



The electronic structures and magnetic properties of N-doped ZnO with and without Zn vacancy

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ARTICLE INFO

Article history:

Received 9 November 2011

Received in revised form 25 December 2011

Accepted 1 January 2012

Available online 10 January 2012

Keywords:

Diluted magnetic semiconductors

First-principles

Magnetic moment

Curie temperature

ABSTRACT

Using first-principles method based on density functional theory, we investigated systematically the electronic structure and magnetic properties of N-doped ZnO with and without Zn vacancy. The calculated results indicate that N-doped ZnO is a weak ferromagnet. Interestingly, the ferromagnetic stability can be increased significantly by doping a Zn vacancy. A Curie temperature of about 490 K can be expected in N-doped ZnO with a Zn vacancy. The ferromagnetism in N-doped ZnO should be attributed to the hole-mediated double exchange interaction.

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1. Introduction

Diluted magnetic semiconductors (DMSs) have been studied extensively in both theory and experiment, because of their potential usage of both charge and spin of freedom of carriers in the electronic device, namely, the spintronics [1,2]. The ideal DMSs should exhibit ferromagnetism at room temperature for practical applications and have a homogeneous distribution of the magnetic dopants. Since Dietl et al. theoretically predicted that room temperature (RT) ferromagnetism might exist in wide-band-gap semiconductors [3], ZnO doped with transition metals (TM) has been extensively studied [4–9]. However, a number of studies indicate that the RT ferromagnetism in TM-doped oxides may come from precipitation of magnetic clusters or from secondary magnetic phases. These extrinsic magnetic behaviors are undesirable for practical applications. Up to the present, the origin of ferromagnetism in oxide DMSs remains a very controversial topic. A possible way to avoid problem related to magnetic precipitate is to dope semiconductors or oxides with nonmagnetic elements instead of magnetic TM. Based on this idea, RT ferromagnetism has been demonstrated in Cu and Ti doped ZnO [10,11]. In addition, theoretical studies predicted that anion substitutions in oxide can also lead to ferromagnetism [12,13]. Recently, experimental magnetic moments and RT

ferromagnetism in N-doped ZnO and C-doped ZnO have been reported [14–16]. Moreover, one can even find several studies that the magnetic state can be observed due to vacancy defect without any doping element [17–20]. It seems that the magnetic behaviors of ZnO-based DMSs are strongly dependent on the preparation methods used and poorly reproducible. The correlation between ferromagnetism and sample preparation conditions suggests that defects may play an important role in the observed magnetic behaviors of these materials.

Theoretical studies have been carried out to investigate the mechanisms of ferromagnetism associated with defects. The results of first-principle calculations indicate that neutral oxygen vacancy in ZnO is nonmagnetic [21], but Zn vacancy (V_{Zn}) does lead to magnetism [22,23]. From the above expression, it is clear that a detailed investigation of electronic structure and magnetic interactions is necessary, taking into account the general features of DMS's. In ZnO, one of the predominant intrinsic defects is V_{Zn} . Here, we focus on the effect of V_{Zn} on the magnetic behavior of N-doped ZnO. In this paper, we investigated in detail the electronic structure and magnetic properties in N-doped ZnO with and without V_{Zn} by using the first-principles calculation. We found that N-doped ZnO is a weak ferromagnet. However, the ferromagnetic stability can be increased significantly by doping V_{Zn} . In addition, we carried out an approximation to calculate the T_{C} value by using mean-field approximation and found a Curie temperature of about 490 K can be expected in N-doped ZnO with a V_{Zn} . Therefore, (N, V_{Zn})-codoped ZnO may present a promising dilute magnetic semiconductor in practical applications.

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2. Computational methods

The first-principles calculations were performed with the CASTEP code, based on density functional theory (DFT) using ultrasoft pseudopotentials [24] and a plane-wave expansion of the wave function [25]. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) scheme [26] was used for treating the exchange and correlation potential. The valence-electron configurations for the O, Zn and N atoms were chosen as $2s^22p^4$, $3d^{10}4s^2$ and $2s^22p^3$, respectively. The electron wave function was expanded in plane waves with a cutoff energy of 380 eV, and a Monkhorst–Pack grid [27] with parameters of $4 \times 4 \times 2$ was used for irreducible Brillouin zone sampling. The crystal structure and the atomic coordinates were fully relaxed without any restriction using the Broyden–Fletcher–Goldfarb–Shanno method [28]. In the geometry optimization process, the energy changes, as well as the maximum tolerances of the force, stress, and displacement were set as 5×10^{-6} eV/atom, 0.01 eV/Å, 0.02 GPa, and 0.0005 Å, respectively. The test calculations with higher cutoff energies and denser k -point grids were also performed, and the overall results remained unchanged. Then the electronic structures were calculated on the basis of the optimized supercells.

