A first-principles study of the magnetic properties in boron-doped ZnO*

Xu Xiao-Guang(徐晓光), Yang Hai-Ling(杨海龄), Wu Yong(吴 勇), Zhang De-Lin(张德林), and Jiang Yong(姜 勇)†

[a] State Key Laboratory for Advanced Metals and Materials, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

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First-principles calculations based on density functional theory are performed to study the origin of ferromagnetism in boron-doped ZnO. It is found that boron atoms tend to reside at Zn sites. The induced Zn vacancy is a key factor for ferromagnetism in $Zn_{1-x}B_xO$ ($0 < x < 1$) systems. The nearest oxygen atoms coordinated with the B–Zn vacancy pair show a few hole states in the 2p orbitals and induce magnetic moments. However, the configuration of two boron atoms inducing one Zn vacancy is nonmagnetic, with a lower formation energy than that of the B–Zn vacancy pair. This explains the difference between the theoretical and experimental magnetic moments.

Keywords: diluted magnetic semiconductors, ZnO, doping

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1. Introduction

Due to peculiar magnetic and semiconductor properties, dilute magnetic semiconductors (DMSs) have become promising materials for spintronic devices. Dietl *et al.*[1] predicted that ZnO is a promising candidate for DMS at room temperature (RT), which opens up a new field for DMS. According to Wang *et al.*[2] and Kim *et al.*,[3] the origin of the ferromagnetic (FM) property in ZnO comes from the magnetic moments of oxygen atoms around Zn vacancies. However, the density of Zn vacancies is hard to control in pure ZnO, which makes the FM property unrepeatable. To design new DMSs, many researchers introduced transition metal (TM) elements into ZnO, which brought many arguments as to whether the FM property is intrinsic or just brought about by second phase.[4−7] The doping of d^0 elements, such as carbon-doped ZnO, has been proved both experimentally and theoretically to be a new way to design intrinsic DMSs.[8,9] For strong electronegativity dopants such as carbon, the dopants tend to reside at oxygen sites and account for the ferromagnetism. However, there is a small second-phase quantity, such as graphite. Peng *et al.*[10] demonstrated the hole-induced ferromagnetism in a p-group element-doped ZnO system. In a previous study, we obtained FM B-doped ZnO films by pulsed laser deposition under high oxygen pressure.[11] It was found that weak electronegativity odd-valent dopants such as boron tend to reside at Zn sites and induce Zn vacancy, which results in intrinsic FM non-TM-doped DMS films. In this paper, we report on our detailed theoretical study of ferromagnetism in the B-doped ZnO films. The ferromagnetism in the B-doped ZnO is caused by oxygen atoms coordinated to the B–Zn vacancy pair. Energy analysis demonstrates that the 2B–Zn vacancy configuration is nonmagnetic with a lower formation energy than that of a B–Zn vacancy pair, which explains the difference between the theoretical and experimental magnetic moments.

2. Calculations

First-principles calculations based on the density functional theory were performed using the Vienna *ab initio* Simulation Package (VASP)[12] to investigate the FM origin in the $Zn_{1-x}B_xO$ system. Exchange correlation interactions were described by the Perdew-Wang 91 (PW91) generalized gradient

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†Corresponding author. E-mail: yjiang@ustb.edu.cn

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approximation (GGA).[13] The projector-augmented wave (PAW) method[14] was used for the treatment of core electrons. For all systems, the kinetic cutoff energy was set to be 400 eV. The bulk ZnO was relaxed to examine the reliability using a 9×9×6 k mesh, and the B-doped ZnO models were constructed by a 3×3×2 ZnO supercell. One or two boron atoms in the supercell correspond to a 2.8% or 5.6% boron concentration. We calculated the supercells with boron atoms occupying Zn, oxygen, and interstice sites, respectively. Considering that trivalent boron cations might induce Zn vacancy (denoted by V_{Zn}) in an oxygen rich environment, we separately calculated the Zn vacancy supercells of $Zn_{35}V_{Zn}O_{36}$ (ZnO+V_{Zn}), $Zn_{34}V_{Zn}BO_{36}$ (B+V_{Zn}), $Zn_{33}V_{Zn}B_2O_{36}$ (2B+V_{Zn}), and $Zn_{32}V_{Zn2}B_2O_{36}$ (2B+2V_{Zn}). In the B-doped models, the V_{Zn} occupies the nearest Zn site to the boron atom. The 2B+2V_{Zn} models with different distances between the B–V_{Zn} pairs were calculated to study the boron segregation. In all the calculations presented in this study, we employed a 3×3×2 mesh of special k-points to perform the summation over the Brillouin zone.

