor [1]. Currently, the search for ferromagnetic properties at room temperature in DMS is one of the most intensively researched topics. And ZnO-based DMS, a wide-gap energy semiconductor, is very attractive as a candidate for integrating optical, magnetic and electronic properties into a single material. After Dietl et al. [2] predicts that ZnO:TM can produce ferromagnetism at room temperature, there are many experiments whose results are inconsistent with these results [3]. Research on ZnO doped TM is mostly done on Co and Mn dopant. However, the ZnO doped system with Cr (ZnO:Cr) is also interesting to study after the calculations of Sato and Katayama Yoshida [4] indicate that the FM state of ZnO:Cr is more stable than the spin-glass or AFM state.

Although the first experiment of ZnO:Cr ($x=0.05-0.25$) on thin films prepared by the Pulsed Laser Deposition (PLD) method by Ueda et al. does not show FM properties [5], but a thin layer of ZnO:Cr ($x=0.905$) obtained through the co-sputtering process which was later carried out by Roberts et al. [6] produces FM at room temperature (RT) without any other magnetic phase in it. Similarly, the FM obtained by Liu et al. [7] on a thin layer using the co-sputtering method, but they also obtained paramagnetic results on the ZnO:Cr sample in the form of nanoparticles made by the sol-gel method. The theoretical ZnO:Cr investigation has been published by Hong; Li; et al. [8,9] in thin layers, while Wang et al. on nanowires ($x=0.02$) [10] and bulk [11]. The results of their analysis stated that the FM condition was preferred in ZnO:Cr. In addition, the Cr dopant in ZnO is known to form several defects that may significantly affect the electronic structure and magnetic properties. As in the observation of photoluminescence (PL) emission on a ZnO:Cr thin layer which shows a decrease in magnetization along with a decrease in the Zn vacancy acceptor (V_{Zn}) [12,13]. Also, as in polycrystalline ZnO:Cr nanoparticles, which were synthesized using the auto-combustion method ($x=0.01$ and 0.02) were studied to have FM which is said to be an important role of the observed Cr^{3+} [14]. The results of their analysis stated that the FM condition was preferred in ZnO:Cr. In addition, they also stated that there was also an involvement of V_o in the observations of several ZnO:Cr samples, but the value of the magnetic moment calculated by them was still far different from the experimental results. We hypothesized this because there is a role for hydrogen impurity in the sample, considering that in its manufacture ZnO:Cr is always involved with water and hydrogen is difficult to separate from ZnO:Cr [15-21]. Therefore, this thesis tries to explain the interaction of defects that may occur in ZnO doped Cr and its effects.

In order to understand the role of intrinsic defects in the mechanism of FM properties in ZnO:Cr DMS, in this study the electronic structure and also the magnetic properties of ZnO:Cr were

calculated using the DFT method. To simplify the calculation, the shape of the calculated sample is in the form of bulk monocrystalline. In contrast to other studies, this study takes into account the role of hydrogen (H) impurity and also the defect of the oxygen plus hydrogen (VoH) vacancy complex in ZnO:Cr. The parameter limit of Cr concentration that is taken into account is low ($x=0.0625$) and has a distance between Cr atoms equal to the lengths of the lattice to see the interaction of defects in ZnO:Cr DMS. The way we research is to calculate: (1) energy bands, to find out the nature of the system through the energy gap, fermi energy and impurity states, (2) total and partial state densities, i.e. histograms of energy levels, calculated to see symmetry/ majority spin asymmetry with minority spin of the ZnO DMS system and of one particular atomic orbital, finally (3) the spin-density distribution is shown to show the interaction and localization of the magnetic moment in ZnO:Cr.

II. Theoretical Review dan Methods

ZnO:Cr crystals in a hexagonal wurtzite structure at room temperature, with a space group P63mc (no.186) [3] and 4 atoms per unit cell, where each Zn atom is positioned tetrahedral with 4 other O atoms. The lattice constants used are $a=b=3.2495$ and $c=5.2069$ [22] and the atomic positions for Zn are $(1/3, 2/3, 0)$ and $(2/3, 1/3, 1/4)$ and for O are $(1/3, 2/3, 0.19)$ and $(2/3, 1/3, 0.44)$. To investigate the effect of hydrogen on the electronic structure and magnetic properties of ZnO:Cr, we inserted one H atom in a unit cell.

