Electronic structure and magnetic moments of 3d transition metal-doped ZnO

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Available online 3 May 2004

Abstract

Ferromagnetism in 3d transition metal-atom-doped ZnO was investigated by ab initio electronic structure calculations based on the generalized gradient approximation (GGA). We also performed GGA + U calculations to further refine our results. We found that Mn-doped ZnO has the largest magnetic moment and Sc-doped ZnO is nonmagnetic. Also, Mn-Co- or Cu-doped ZnO are ferromagnetic semiconductors. For the other 3d transition metal atoms the doped ZnO are metals. The appearance of ferromagnetism in these systems suggests the possibility for fabrication of a transparent ferromagnet which may have a great impact on industrial applications in magneto-optical devices.

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PACS: 75.50.p

Keywords: Zinc oxide; Transition metal; Transparent ferromagnet

1. Introduction

Diluted magnetic semiconductors (DMSs) have attracted a great deal of attention because of the possibility of incorporating magnetic degrees of freedom in traditional semiconductors [1,2]. DMSs are semiconductors which contain some magnetic atoms as impurities. They have the possibility to create functional material using the carrier control techniques in semiconductors. They are widely used in high- and low-tech applications such as anti-static coatings, touch display panels, solar

cells, flat panel displays, heaters, defrosters, and optical coatings [3]. All these applications use transparent conductive oxides as simple passive electrical or optical coatings. ZnO is a direct band-gap semiconductor which is piezoelectric and has been used for transparent thin film transistors, blue and UV light-emitting diodes and laser diodes [4]. Recently ZnO attracts much attention because of its cheapness and abundance.

From a physical/chemical point of view, ZnO is a very interesting material because of the mixed covalent/ionic aspects in the chemical bonding. ZnO crystallized in the hexagonal wurzite structure (B4), which consists of hexagonal Zn and O planes stacked alternately along the c -axis. Anions and cations are fourfold coordinated like in the

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closely related zinc-blende structure. A tetrahedral coordinated bulk structure is typical for covalent semiconductors. On the other hand, ZnO shows great similarities with ionic insulators such as MgO [5]. This is why ZnO is often called the “ionic extreme” of tetrahedral coordinated semiconductors.

In this paper, we investigate the magnetic properties of $\text{Zn}_{1-x}(\text{TM})_x\text{O}$ (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) DMS. The purpose of the present study is to give a guideline to synthesize new magnetic materials according to ab initio calculations.

2. Computational methods

The calculations were carried out based on density functional theory (DFT) with the generalized gradient approximation (GGA) [6]. We used the highly accurate full-potential projected augmented wave (PAW) method, as encoded in Vienna Ab-initio Simulation Package (VASP) [7,8]. Since the 3d electrons on the transition metal atoms are presumably strongly correlated, the on-site Coulomb energy U was also taken into account with the so-called GGA + U scheme. The corresponding parameters U and J for the 3d transition metals [9] used are listed in Table 1.

ZnO has a wurtzite structure in which anions and cations, respectively, form hexagonal close-packed lattices separated from each other along the c -axis by the internal coordinate u [10]. To simulate the $\text{Zn}_{1-x}(\text{TM})_x\text{O}$ alloys, the supercell approach was employed. We thus extended the original ZnO unit cell of four atoms [11] to a

$2 \times 2 \times 2$ supercell of 32 atoms, i.e., the unit cell size was doubled in all the three crystallographic axes. The supercell contains 16 molecules of ZnO. One of the 16 Zn atoms in the supercell was then substituted with one 3d transition metal atom. The substitution leads to an impurity concentration x of 3.125%. We adopted the experimental lattice constants of $a_0 = 3.25 \text{ \AA}$ and $c_0 = 5.21 \text{ \AA}$, where a_0 and c_0 were the lattice constants of the primitive unit cell of the wurtzite structure. The internal coordinate $u = 0.345$ was used for doped ZnO [10].