3. Results and discussion

The calculated lattice constants ($a = 3.281$ Å, $c = 5.315$ Å) for wurtzite ZnO are in good agreement with the experimental values ($a = 3.25$ Å, $c = 5.21$ Å) [29], which indicates the calculation model and parameters are reasonable. Based on the unit cell, a $2 \times 2 \times 2$ supercell of ZnO was constructed, in which two O atoms were substituted with two N atoms, as shown in Fig. 1. This gives a dopant concentration of 12.5% and allows for calculation of the relative energies of ferromagnetic (FM) and antiferromagnetic (AFM) orderings. The total energy of ferromagnetic (FM) and antiferromagnetic (AFM) configuration were calculated for the defective system of $\text{Zn}_{16}\text{N}_2\text{O}_{14}$. The energy difference between FM and AFM orderings, $\Delta E = E_{\text{AFM}} - E_{\text{FM}}$, was used as an indicator of the magnetic stability. If ΔE is negative, the AFM configuration is more

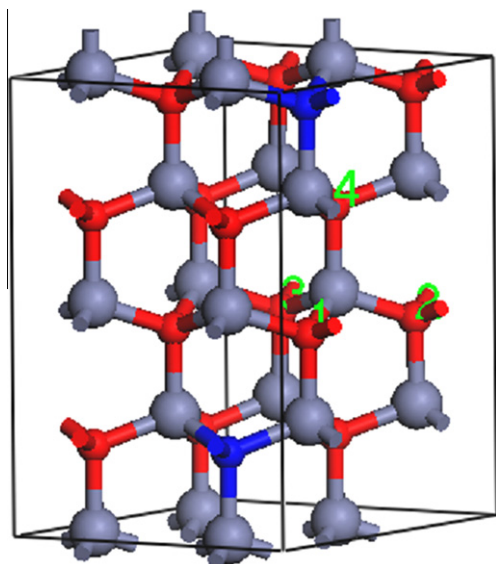


Fig. 1. Schematic illustration of wurtzite $2 \times 2 \times 2$ supercell ZnO with 12.5% N dopant, where larger (gray) balls, small (red) balls and blue balls stand for Zn, O and dopant N, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

stable, and vice versa. The calculated results show that the FM ground state is found to be slightly more stable than the AFM state with a total energy difference of 6 meV. This indicates that N-doped ZnO is a weak ferromagnet, which is in agreement with other theoretical results [30].

Spin-polarization calculations show the total magnetic moment is $1.86\mu_B$ per supercell. The local moment at N is about $1\mu_B$ and the rest magnetic moment mainly arises from the spin polarized O atoms. Fig. 2 shows the calculated band structure of ZnO doped with 12.5% of N. It can be seen that the spin splitting occurs between up spin and down spin channels near the Fermi level, which implies the N dopants can order magnetism in the ZnO hosts. In addition, an interesting feature of the band structure is the occurrence of impurity bands (N-induced bands) in the spin-down bands over the whole Brillouin zone, as can be seen in Fig. 2b, moreover, the Fermi level is within the impurity bands.

The origin of ferromagnetism in DMSs has been intensively discussed over the past years. In this work, the ferromagnetism in N-doped ZnO can be explained by using the hole-mediated mechanism. Dalpian et al. proposed that there are two distinct mechanisms related to the stabilization of ferromagnetism for hole-mediated ferromagnetism [31]. The difference between them is related to the position of the impurity levels with respect to the valence band edge. If the impurity states are in the band gap, ferromagnetism can be explained by double exchange interaction. That is, given the incomplete filling of bands, when the exchange splitting is bigger than the bandwidth, the ferromagnetic state is more stable than the antiferromagnetic state if a larger (usually rather small) number of holes (or electrons) exist. Whereas if the filled impurity states are below the valence band maximum, ferromagnetism can be explained by the Zener model [32], which is related to the coupling between the impurity levels and the host valence states. In both cases, it is necessary to have holes, either free or localized, to stabilize the ferromagnetism. In this work, the holes were introduced by N substitution of O, as can be seen in Fig. 2, in addition, one can also see that the impurity bands are located within the band gap, and the Fermi level falls in the gap of the spin-up band structure but within the impurity bands of the spin-down channel. The exchange splitting is bigger than the valence band, and there are a considerable number of holes. We can therefore conclude that hole-mediated double exchange is responsible for the observed ferromagnetism in N-doped ZnO.

To explore the effect of V_{Zn} on the electronic structure and magnetic properties of N-doped ZnO, one V_{Zn} was created by removing a Zn atom in the defective system of $\text{Zn}_{16}\text{N}_2\text{O}_{14}$, as shown in Fig. 3. In order to establish whether the defective system with one V_{Zn}

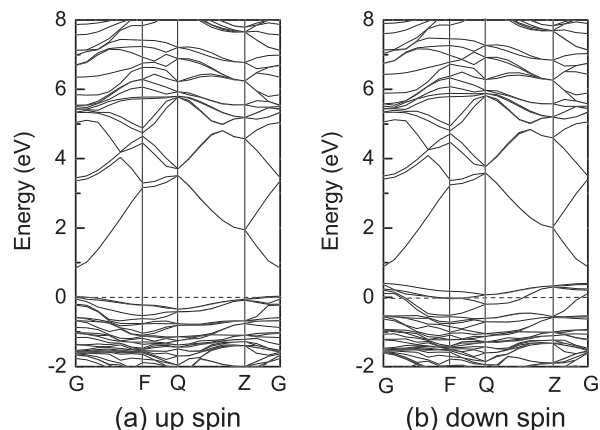


Fig. 2. Band structure of up spin (a) and down spin (b) of ZnO doped with 12.5% of N. Fermi level is set to zero.

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