We analyzed the electronic structure and magnetic properties of the model with the help of the Quantum ESPRESSO program based on density-functional theory (DFT), plane waves, and pseudopotentials [23]. The gradient-generalized approach (GGA) was used for the exchange correlation function in the Perdew-Bueke-Ernzerhof (PBE) framework [24] and with the Hubbard potential GGA+U ($U_{Zn}=7.5$ eV, $U_{Cr}=2.6$ eV) [25]. Ultrasoft pseudopotentials (Vanderbilt) according to the Projector Augmented Wave (PAW) method have been used to construct orthonormalized all-electron like wavefunctions for their valence electrons [26].

Computing has been done for the supercell ($2 \times 2 \times 2$). For the case of using hydrogen atoms, the system corresponds to an H concentration of 3.013×10^{-2} per supercell. According to Van de Walle's research [17], there are 4 positions around the oxygen atom that can be occupied by hydrogen atoms, two of which are bond-centered positions and the rest are antibonding positions. The details about the orientation and relaxation of hydrogen have very little effect on the energy, this is because the strength of the O-H bond determines the stability of the configuration the most. We used bond-centered positions parallel to the hexagonal axes as Lavrov et al. [19] in the results of the measurement of their

polarized raman and the hydrogen is labeled H-I. A plane wave cutoff of 30 Ry was used, to ensure convergence in the calculations and proved sufficient to reproduce the ground state properties. Convergence is reached if the total energy difference between two successive iterations is $<10^{-6}$ eV. For all these self-consistent calculations, the k-point mesh size (12,12,8) was used in the Monkhorst-Pack lattice. This measure is as used by Karmakar et al. [22].

III. Results and Discussion

The state density of pure ZnO:Cr is shown in **Figure 1.(a)**. The figure shows a state in the energy gap due to the Cr dopant ion, which is at -2 eV. The electron in this state has a spin that is 100% polarized. Research results Wang et al. [27] also stated the same thing as the results of this study, only that the localized peak results in this study were higher and located below the Fermi level. While the results of Wang et al. has a lower peak and is located around the Fermi level. Both DOS results both stated that the FM state of ZnO:Cr with low Cr concentration and without defects was unstable, and the mechanism could be caused by carrier induced ferromagnetism.

This statement is based on the observation that there is a state density in the Fermi energy, although it is very small. The polarized electron charge carrier at the Fermi energy is contributed by the 3d orbital of the Cr atom, which carries out exchange interactions between Cr ions. This mechanism could explain the experimental results of Li et al's ZnO:Cr. [28] and Hong et al. [29]. The 3d orbitals of Zn atoms contribute greatly to the density of the spin-up and spin-down states which are distributed around -10 to -12 eV which is the electron state region near the atomic nucleus. While most of the 4s orbitals of Zn atoms are distributed in unoccupied states. The O atom contributes to both peak up and down around -10.5 eV and contributes to the line density state at the state density between -8 eV and the maximum value of the valence band. The absence of splitting at the peak density of the 3d Cr state indicates that the crystal-field has a small effect so that the 3d suborbital levels are degenerated [30] at the energy level of -2 eV.

Figure 1.(b) depicts the spin-density distribution of ZnO:Cr at an isovalue of 0.005. The red isosurface represents the spin-majority region (spin-up) and the dark blue isosurface represents the spin-minority region (spin-down). The green, black and light blue spheres represent Zn, O and Cr atoms, respectively. From the figure, it can be seen that most of the spin-ups are localized in the Cr atom and induce electrons in the surrounding O 1s, while the opposite spin is observed in the O 2p orbitals on the basal axis of the Cr atom. The spin-density shape around the Cr atom is in accordance with the predictions of Ruiz et al. [31] to the shape of the partially filled spin-density TM, in tetragonal coordinates.

