Effect of oxygen vacancy defect on the magnetic properties of Co-doped ZnO*

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The influence of oxygen vacancy on the magnetism of Co-doped ZnO has been investigated by the first-principles calculations. It is suggested that oxygen vacancy and its location play crucial roles on the magnetic properties of Co-doped ZnO. The exchange coupling mechanism should account for the magnetism in Co-doped ZnO with oxygen vacancy and the oxygen vacancy is likely to be close to the Co atom. The oxygen vacancy (doping electrons) might be available for carrier mediation but is localized with a certain length and can strengthen the ferromagnetic exchange interaction between Co atoms.

Keywords: Co-doped ZnO, oxygen vacancy, ferromagnetism

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1. Introduction

Transition metal (TM)-doped diluted magnetic semiconductors (DMSs) have become a highly desirable goal in the last years because of their potential applications in the field of spintronics.[1] Among DMSs II–VI compounds doped with TM, ZnO have attracted great attention due to their abundance and environment-friendly nature and also due to their potential as a suitable optoelectronic material with a wide-gap (3.3 eV) and high exciton binding energy of 60 meV. Moreover, since Dietl *et al.* have predicted that a high-Curie temperature (T_c) DMSs could be obtained in p-type Mn-doped ZnO,[2] great interests in TM-doped ZnO have been generated. In particular, the Co-doped ZnO system is promising for applications requiring ferromagnetism above room temperature.[3,4] For practical applications, enhancing the T_c of DMSs to above room temperature is a key issue. Despite a great deal of studies focusing on the Co-doped ZnO, there have been many contradictory reports on its magnetic states. Theoretically, Sato *et al.* predicted that Co-doped ZnO might be ferromagnetic (FM) without any carrier doping[5] and some other computational results also predicted the existence of high T_c for it.[6−8] Experimentally, Ueda *et al.* reported ferromagnetic behaviour of Co-doped ZnO synthesized by pulsed-laser deposition and with a T_c above 300 K;[9] Janisch *et al.* showed that magnetic moments of $Zn_{1-x}Co_xO$ films grown by various techniques spread over a relatively wide range from 0.56 to 2.6 μ_B/Co.[10] However, other reports claimed no trace of ferromagnetism in these systems.[11,12] Recently, it has been found that the magnetic properties of DMSs are sensitive to the growth methods and growth conditions.[13−17] Hsu *et al.* have investigated the FM dependence of oxygen vacancies in the Co doped ZnO films by x-ray near edge spectroscopy. It was found that the enhancement (suppression) of ferromagnetism is strongly correlated with the increase (decrease) of the oxygen vacancies in ZnO.[18] Also, Seghier *et al.* have suggested that the oxygen vacancy (V_O) is likely to be a main mediator for the ferromagnetism in the Co-doped ZnO.[19] Therefore, it is necessary to investigate the effect of V_O on the magnetic properties of Co-doped ZnO.

In this paper, we report the effect of V_O on the electronic structure and magnetic coupling for Co-doped ZnO with first-principles method. We first cal-

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culate the electronic structure and magnetic properties of $Zn_{1-x}Co_xO_{1-\delta}$ ($x = 0.028$) with and without single V_O ($\delta = 0.028$, $\delta = 0.0$) to find out the stable site of V_O. Next, we calculate the interatomic exchange interactions of $Zn_{1-x}Co_xO_{1-\delta}$ ($x = 0.055$) with and without single V_O ($\delta = 0.028$, $\delta = 0.0$) for seven configurations with different magnetic atom lattice arrangements. The role of V_O on the magnetism of Co-doped ZnO is finally discussed.

2. Model and calculations

The electronic structure and magnetism of $Zn_{1-x}Co_xO_{1-\delta}$ ($x = 0.028, 0.055$; $\delta = 0, 0.028$) are investigated using first-principles calculations based on the spin density functional theory (DFT). The projector augmented wave (PAW)[20] is used to represent the interactions between the valence electrons and the core, as implemented in the Vienna *ab initio* simulation package (VASP).[21−25] The Perdew and Wang parameterization of generalized gradient approximation (GGA) is adopted for the exchange–correlation potentials.[26] The experimental lattice constants of ZnO unit cell with $a = b = 3.249$ Å (1 Å = 0.1 nm) and $c = 5.205$ Å are employed. Based on the unit cell, 3×3×2 ZnO supercell is built with Zn atom replaced by Co atom. A plane-wave energy cutoff of 520 eV is used throughout the calculations. Gamma-centered k-meshes of 3×3×2 is used to sample the irreducible Brillouin zone of 3×3×2 ZnO supercells. The internal coordinates are fully relaxed until the forces on each ion are converged to less than 0.02 eV/Å. Figure 1 shows a wurzite ZnO supercell with one substitutional Co atom and two different V_O sites.

