Half-metallic ferromagnetism in C-doped zinc-blende ZnO: A first-principles study*

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(Received 15 November 2012; revised manuscript received 28 December 2012)

We perform a first-principles study of electronic structure and magnetism of C-doped zinc-blende ZnO using the full-potential linearized augmented plane wave method. Results show that C-doped zinc-blende ZnO exhibits half-metallic ferromagnetism with a stable ferromagnetic ground state. The calculated magnetic moment of the 32-atom supercell containing one C dopant is 2.00 μ_B, and the C dopant contributes most. The calculated low formation energy suggests that C-doped zinc-blende ZnO is energetically stable. The hole-mediated double exchange mechanism can be used to explain the ferromagnetism in C-doped zinc-blende ZnO.

Keywords: half-metallic ferromagnetism, first-principles, electronic structure

PACS: 75.50.Pp, 71.15.Mb, 71.20.–b **DOI:** 10.1088/1674-1056/22/4/047507

1. Introduction

Recently, diluted magnetic semiconductors (DMSs) have aroused wide research interest because of their potential applications in spintronic devices. The practical spintronic applications require the DMSs to have ferromagnetism at or above room temperature (RT). Dietl *et al.*,[1] and Sato and Yoshida[2] predicted that a Curie temperature higher than RT can be achieved in ZnO by transition metal (TM) doping, and RT ferromagnetism was indeed observed in ZnO-based DMSs.[3–6] However, the origin of the observed ferromagnetism is still under debate. Usually, doping with TM elements can induce such problems as clusters or second phases, which has been verified by several experimental studies.[7–9] To avoid these questions, some semiconductors doped with nonmagnetic elements such as Cu, Ca, C, and N were investigated, and the results verified that nonmagnetic elements can induce ferromagnetism.[10–14]

Pan *et al.*[15] predicted ferromagnetism in C-doped wurtzite ZnO by first-principles calculations and then confirmed their prediction by fabricating C-doped ZnO films with Curie temperature higher than 400 K via pulsed laser deposition. Subsequently, Zhou *et al.*[16] produced C-implanted ZnO films with RT ferromagnetism by ion implantation. First-principles calculations performed by Shen *et al.*[17] suggested that the long-range ferromagnetic coupling of N-doped wurtzite ZnO is attributed to a *p–d* coupling interaction involving holes. Very recently, Jindal *et al.*[18] reported on the RT ferromagnetism in N-doped wurtzite ZnO films grown by pulsed laser deposition, and their first-principles calculations showed that the origin of RT ferromagnetism in ZnO:N system is mainly due to the induced hybridization between O 2*p* states and N 2p states. ZnO has three commonly encountered polymorphs in nature: rocksalt, zinc-blende (ZB), and wurtzite.[19–21] ZnO in wurtzite structure doped by nonmagnetic elements has been widely studied as mentioned above, but research on ZB ZnO is relatively little. To the best of our knowledge, there have been no systematic theoretical studies about C-doped ZB ZnO till now.

In this work, we investigate the electronic structure and magnetism of C-doped ZB ZnO using the first-principles full-potential linearized augmented plane wave (FLAPW) method. Our results show that C-doped ZB ZnO exhibits a half-metallic behavior with a ferromagnetic ground state and a Curie temperature above RT, which suggests that C-doped ZB ZnO should be useful for the spintronic applications. The rest of the present study is organized as follows. The calculational method is described in Section 2, and the results are presented and discussed in Section 3. Some conclusions are drawn from our calculations in Section 4.

2. Computational method

To study the magnetism and electronic structure of C-doped ZB ZnO, we construct a 1×2×2 supercell containing four unit cells of ZB ZnO and use a C atom to substitute an O atom (Fig. 1), hence, the structure of $Zn_{16}CO_{15}$ is obtained. Calculations are performed using the FLAPW method as implemented with the WIEN2K code.[22] Generalized gradient approximation (GGA)[23] is used to treat the exchange correlation potential. Relativistic effects are taken into account. The convergence threshold for self-consistent energy

*Project supported by the National Natural Science Foundation of China (Grants Nos. 11004066 and 11074081) and the Research Foundation for the Doctoral Program of Higher Education of China (Grant Nos. 20100142120080 and 20090142110063).