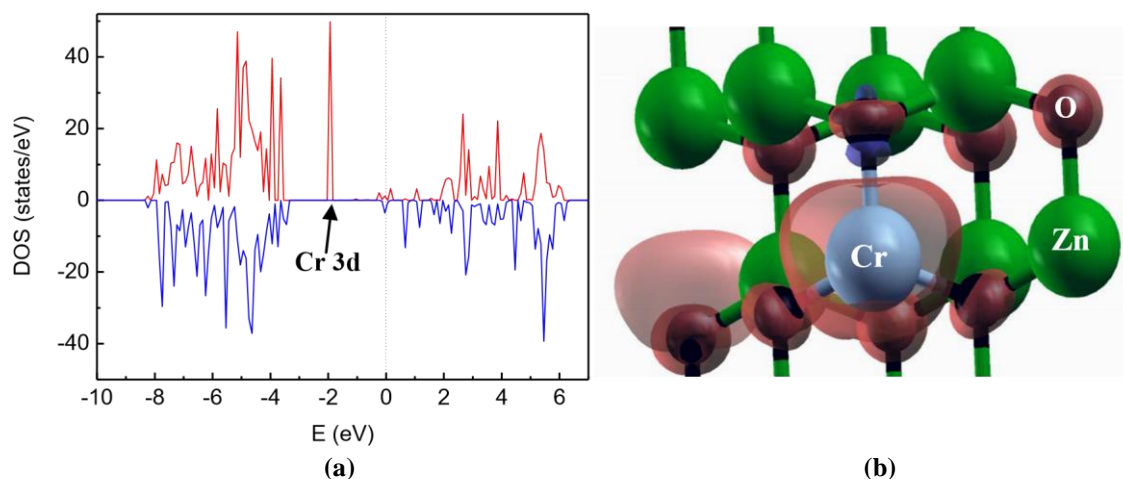


Figure 1. (a) the total state density, and (b) the spin-density distribution of pure Cr doped ZnO.

Spins that are localized in the region are non-itinerant and have a large number of states, such as the DOS representation obtained in this study. Although there are opposite spins filling the 2p orbitals of the O atom, which are evenly distributed in the valence band, it does not significantly affect the total magnetic moment of pure ZnO:Cr. Maybe this will start to affect the FM state when the Cr-OCr bond occurs if the concentration of Cr increases, considering that it is the opposite spin that affects the FM or AFM state between TM through bonds. The results of the calculation of the magnetic moment state that the value of the magnetic moment per Cr atom is 3.15 B/Cr. This value is higher than the value of the magnetic moment obtained from the experimental measurements on the ZnO:Cr thin film Hong et al. [32] and Roberts et al. ($\sim 1.4\mu\text{B/Cr}$) [33]. This is predicted to be the effect of the existence of the defect, because it is known that the FM state of the ZnO:Cr thin layer if there is no unstable defect [34,35]. However, when compared with the results of other theoretical calculations, the magnetic moment value obtained in this study is smaller than the calculation results of Li et al. [34] with ARF (3.7 B/Cr) and Raebiger et al. [36] with the theory of band structure correction (3.3 B/Cr).

Figure 2.(a) shows the density of the total state of ZnO:Cr with oxygen vacancies. The figure shows the presence of spin polarization in the maximum energy region of the valence band and below the Fermi energy level up to about -2 eV delocalized. As a result of the discovery of more partially filled electron states around the Fermi level region, if the mechanism that occurs in the system is carrier induced ferromagnetism, then besides the magnetization in this system becomes greater, the FM state also becomes more stable due to the polarization of the spin state to below Fermi energy level indicated after the presence of V_o in ZnO:Cr. The figure also shows the polarized region under the Fermi energy, which dominates the magnetization in this system, dominated by Cr 3d. The Cr^{2+} ion in the tetrahedral coordination of this system undergoes crystalfield splitting, causing the 3d state to be divided into two-degenerate (e_g) and

three-degenerate (t_{2g}) states, both in spin-up and spin-down, where the e_g level is lower in energy than t_{2g} [22,30]. In this calculation, the exchange splitting is greater than the crystal-field splitting which indicates the spin configuration is in a high-spin state [22]. And from the picture, the e_g level is found at -1.5 eV while the t_{2g} level is found between -1 eV to the Fermi level (0 eV). Passing the Fermi level within the level t_{2g} , indicating that the t_{2g} level is partially occupied.