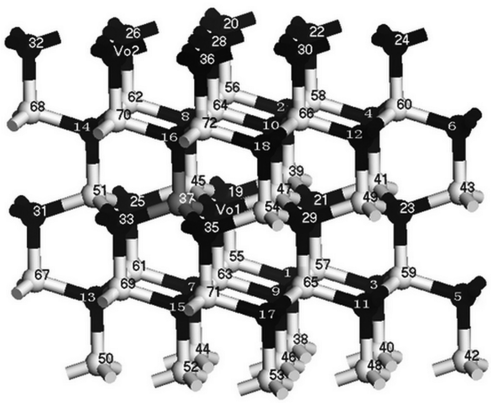


Fig. 1. The 3×3×2 supercell of wurtzite ZnO containing 35 Zn (white), 36 O (black) atoms and one Co (gray) atom with the labled V_O's sites. The positions of different V_O are labeled with V_O1, V_O2, respectively. All the atoms are labeled from 1 to 72.

Figure 2 shows a wurzite ZnO supercell with two substitutional Co atoms and V_O site being labled. To study the magnetic coupling, seven different configurations of two doped Co atoms in the supercell are considered. Configurations I–VII correspond to two Co atoms substituting for Zn at sites marked by (0, 1), (0, 2), (0, 3), (0, 4), (0, 5), (0, 6) and (0, 7) in Fig. 2, respectively.

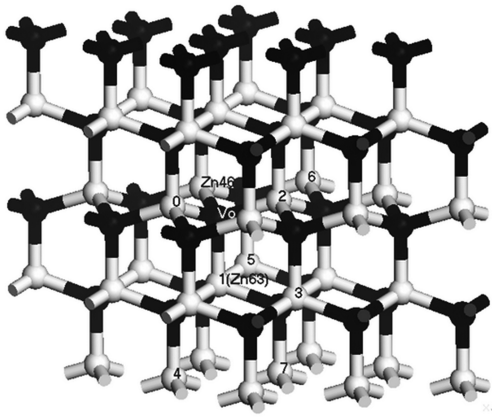


Fig. 2. The 3×3×2 supercell of wurtzite ZnO containing 36 Zn (white) and 36 O (black) atoms with the labled magnetic atomic sites. Here, Zn atoms at different sites are replaced by two Co atoms, which gives seven distinct pairs of Co atoms, such as (0, 1), (0, 2), (0, 3), (0, 4), (0, 5), (0, 6), (0, 7) respectively. The position of V_O is labled with 'V_O'. Two Zn atoms bonded with the O atom at the site V_O are numbered by 46 and 63 for configuration II.

3. Results and discussion

First, one Zn atom substituted by Co atom in 3×3×2 ZnO with single V_O was investigated in order to find the stable site of V_O. Two different sites of V_O are considered. As seen in Fig. 1, one is near to the Co atom labeled with V_O1; the other is far from Co atom labeled with V_O2. The electronic structures of $Zn_{0.972}Co_{0.028}O$ with and without single oxygen vacancy are shown in Fig. 3. The Co-3d orbitals in the tetrahedral coordination are split into e states with lower energy and t_2 states with higher energy. Exchange splitting is larger than the role of crystal field, which results in the nearly full-filled spin-down e states and the empty t_2 states,[27] as seen in Fig. 3(b). Clearly, the oxygen vacancy in Co-doped ZnO will give rise to the increase of n-type carriers. Comparing Fig. 3(b) with Fig. 3(e), one can note that the increased electron carriers occupy the t_2 state of minority spins partially and broaden the bandwidth of the t_2 band. However, in Figs. 3(g)–3(i), it is found that the Fermi level does not lie in a hybridized Co 3d–O 2p impurity band when V_O is far away from the Co atom. This indicates that V_O and the location of

