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First-principles study on electronic and magnetic properties of (Mn,Fe)-codoped ZnO

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ABSTRACT

First-principle calculations have been performed to investigate the electronic and magnetic properties of (Mn,Fe)-codoped ZnO within the generalized gradient approximation (GGA) and GGA+U schemes. The formation energy of five different configurations is investigated and the ground state is demonstrated to be ferromagnetic ordering. By applying the U correction, the band gap energy of pure ZnO is close to the experimental values, while the ferromagnetic ordering of the ground state remains unchanged. The ferromagnetic stabilization is mediated by double exchange mechanism. In addition, defects corresponding to Zn-vacancy and O-vacancy cannot enhance the ferromagnetism obviously. These results indicate that (Mn,Fe)-codoped ZnO are promising magneto-electronic and spintronic materials.

1. Introduction

Dilute magnetic semiconductors (DMS) are considered promising materials to build novel magneto-electronic and spintronic devices [1]. This opens the door to combine the advantage of having logic, memory and communication on a single chip by the use of spin and charge properties of electrons [2,3]. In the extensive study on DMS, the focus is mainly concentrated in two aspects.

It is known that the Curie temperature (T_c) of most DMS materials is below room temperature and it has been the major challenge for the commercial applications. The first task is to search for DMS with room temperature ferromagnetism. Various theoretical and experimental attempts have shown that chemical doping, especially the 3*d* transition metal doping is a key process to raise T_c to the values above room temperature. Ohno H [1,4] et al. fabricated GaMnAs magnetic films with T_c as high as 110 K by molecular beam epitaxy (MBE). Matsumoto [5] et al. reported on the observation of 400 K ferromagnetism in Co doped anatase thin films. As the ferromagnetic (FM) mechanisms of DMS are still controversial, the second task is to explore the origin and exchange manner of ferromagnetism.

ZnO based DMS are predicted to be promising host materials to obtain room temperature FM properties [6]. In the past few years, there have been systemic studies of 3d TMs (Fe, Mn, Cr, Co, Ni and Cu) doped ZnO bulk or film and a large number of ideal high T_c results have been reported [7–10]. By plasma assisted molecular beam epitaxy (*p*-MBE) techniques, Fe doped ZnO with different Fe concentrations have been successfully prepared that display FM ordering at room temperature [11]. However, with different Mn concentration and sample preparation conditions at room temperature, both FM and nonmagnetic orderings were observed by Bondino [12] et al., which was confirmed by the recent researches [13–15]. Taking into account the controversial results of Mn doped ZnO DMS, an effective route to obtain room temperature ferromagnetism is codoping with two different 3*d* TM impurities. Hailing Yang [16] et al. performed (Mn,Fe)-codoped ZnO thin films by pulsed laser deposition (PLD) and observed room temperature ferromagnetism through the magnetic hysteresis loops. Furthermore, similar results have been confirmed by hydrothermal method [17]. These relevant experiments stimulate us to give a theoretical investigation of (Mn,Fe)-codoped bulk ZnO.

In this article, we systematically investigate the electronic structure and magnetic properties of (Mn,Fe)-codoped ZnO.

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The theoretical simulations are based on density functional theory (DFT) via first-principle calculations. The purpose of this article is to provide a theoretical foundation for the fabrication of high T_c of ZnO materials. This article is presented as follows. The theoretical method and computational details are described in Section 2. Our results and discussions are given in Section 3. Finally, a brief summary is made in Section 4.

2. Theoretical method and computational details

Our calculations are performed with the Vienna ab initio simulation package (VASP) [18] code, which is based on the spin-polarized density functional theory (DFT) [19] and the plane-wave pseudo potential method. The electrons exchange-correlation function is treated using generalized gradient approximation (GGA) [20] with Perdew-Wang 91 (PW91) [21] approach. To give a proper description of the strong correlation effects, GGA+U methods [22,23] are considered. The on-site Coulomb parameter U for 3*d* states of Mn, Fe, Zn and 2*p* states of O are 5, 3.5, 10.5 and 7 eV. The exchange parameter is set to the typical value of $J=1$ eV [23,24]. In order to ensure a good convergence of the geometry optimization, the cutoff energy is chosen as 460 eV after a series of test. The valence electron configurations for Zn, O, Mn, Fe atoms are selected as: $4s^2 3d^{10}$, $2s^2 2p^4$, $4s^2 3d^5$ and $4s^2 3d^6$, respectively. For the self-consistent Brillouin zone integration, the Monkhorst-Pack *k*-points mesh for pure ZnO and (Mn,Fe)-codoped ZnO are $7\times7\times4$ and $4\times4\times2$ respectively, in order to provide sufficient accuracy. The process of geometry optimization is considered to be finished when the following parameters are satisfied (maximum force on each atom is 0.01 eV/Å, maximum energy change between two ionic steps is 10^{-5} eV and maximum stress is 0.1 GPa).