3. Results and discussion

To examine the accuracy of our calculations, the bulk ZnO model was optimized first. The theoretical lattice parameters a and c are 3.283 Å (1 Å=0.1 nm) and 5.283 Å respectively, which are in good agreement with the experimental values. All the possible vacancy-free models of B-doped ZnO were calculated to find the energetic stable sites for boron in the ZnO system. The theoretical lattice parameters, free energies, formation energies, and magnetic moments of pure ZnO and B-doped ZnO supercells are listed in Table 1. The most possible sites for the boron atoms doped in ZnO should be tetrahedral or octahedral interstices due to their small radius. However, according to our calculations, the tetrahedral interstice is too small for the boron atoms to be stable. On the other hand, if the boron atoms occupy the octahedral interstice, the formation energy is 0.004 eV. The lattice parameters expand to 3.311 Å and 5.331 Å, and the model converges to a nonmagnetic configuration. At the supercell of the boron occupying oxygen sites, the formation energy is 4.393 eV, which is too high for the supercell to be stable. The lattice parameters are also expanded as expected. When the boron atoms substitute Zn sites, the formation energy is −7.063 eV for each boron atom, indicating that the Zn sites are energetic favourable sites for the boron dopants. However, the supercell converges to a nonmagnetic ground state, even though the lattice shrinks to 3.263 Å and 5.272 Å. According to the above analyses, no vacancy-free B-doped ZnO supercell can converge to a stable FM ground state accompanied by lattice contraction, and according to the experimental results that the fabricated B-doped ZnO films are FM-accompanied by a lattice contraction,[11] none of the vacancy-free models can represent the real distribution of the boron atoms. Therefore, the FM mechanism of the B-doped ZnO is quite different from that of the C-doped system.[8]

Table 1. The calculated lattice parameters, free energies, formation energies, and magnetic moments of the pure ZnO and B-doped ZnO supercells.

		ZnO	B-doped ZnO		
			Zn site	O site	Octahedral interstice
Lattice parameter/Å	a	3.283	3.263	3.294	3.311
	b	3.283	3.263	3.294	3.311
	c	5.283	5.272	5.317	5.331
Free energy/eV		–18.076	–331.604	–314.172	–325.947
Formation energy/eV			–7.063	4.393	0.004
Magnetic moment/μ_B		0	0	0	0

Since the vacancy-free models cannot explain the FM property in the B-doped ZnO films, it is necessary to study the effects of vacancies. In our experiments, all the B-doped ZnO films were deposited under a high oxygen pressure of 10 Pa.[11] It is impossible for oxygen vacancies to exist. Therefore, we focused on Zn vacancies which might be induced by the trivalent B^{3+} dopants. To study the effect of boron atoms

on the stability of ZnO films, we average the formation energy of the configuration to each boron atom. So the formation energy $E_{\rm f}$ is calculated by formula (1), where m and n represent the numbers of boron atoms and Zn vacancies in the supercell, respectively

$$E_{\rm f} = \frac{E_{(m{\rm B}+n{\rm V_{Zn}})} - E_{\rm ZnO} - mE_{\rm B} + (n+m)E_{\rm Zn}}{m}. \quad (1)$$