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error is 10^{-5} Ry. The $R_{\min}K_{\max}$ is chosen to be 8.0. Atomic sphere radii of Zn, O, and C atoms are set to be 1.97, 1.77 and 1.75 a.u., respectively. The $7\times3\times3$ k-point meshes are used for the first Brillouin zone integration. Moreover, both atomic positions and lattice constants are optimized whenever applicable.

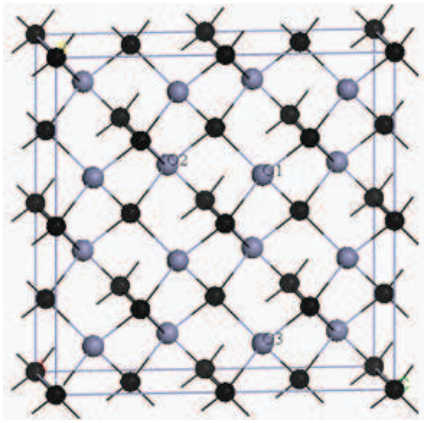


Fig. 1. The $1\times2\times2$ supercell of zinc blende ZnO. Black and gray balls represent Zn and O atoms, respectively.

3. Results and discussion

We firstly discuss the relative stability of the C-doped ZB ZnO system by calculating the defect formation energy, which is defined by the following formula:

$$E_{\rm f} = E_{\rm doped} - E_{\rm pure} + n_{\rm O}\mu_{\rm O} - n_{\rm C}\mu_{\rm C}, \qquad (1)$$

where $E_{\rm doped}$ and $E_{\rm pure}$ are the total energies of the supercell with and without C impurities, $n_{\rm O}$ and $n_{\rm C}$ are the numbers of O and C atoms that are removed and added to the host respectively, $\mu_{\rm O}$ and $\mu_{\rm C}$ are the chemical potentials of O and C, respectively. The chemical potentials are dependent on the experimental growth conditions, and we adopt the same method as that in Ref. [24], i.e., we use the energies of an isolated carbon and oxygen atoms to replace the chemical potentials of C and O, respectively. The calculated formation energy of $Zn_{16}CO_{15}$ is about 0.87 eV. The low formation energy indicates that C-doped ZnO is energetically stable.

Figure 2 shows the calculated spin-resolved band structures of the C-doped ZB ZnO. We can see that the splitting of the energy level occurs between the majority-spin (spin-up) and minority-spin (spin-down) channels near the Fermi level, which indicates the existence of magnetism in such a doped system. The majority-spin channel keeps a semiconductor behavior with a band gap of 0.56 eV, while the minority-spin electrons cross the Fermi level, exhibiting metallic properties. As a consequence, the C-doped ZB ZnO shows a half-metallic behavior[25,26] with a half-metallic band gap of 0.3 eV in the majority-spin channel, which is useful in the spintronic applications. The impurity bands lie at an energy level of about -0.6 eV, which is higher than the valence band maximum (about -1.1 eV for undoped ZnO), indicating that C-doped ZB ZnO is a p-type semiconductor.

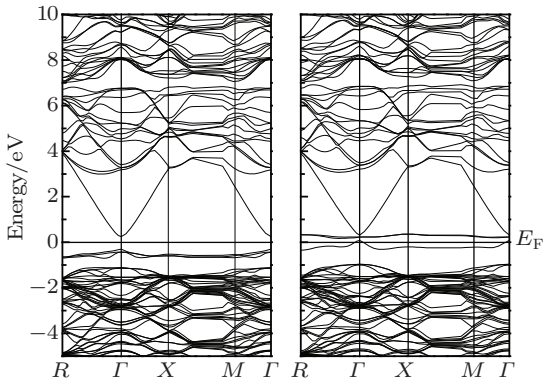


Fig. 2. Calculated spin-polarized band structures for zinc-blende $ZnO_{1-x}C_x$, $x = 0.0625$. The left (right) represents the majority (minority) spin channel. The Fermi level is set to be at 0 eV.