V_O play an important role on the electron structure and magnetism of Co-doped ZnO. In our calculations, the magnetic moment per supercell is found to reduce from 3.07 μ_B to 1.92 μ_B for V_O1, and from 3.07 μ_B to 2.90 μ_B for V_O2, respectively. These results can be illustrated by the exchange coupling mechanism proposed by Dietl *et al.*[2] The key elements of the mechanism are unpaired electrons produced by defect in the valence band whose wave function overlaps with that of the transition-metal ion and whose spin is opposite to that of the transition-metal ion as long as the defect is not too distant from the transition metal. When V_O is produced in Co-doped ZnO, more electrons transfer to the Co impurity and distribute in antiparallel as minority spin electrons, so the net spin decreases, which results in the decrease of the magnetic moment. While for the V_O far away from the Co atom, the doped electrons have not enough energy to hop to the t_2 level of Co, namely, the number of electrons transferring to the Co 3d band becomes fewer. Therefore, the value of the magnetic moment of the supercell with V_O far away from the Co atom is higher than that of supercell with V_O near to the Co atom. The above discussion can also be certified by Fig. 4. Figure 4 shows the electron transferring structures of single Co-doped ZnO without and with V_O located in V_O1 and V_O2, respectively. For the $Zn_{0.972}Co_{0.028}O$, Co atom loses about 1.27 electrons. When an oxygen atom is removed, the number of the lost electrons for Co atom is decreased. Moreover, comparing Fig. 4(a) with Fig. 4(b), we can find that the number of the lost electrons for V_O1 is much less than that for the configuration for V_O2. Therefore, it is suggested that the doped carriers induced by V_O are localized with a certain length. In addition, it is found that the configuration energy for V_O1 is –0.56 eV lower than that for V_O2, which suggests that the V_O is likely to be close to Co atom.

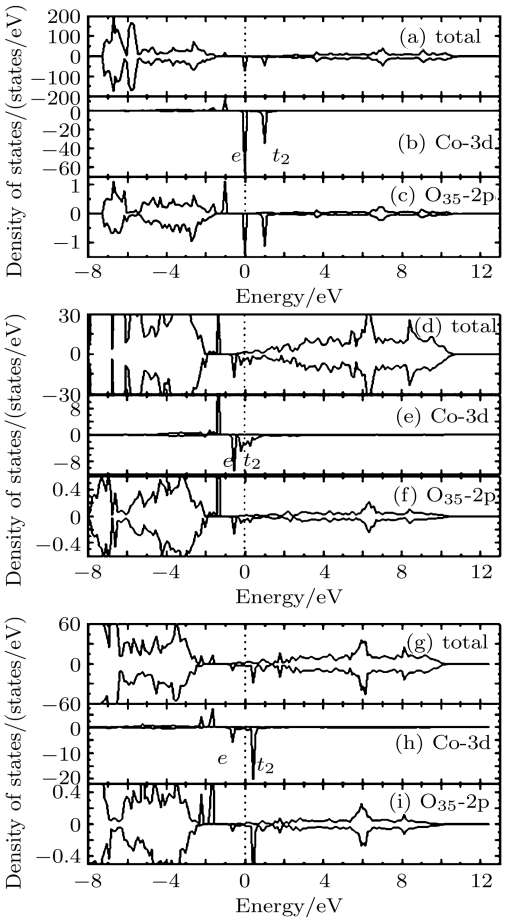


Fig. 3. Panels (a), (d) and (g) are total density of states (DOS) and panels (b), (e) and (h) are Co-3d projected density of states (PDOS) and panels (c), (f) and (i) O-2p PDOS of the case without V_O for $Zn_{0.972}Co_{0.028}O$, V_O1 for $Zn_{0.972}Co_{0.028}O_{0.972}$ when O atom is removed from V_O1, and $Zn_{0.972}Co_{0.028}O_{0.972}$ when O atom is removed from V_O2 (panels (g)–(i)). The Fermi level (dashed line) is set as the zero energy. Positive (negative) values correspond to the majority (minority) spin.