3. Results and discussions

Fig. 1 shows the magnetic moment of $\text{Zn}_{1-x}(\text{TM})_x\text{O}$ (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu). Both GGA and GGA + U calculations produce the similar results. In both calculations, the Sc-doped ZnO is nonmagnetic. Of the atomic number increases, the magnetic moment of 3d transition metal-doped ZnO increases as well. The moment distribution reaches its maximum ($4.5 \mu_B$ for GGA and $4.78 \mu_B$ for LDA + U) at Mn doped ZnO. The trend decreases as the atomic number increases.

The band structures of selected $\text{Zn}_{1-x}(\text{TM})_x\text{O}$ (TM = V, Cr, Mn, Fe, Co, and Cu) are shown in Fig. 2 and the energy band-gap values for the ferromagnetic semiconductors are listed in Table 2. Although, the full figures of the band structure

Table 1
Coulomb (U) and exchange (J) parameters (eV), and the magnetic moments (μ_B) from GGA + U calculations

	U	J	μ_B
Sc	6.6	0.78	0.0
Ti	6.6	0.78	1.62
V	6.7	0.81	2.02
Cr	6.8	0.84	3.58
Mn	6.9	0.86	4.77
Fe	6.8	0.89	4.30
Co	7.8	0.92	2.93
Ni	8.0	0.95	1.99
Cu	8.0	0.95	0.96

Fig. 1. Total magnetic moment per one transition metal atom of $\text{Zn}_{1-x}(\text{TM})_x\text{O}$. Diamonds represent GGA and stars represent GGA + U calculations.

Fig. 2. Band structure of spin up (up arrows) and spin down (down arrows) of selected $\text{Zn}_{1-x}(\text{TM})_x\text{O}$ ($\text{TM} =$ (a) V, (b) Cr, (c) Mn, (d) Fe, (e) Co, and (f) Cu).

Table 2
Energy band gap of $\text{Zn}_{1-x}(\text{TM})_x\text{O}$ semiconductors from GGA + U calculations

System	Mn	Co	Cu
Gap $\uparrow$ (eV)	0.26	0.76	0.81
Gap $\downarrow$ (eV)	0.93	0.92	0.53

Fig. 3. The total and partial densities of states (DOS) of Mn doped ZnO from GGA + U calculation.

are not shown here for all the transition metal-doped ZnO, it is clear from our calculations that Sc-, Ti-, V-, Cr-, Fe-, and Ni-doped ZnO are metal. On the other hand, Mn-, Co-, or Cu-doped ZnO are ferromagnetic semiconductor with a band gap of 0.26, 0.93, 0.76, 0.92, 0.81 and 0.53 eV, for spin up and down, respectively. Fig. 3 shows the total and partial densities of states of Mn-doped ZnO from our GGA + U calculation. As we can see in the partial density of states, the Zn atoms contribute to the majority density of states in both up and down spins. O atoms contribute to both the up and down peaks around -15.0 eV and smoothly contribute to the density of states between -5.0 eV and Fermi energy 1.54 eV. Mn atom are distributed differently in the up and down spin density of states. For the spin up configuration, Mn atom contributes to several peaks up to Fermi energy, and the spin down starts from 6 to 10 eV. The up spin insulating gap is 0.26 eV and the down spin gap is 0.93 eV (Table 2). Similarly, Co- and Cu-doped ZnO are also ferromagnetic semiconductors with

different band gap for different spin band structures (Table 2).

4. Summary

We studied the electronic structure and magnetism in ZnO-based DMS by ab initio calculations based on the GGA and GGA + U schemes. We obtained the trend of magnetic moments for 3d transition metal-atom-doped ZnO. It is found that Mn-doped ZnO has the largest magnetic moment in both our GGA and GGA + U calculations. On the other hand, Sc-doped ZnO is nonmagnetic. Mn-, Co- or Cu-doped ZnO was found to be a ferromagnetic semiconductor. The other 3d transition metal-atoms-doped ZnO are metals.

Acknowledgements

This work was supported by the National Science Council of the Republic of China (Grant No. NSC91-2120-M-001-004).

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