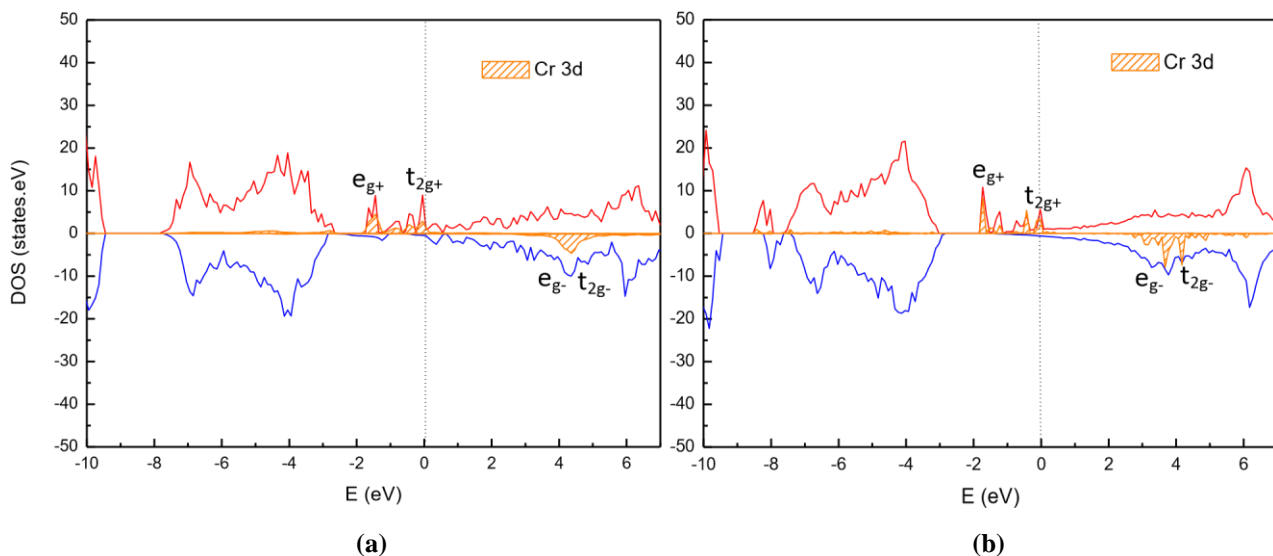


Figure 2. the density of the total state of ZnO doped Cr with (a) oxygen vacancy ($x = 0.0625$), (b) hydrogen ($x = 0.0312$).

So if considering that four electrons are in Cr 3d, it can be said that these two electrons accommodate the low level of e_g and the rest fill the level of t_{2g} in this spin polarized calculation. Widening of the distribution of the peaks of the density of the 3d Cr state due to crystal-field splitting, causing the t_{2g} level to overlap with the deep donor V_o level (-2 eV). This overlap resulted in hybridization interactions between the t_{2g} level and the dangling-bond state of the host. The t_{2g} level rises to a higher level after hybridization fills the conduction band, causing a charge transfer to the host conduction band, resulting in a non-integer magnetic moment value [37].

The total state density of ZnO:Cr with hydrogen shown in Figure 2.(b) shows a slight magnetization in the maximum valence band region and below the Fermi energy level. Peaks in the energy gap present in pure ZnO:Cr (at -0.2 eV) were also observed to appear in this DOS with a lower number of states but still contributed the most to the magnetization of this system. In addition, in the area between these peaks and the Fermi energy level, there are four peaks that are similar to the impurity donor peaks in ZnO:Cr with V_o , only the density is lower. This indicates that the nature of pure ZnO:Cr still dominates even after being hydrogenated, and the role of hydrogen in ZnO:Cr is the same as that of V_o even though the electron donor is not as

much as Vo. No loss of peak at -0.2 eV indicates that no hybridization occurred in this system.