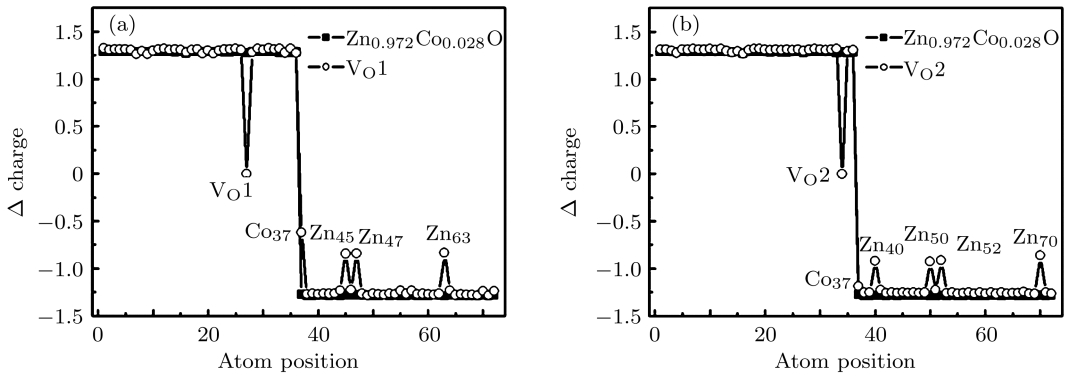


Fig. 4. The electron transferring structure of $Zn_{0.972}Co_{0.028}O$ with V_O located in (a) V_O1 and (b) V_O2. The electron transfer structure of $Zn_{0.972}Co_{0.028}O$ without V_O is displayed for comparison. The atom positions from "1" to "36", "37", from "38" to "72" represent O, Co, Zn atoms, respectively.

To study the magnetic coupling, for each configuration in Fig. 2, the total energies of the ferromagnetic ($E_{\rm FM}$) and antiferromagnetic ($E_{\rm AFM}$) spin configurations with and without V_O are calculated. The magnetic coupling strength J for the pair of Co atoms is obtained from the energy difference between the FM and AFM configurations ($J = E_{\rm AFM} - E_{\rm FM}$). Figure 5 shows the magnetic coupling strength of $Zn_{0.945}Co_{0.055}O$ for different configurations with and without V_O. From the figure, it is found that the system has an FM ground state when the V_O is absent. The trend is consistent with the previous results.[23,28] When V_O is generated, the magnetic coupling strength J is found to be notably increased. The calculated results show that the doped electrons due to V_O strengthen the exchange interaction between Co atoms. The above results are similar to the experimental facts.[29] To explore further the influence of V_O on the ferromagnetism of Co-doped ZnO, the electronic structure and transferring are carried out.

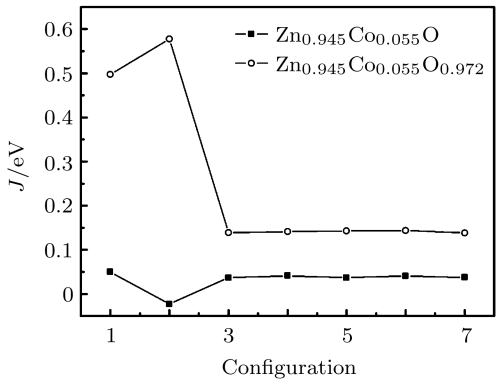


Fig. 5. The magnetic coupling strength J between two substitutional Co atoms at site 0 and site i for $Zn_{0.945}Co_{0.055}O$ with and without V_O.

Figures 6 and 7 show the total density of states (DOS), Co-3d, O-2p and Zn_{46}-3d projected density of states (PDOS) of $Zn_{0.945}Co_{0.055}O$ and $Zn_{0.945}Co_{0.055}O_{0.972}$ without and with V_O for configuration II, respectively. Figure 8 shows the electron transfer structures of $Zn_{0.945}Co_{0.055}O_{0.972}$ for configurations II. From Fig. 6, it is found that the ferromagnetism originates only from the hybridization between Co-3d and O-2p electrons in the vicinity of the Fermi level. The Zn-3d electrons do not contribute to the peak at the Fermi level. However, when V_O is generated, the Zn-3d electrons are also responsible for the ferromagnetism, and the hybridization between O-2p and Zn-3d electrons is also observed. When Co–V_O is formed, the added electrons are doped into the system, transferring primarily to the Co atoms and Zn atoms (Zn_{46} and Zn_{63}) bonded with the removed oxygen atom, as seen from Fig. 8. Compared with that of $Zn_{0.945}Co_{0.055}O$, the number of the lost electrons for Co, Zn_{46} and Zn_{63} atoms of $Zn_{0.945}Co_{0.055}O_{0.972}$ is decreased. The above results suggest that V_O is available for carrier mediation of hybridization between Co-3d, O-2p and Zn-3d electrons, which strengthens the exchange interaction between Co atoms. From Fig. 5, one can also note that the values of J for nearest neighbours are larger than that for distant neighbours, which can be ascribed to a dimmer formed by the two nearest Co atoms due to the creation of Co–V_O–Co. Figures 9(a) and 9(b) show the charge density distribution of $Zn_{0.945}Co_{0.055}O$ for configuration II without and with V_O, respectively. Comparing Fig. 9(a) with Fig. 9(b), it is found that a bonding has been formed between the two Co atoms, which results in a strong hybridization between them.