The calculated total density of states (DOS) of the doped system and the local DOS of the C atom and its nearest neighboring Zn atom and next neighboring O atom are plotted in Fig. 3 and Fig. 4, respectively. Evidently, C doping results in the spin splitting near the Fermi level. The spin-up states are fully occupied while the spin-down states are partially filled, leading to a total magnetic moment of 2.0 $\mu_{\rm B}$ per supercell. Comparing Fig. 3 with Fig. 4, we can find that the total DOS near the Fermi level is mainly formed by the C $2p$ states, which provides the main atomic magnetic moment (0.74 $\mu_{\rm B}$/C), while the nearest neighboring Zn atom contributes 0.08 $\mu_{\rm B}$/Zn resulting from the strong hybridization between C $2p$ states and Zn $3d$ states near the Fermi level. Meanwhile, the C $2p$ states also hybridize with the O $2p$ states, inducing 0.05 $\mu_{\rm B}$/O for the next neighboring O atom. Zn $3d$ levels are located only below -4 eV, suggesting that the Zn^{2+} ion is chemically stable. Figure 5 shows the plots of the partial DOSs of C $2p_x$, $2p_y$, and $2p_z$ states. One can find that the spin-up C $2p_x$, $2p_y$, and $2p_z$ states are fully occupied, but the spin-down C $2p_x$, $2p_y$, and $2p_z$ states are not, and the energies of C $2p_y$, and $2p_z$ states are doubly degenerate. Our spin-polarization calculations show that all the magnetic moments of the atoms in the supercell are positive, implying that there are ferromagnetic interactions between these atoms, which is different from magnetic semiconductors doped with TM elements, where the spin of TM element is always antiparallel to that of the neighboring atoms, i.e., there is antiferromagnetic coupling between the TM element and ambient atoms. Furthermore, we conclude that the ferromagnetism in C-doped ZB ZnO is intrinsic since the Zn, C, O elements and their compounds are all nonmagnetic.

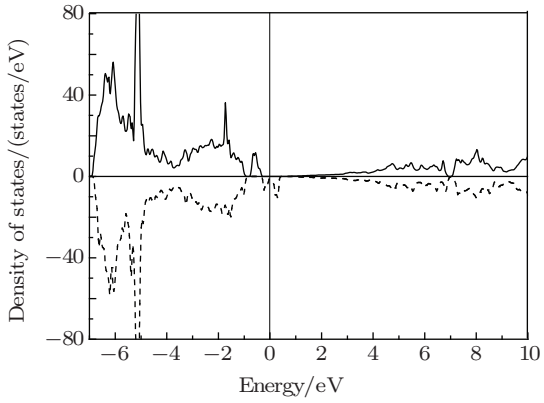


Fig. 3. Spin-dependent total DOSs for $ZnO_{1-x}C_x$, $x = 0.0625$. The solid (dashed) line represents the majority (minority) spin channel. The vertical line set at 0 eV indicates Fermi level.

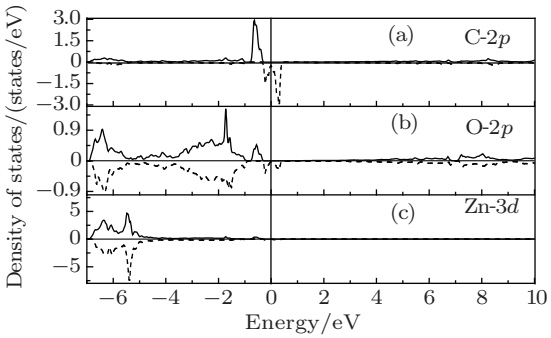


Fig. 4. Local DOSs of the C atom and its nearest neighboring Zn atom and next neighboring O atom.