If the picture is examined, several small gaps are found

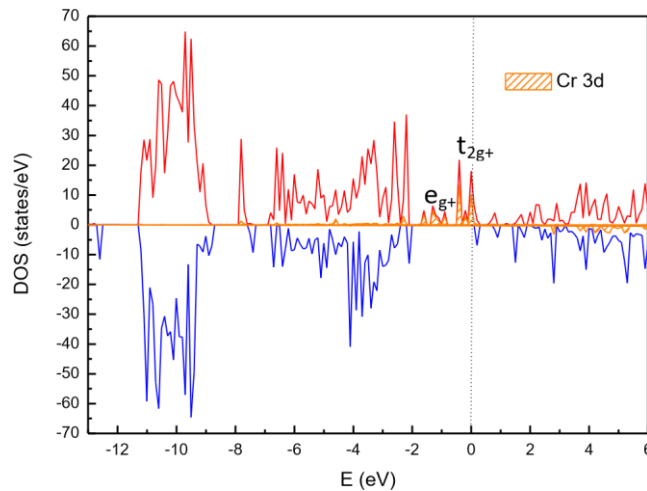
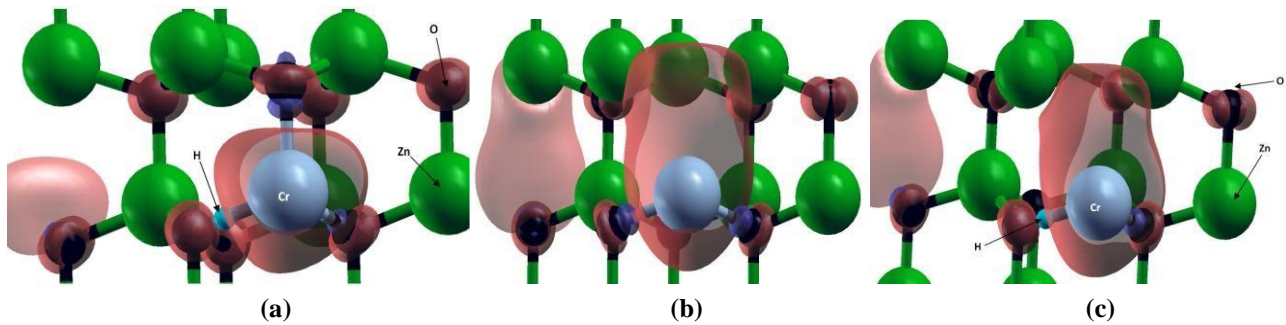


Figure 3. total state density in Cr doped ZnO with oxygen plus hydrogen vacancies

between the t_{2g} (~ -0.1 eV) and e_g (~ -0.2 eV) levels. These gaps, accompanied by the Fermi level crossing the t_{2g} level, indicate that the magnetization in this system makes the ions around Cr choose to be distorted from their tetragonal symmetry because their energy will be lower. This effect is known as the Jahn-Teller effect [30].

Figure 3 shows the total state density for ZnO:Cr with oxygen plus hydrogen vacancies. The figure shows that the peak at the Fermi energy level is 100% polarized, then in the spin-up section it is observed that the conduction band overlaps with the valence band. In the spin-down, there is a deep donor level near the valence band, and the Fermi energy level enters the n-type doping region. It is predictable that the spin-down state will not conduct current at room temperature because there is no energy level between the Fermi level and the deep donor level. Thus, room temperature does not have sufficient energy to excite electrons at the deep donor level until they reach the Fermi energy level [38]. This indicates that this system is semi-metallic and effective for spin-injection applications in spintronics.