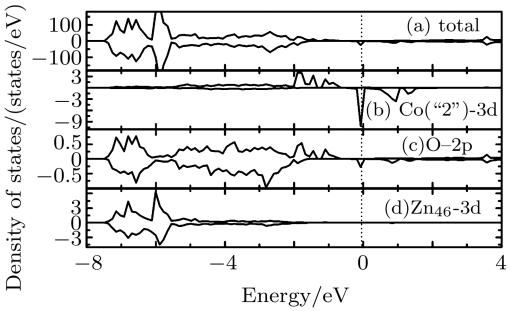


Fig. 6. (a) Total density of states (DOS), (b) Co-3d (at site "2"), (c) O-2p, and (d) Zn_{46}-3d projected density of states (PDOS) of $Zn_{0.945}Co_{0.055}O$ for configuration II. The Fermi level (dashed line) is set as the zero energy. Positive (negative) values correspond to the majority (minority) spin.

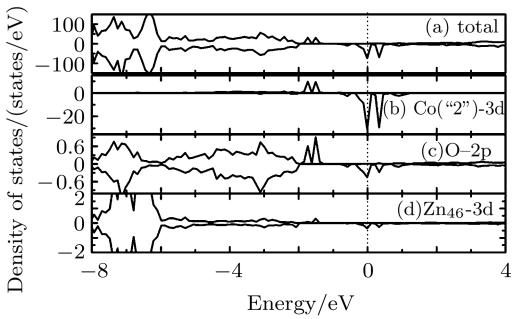


Fig. 7. (a) Total density of states (DOS), (b) Co-3d (at site "2"), (c) O-2p, and (d) Zn_{46}-3d projected density of states (PDOS) of $Zn_{0.945}Co_{0.055}O_{0.972}$ for configuration II. The Fermi level (dashed line) is set as the zero energy. Positive (negative) values correspond to the majority (minority) spin.

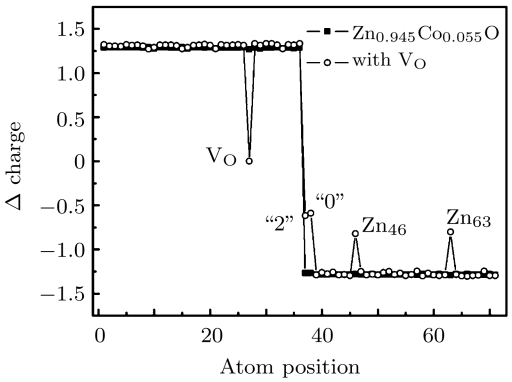
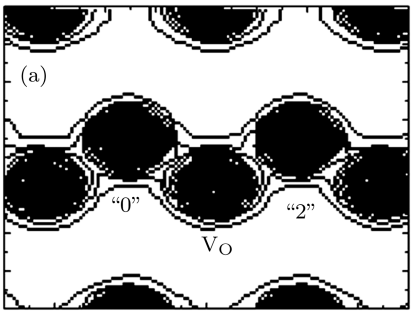


Fig. 8. The electron transfer structures of $Zn_{0.945}Co_{0.055}O_{0.972}$ for configurations II. The electron transfer structure of $Zn_{0.945}Co_{0.055}O$ without oxygen vacancy is displayed for comparison. The atom positions from "1" to "36", "37"and "38", from "39" to "72" represent O, Co, Zn atoms, respectively. "0", "2" represent the different sites of Co atoms, respectively.



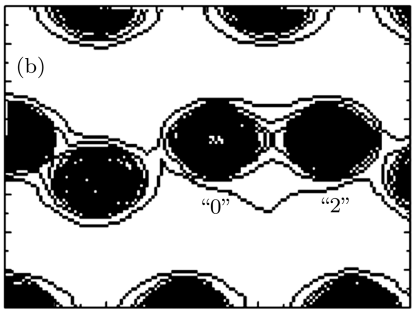


Fig. 9. Charge density distribution of $Zn_{0.945}Co_{0.055}O$ for configuration II, (a) without and (b) with V_O in the plane consisted of two Co atoms and V_O.

4. Conclusions

In conclusion, the electronic structure and magnetic properties of $Zn_{1-x}Co_xO_{1-\delta}$ ($x = 0.028$, 0.055; $\delta = 0.0$, 0.028) are calculated by using the first-principles method. The effects of oxygen vacancy on the electronic structure and magnetism of Co-doped ZnO are discussed. The calculated results indicate that the V_O (doping electrons) prefers to stay in the near neighbour site of Co atoms and the exchange coupling mechanism should be responsible for the magnetism of Co-dope ZnO with V_O. The V_O might be available for carrier mediation but is localized with a certain length and can strengthen the ferromagnetic exchange interaction between Co atoms.

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