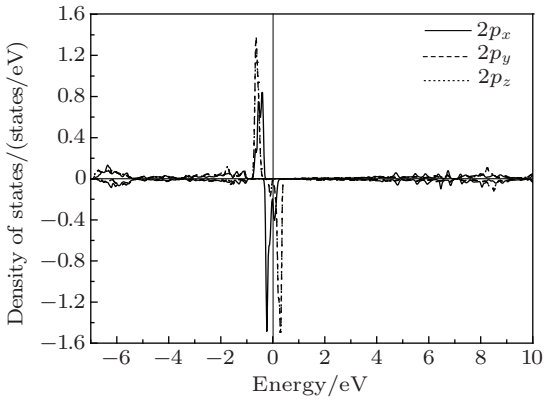


Fig. 5. Partial DOSs of C $2p_x$, C $2p_y$, and C $2p_z$ states.

According to Akai's double exchange mechanism, the half-metallic material should prefer the ferromagnetic ground state.[27] To determine the stable ground state of the C-doped ZB ZnO, we investigate the structure of a 32-atom supercell in which two O atoms are replaced by two C atoms. For this case, there are two different configurations: the O(1) and O(2) atoms, the O(1) and O(3) atoms (see Fig. 1), respectively, are substituted by two C atoms. We designate these two different configurations as C1 and C2, respectively. Then we calculate total energies in ferromagnetic (FM) and antiferromagnetic (AFM) states corresponding to parallel and antiparallel for the spin directions of the two C atoms, respectively. Results show that for the C1 configuration, the total magnetic moment of the supercell and the magnetic moment of each atom in the supercell are all close to zero in FM and AFM states, i.e., in the C1 configuration, the doped system is nonmagnetic. However, for the C2 configuration, the total energy in FM state is about 139.6 meV smaller than that in AFM state, which means that FM state is the stable ground state for the C2 configuration. A similar situation was found in the case of C-doped anatase TiO_2 studied by Yang *et al*.[28] In Ref. [28], Yang *et al*. found that magnetic coupling between adjacent C sites depends strongly on C–C distance, leading to a nonmagnetic state for the short C–C distance and an FM or AFM state when the C–C distance becomes long. In our work, the optimized C–C distances are 2.96 Å (1 Å = 0.1 nm) and 3.52 Å for the C1 and C2 configurations, respectively. Therefore, our obtained nonmagnetic and ferromagnetic ground states for the C1 and C2 configurations in C-doped ZB ZnO are consistent with those of C-doped TiO_2 obtained by Yang *et al*.[28]

Many theories have been proposed to expound the ferromagnetism of the DMSs. Our calculations suggest that the hole-mediated double exchange mechanism can be used to explain the ferromagnetism between the two carbon atoms. Holes induced by the carbon dopants are the main carriers and the spin-polarized holes in C $2p$ states couple with the O $2p$ localized spins via a p–d type p–p interaction, which results in the long-range ferromagnetic interaction between the two C dopants. Similar phenomena have been found in both N-doped ZnO and C-doped GaN.[15,29]

In addition, we can estimate the Curie temperature (T_C) of C-doped ZB ZnO using the classical Heisenberg model in mean-field approximation, i.e., $K_B T_C = 2\Delta E/3x$,[1] where ΔE is the energy difference between FM state and AFM states and x is the concentration of doping atoms. According to the calculated value of ΔE (139.6 meV) in the C2 configuration mentioned above, we obtain a T_C of about 476 K for C-doped ZB ZnO, and this value is higher than those of Cu-doped ZnO (above 380 K[30]) and Cu-doped GaN (around 350 K[31]), which indicates that C-doped ZB ZnO is more promising for the practical applications in spintronic devices.

4. Conclusions

In this work, we perform the first principles calculations of electronic and magnetic properties of C-doped ZB ZnO using FLAPW method based on spin-polarized density functional theory. Results show that C-doped ZB ZnO exhibits half-metallic ferromagnetism with a stable ferromagnetic ground state. The calculated magnetic moment of the 32-atom supercell containing one C dopant is 2.00 μ_B and the C atom contributes most. Low formation energy suggests that

C-doped ZnO is energetically stable. Moreover, C-doped zinc-blende ZnO is a p-type semiconductor, and hole-mediated p–p like long-distance coupling is considered to be the origin of the ferromagnetism in such a doped system. Our calculations also show C-doped zinc-blende ZnO has a T_C above room temperature, which makes it a promising candidate for the spintronic applications.

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