Figure 4 shows the spin-density distribution of ZnO:Cr with (a) H, (b) VO, and (c) both at the isovalue 0.005. If you compare the three images with **Figure 1.(b)**, it can be concluded that: H reduces the symmetry belonging to the red isosurface (spin dominant) but holds a blue isosurface at the unfilled H site; Significantly polarized VO due to the hybridization process; and so is VOH due to the



Gambar 4. distribusi densitas-spin pada ZnO didop Cr dengan (a) hidrogen, (b) vakansi oksigen, dan (c) keduanya.

polarization of dangling-bond O by the conduction electron. In more detail, each addition of H to the ZnO:Cr system can reduce the spin-electrons in the H region, due to precipitation forming O-H bonds. Then the field generated due to the polarization in VO can transfer some of the O electrons from the s-orbital to the p-orbital, but the spin-down state has a lower energy in the p-orbital. The magnetic moments per Cr atom due to H, VO, VOH on ZnO:Cr are 3.2 B/Cr, 4.7 B/Cr, 4.05 B/Cr, respectively. VO plays a more significant role than H on the magnetic properties of ZnO:Cr. However, when viewed from the total state density analysis, it appears that H plays a more significant role than VO in the electronic properties of ZnO:Cr.

H along with Vo incorporated into ZnO:Cr may contribute greatly to the magnitude of the FM properties and conductivity, considering that the conduction electrons and magnetic moments in this system are both significantly increased. However, the two properties are not directly related. The properties that appear in these calculations may explain the experimental results of Roberts et al. [39]. In their observations on the $Zn_{0.99}Cr_{0.01}O:H$ thin layer, it was said that there was an interaction between Vo in the sample and H and it played a role in increasing the conductivity and magnetism of their sample. However, hydrogen in this study does not act as a multicenter-bond (ie the H atom is trapped in Vo and binds to Zn^{2+} ions) as hypothesized by Roberts et al. but rather as a donor in the conduction band.

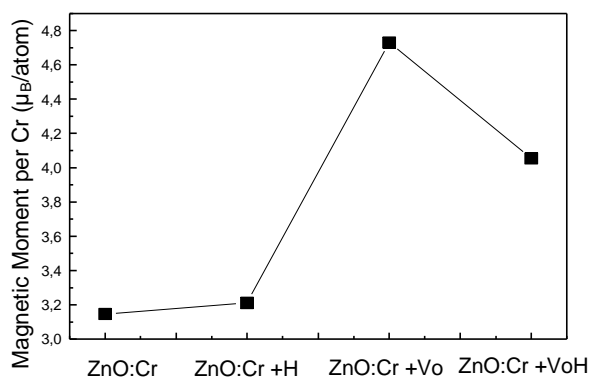


Figure 5. Magnetic moments per Cr for pure ZnO:Cr systems, with hydrogen impurities, with oxygen vacancies, and with oxygen plus hydrogen vacancies.

IV. Conclusion

The electronic structure and magnetic properties of Cr-doped ZnO with and without V_o and H were investigated using DFT calculations. The results indicate that by substituting the Cr atom in ZnO undop can produce a polarized spin of 3.15 B/Cr with a high localized DOS below the Fermi energy level. Then V_o in the ZnO:Cr lattice is able to stabilize the ferromagnetic state of the system due to the higher magnetization and the precise density of states at the Fermi energy level. This stability can indicate a high T_c in the oxygen vaccinated ZnO:Cr system. In contrast to hydrogen, which donates electron donors to ZnO:Cr, it does not change its magnetic properties much. This may be because V_o acts as a deep donor and is able to hybridize with the t_{2g} level of the 3d orbital of the Cr atom, while H which acts as a shallow donor in both ZnO undop and ZnO:Cr does not hybridize but only slightly distorts the crystal lattice. When H interacts with V_o , the results show metallic properties in ZnO undop and spin the majority of ZnO:Cr. While the spin minority of the system exhibits n-type semiconductor properties, it can be said that ZnO:Cr with V_o plus H can be an effective half-metallic for spin injection applications in spintronics.

V. Suggestion

As a suggestion, it is necessary to find a more complex combination of defects that act as shallow donors but also capable of hybridization to explain magnetic phenomena in ZnO:Cr.

VI. References

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