Moreover, a periodic $2\times2\times2$ wurtzite (WZ) bulk ZnO supercell is employed in our simulation and the size has been verified to satisfy the calculations [25]. The supercell contains 32 atoms with 16 O and 16 Zn atoms as shown in Fig. 1(a). In order to simulate (Mn,Fe)-codoped ZnO, two Zn atoms are substituted with one Mn and Fe atoms corresponding to the dopant concentration about 6.25% Mn and 6.25% Fe. As we all know, the ionic states of Mn and Fe atoms are divalent and their substitutions are readily for divalent Zn cations. Furthermore, the ionic radius of Mn^{2+} (0.80 Å) and Fe^{2+} (0.76 Å) are close to that of ion Zn^{2+} (0.74 Å). Five possible magnetic coupling configurations are introduced. For configuration I and II, Mn and Fe atoms are paired via intermediate O atom. While in configuration III, VI and V, Mn and Fe atoms are separated by O–Zn–O or O–Zn–O–Zn–O. The 5 dopant configurations are plotted in Fig. 1. The simulation is arranged as follows: first, all these five configurations are subjected to the spin polarized calculations corresponding to the FM and antiferromagnetic (AFM) orderings. Second, both the Zn-vacancy and O-vacancy are investigated to verify whether defects can induce FM coupling. Finally, the origin of FM coupling is discussed from the above-mentioned calculations.

3. Results and discussion

3.1. Structural optimization

The lattice constants of unrelaxed ZnO with stable hexagonal WZ structure in $P6_3mc$ space group are: $a=b=3.249$ Å and

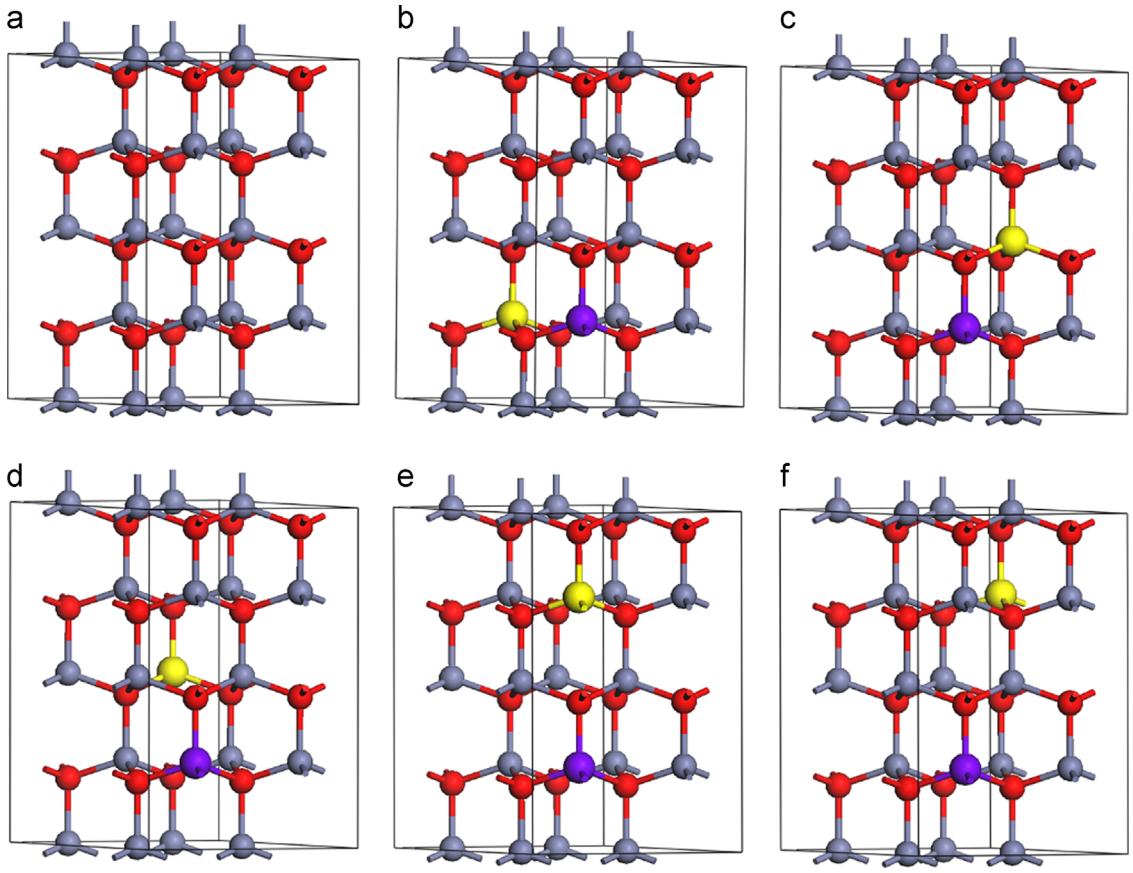

Fig. 1. Pure bulk $Zn_{16}O_{16}$ supercell and five configurations of (Mn,Fe)-codoped ZnO (the red, gray, blue, yellow spheres represent O, Zn, Mn and Fe atoms, respectively. For the sake of highlighting Mn and Fe atoms, their dimensions are enlarged). (a) Pure bulk $Zn_{16}O_{16}$, (b) Configuration I, (c) Configuration II, (d) Configuration III, (e) Configuration IV and (f) Configuration V. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).