Table 2 presents the optimized lattice parameters, free energies, formation energies, and magnetic moments of ZnO and B-doped ZnO supercells with Zn vacancies. The ZnO+V_{Zn} supercell shows both lattice shrinking and an FM ground state with a magnetic moment of 1.27 μ_B, which is mainly attributed to the induced magnetic moment ∼0.13 μ_B of the nearest neighbour oxygen atoms to the V_{Zn} sites, and is consistent with the results of Kim *et al.*[3] However, the formation energy of the ZnO+V_{Zn} configuration is 5.097 eV, indicating that the Zn vacancy is unstable in pure ZnO and may greatly depend on experimental conditions. It is therefore difficult to control the density of Zn vacancies to obtain a pure ZnO DMS. The configuration with formal valences in the B-doped ZnO is represented by the 2B+V_{Zn} model. The formation energy of each boron dopant in 2B+V_{Zn} is −6.126 eV, which is low enough for the configuration to be stable. However, the model has no net spin polarization as expected because there is no unpaired electron. So the FM property is not caused by 2B+V_{Zn}, in spite of its stability and lattice shrinking. The situation of each boron dopant inducing one Zn vacancy can be represented by the configurations of B+V_{Zn} and 2B+2V_{Zn}, in which the oxygen atom presents a $-2+\delta$ fractional valence. The formation energies of boron dopant in the B+V_{Zn} and 2B+2V_{Zn} are −4.619 eV and −4.807 eV, respectively, which are higher than those of 2B+V_{Zn}. However, the negative $E_{\rm f}$ values indicate that the B+V_{Zn} and 2B+2V_{Zn} configurations can exist stably. The magnetic moments of B+V_{Zn} and 2B+2V_{Zn} are 0.82 μ_B and 1.74 μ_B, respectively, accompanied by a lattice shrinking with the increased boron content. The magnetic moment per B–V_{Zn} pair is smaller than that in ZnO+V_{Zn} due to one hole less than the latter. The FM property comes from the induced magnetic moment of oxygen ranging from 0.09 μ_B to 0.14 μ_B, which is smaller than that in ZnO+V_{Zn} and indicates more occupied O-2p states. The induced magnetic moment of Zn is smaller than 0.03 μ_B, which can be omitted. As presented in our previous study,[11] the theoretical magnetic moment of the B-doped ZnO increases monotonically with the boron content, which is qualitatively consistent with the experimental results. However, the experimental $M_{\rm s}$ values are only ∼5% of the theoretical ones.[11] According to the formation energies in Table 2, 2B+V_{Zn} is the most stable configuration with Zn vacancies, while B+V_{Zn} and 2B+2V_{Zn} are metastable configurations with negative formation energies. Therefore, in the B-doped ZnO films, only minor boron dopants can form the B+V_{Zn} or 2B+2V_{Zn} configuration and contribute to the observed ferromagnetism, and others form nonmagnetic configurations to lower free energy. This corresponds to the quantitative difference between the experimental and theoretical $M_{\rm s}$ values. As listed in Table 2, the free energy of the 2B+2V_{Zn} with near neighbour B–V_{Zn} pairs is about 0.7 eV lower than that of the 2B+2V_{Zn} with far neighbour B–V_{Zn} pairs, indicating that the B–V_{Zn} pairs tend to occupy neighbour sites to decrease the free energy and lattice distortion.

Table 2. The calculated lattice parameters, free energies, formation energies, and magnetic moments of ZnO and B-doped ZnO supercells with Zn vacancies. Far and neighbour represent the distance between two B–V_{Zn} pairs. The formation energy corresponds to one boron dopant in each configuration.

		ZnO+V_{Zn}	2B+V_{Zn}	B+V_{Zn}	2B+2V_{Zn}	
					Far	Neighbor
Lattice parameter/Å	a	3.245	3.252	3.227	3.183	3.209
	b	3.245	3.241	3.245	3.241	3.239
	c	5.228	5.212	5.187	5.122	5.165
Free energy/eV		–319.149	–334.855	–328.044	–329.709	–331.102
Formation energy/eV		5.097	-6.126	–4.619	–4.111	–4.807
Magnetic moment/μ_B		1.27	0	0.82	1.85	1.74

Figure 1 shows the partial density of states (PDOS) of the oxygen and Zn atoms nearest to the B–V_{Zn} pair in the B+V_{Zn} supercell. The Fermi energy is set to be zero. The O-p states are almost fully occupied and nonmagnetic in pure ZnO. When the B–V_{Zn} pair is introduced into the supercell, the majority spin states are still fully occupied, while the minority spin states are partially filled, resulting in a net magnetic moment. Similar changes are observed in the Zn-d states. However, the magnetic moment is too small to influence the magnetic property of the system. The Zn-s state has no contribution to the FM property according to Fig. 1(b). Therefore, the ferromagnetism of the B-doped ZnO comes mainly from the induced magnetic moment of the oxygen atoms nearest to the B–V_{Zn} pair. As shown in Fig. 1, the B+V_{Zn} model is expected to be metallic, while all the calculated non-magnetic models are insulating. Since most boron dopants form nonmagnetic configurations and only minor quantities of boron can form the magnetic metallic B+V_{Zn} or 2B+2V_{Zn} configurations according to the above discussion on the formation energy, the films can be regarded as an insulating background inserted by metallic units. Therefore, the deposited films should be insulated. This is also supported by the experimentally measured resistance above 2×10^6 Ω for all the films.

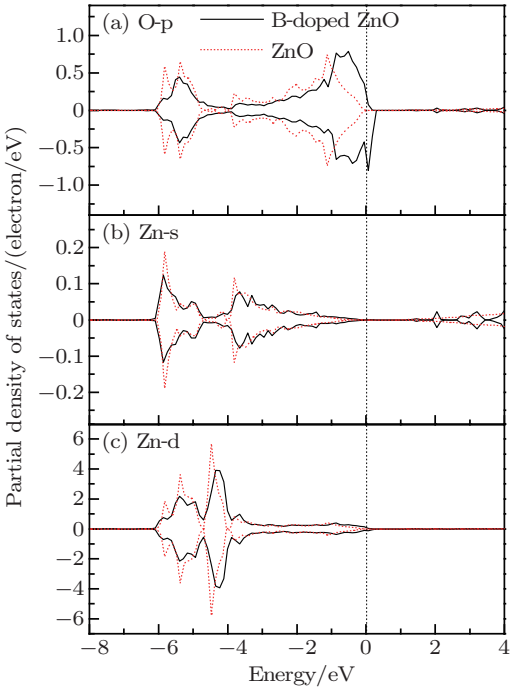


Fig. 1. (colour online) The partial density of states of (a) O-p, (b) Zn-s, and (c) Zn-d electrons in pure (dashed line) and 2.8% B-doped ZnO in B+V_{Zn} supercells (solid line).

In order to clearly display the origin of ferromagnetism, the spin resolved electron density slices of the B+V_{Zn} (100) plane near the Fermi level are presented in Fig. 2. The O_n atom noted in the map is one of the nearest neighbour oxygen atoms to the B–V_{Zn} pair. It is obvious that the majority electron density of O_n is similar to that of other oxygen atoms, while its minority electron density is much larger than the others. The difference between the majority electron density and the minority electron density near the Fermi level indicates spin polarized O-2p states of the O_n atom, which is the origin of the ferromagnetism in the B+V_{Zn} model.

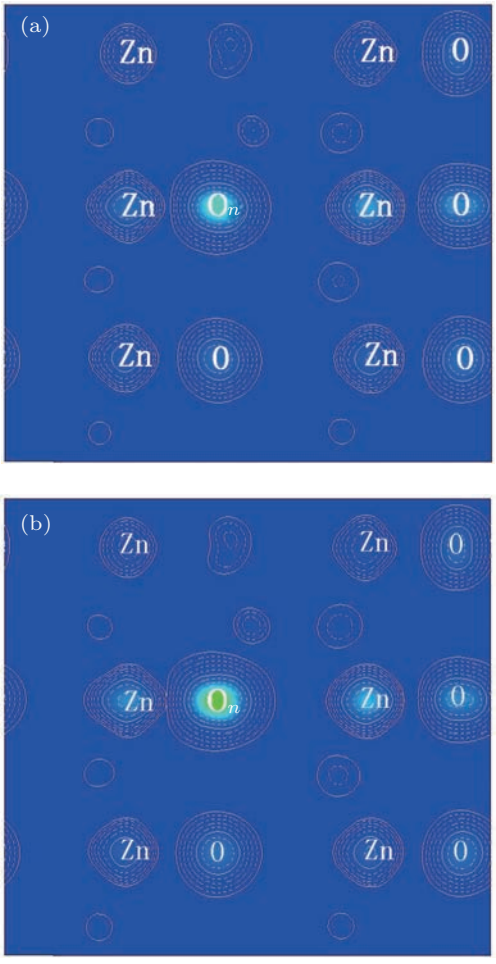


Fig. 2. (colour online) Majority (a) and minority (b) charge density slices of the B+V_{Zn} (100) plane at 0.2141, associated with the states within the energy region from −0.5 eV to 0.5 eV.

4. Conclusion

In summary, we demonstrated the origin of ferromagnetism in the B-doped ZnO film by first-principles calculations. Zn sites are calculated to be the suitable sites for boron dopants. The Zn vacancy is a key factor for ferromagnetism in the $Zn_{1-x}B_xO$ sys-

tem. Odd-valent boron dopants can induce a few hole states in oxygen 2p orbitals, which produces magnetic moments. The formation energies of the different configurations can explain the difference between the theoretical and experimental magnetic moments.

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