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Electronic structure and magnetic interactions in Zn-doped β-Ga_2O_3 from first-principles calculations

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ABSTRACT

By using first-principles calculation method, the electronic structure and magnetic interactions of Zn-doped β-Ga_2O_3 have been investigated. The calculated results indicate that Zn-doped β-Ga_2O_3 with spin-polarized state has lower energy than that with nonspin-polarized state. Zn-doped β-Ga_2O_3 is a ferromagnetic (FM) semiconductor with 100% spin polarization. The magnetic moment of Zn-doped β-Ga_2O_3 is about 1.0 μ_B per cell, which mainly comes from the unpaired 2p electron of O atoms around Zn dopant. The magnetic moment decreases to 0.49 μ_B when oxygen vacancy is introduced. It suggests that the ferromagnetism in Zn-doped β-Ga_2O_3 originates from the p–d hybridization of oxygen and zinc atoms. FM coupling is always favorable for configurations in which two Zn atoms substitute either tetrahedral or octahedral sites. Zn-doped β-Ga_2O_3 can be free from clustering effect.

1. Introduction

Dilute magnetic semiconductors (DMSs) have elicited much attention because of their potential applications in spintronic devices, which combine the charge and spin property of electrons in the materials [1,2]. Ideally, engineerable DMSs with the Curie temperature (T_C) higher than room temperature (RT) and high spin polarization are preferred in the industry. To achieve this goal, magnetic 3d transition metal (TM)-doped DMSs with RT ferromagnetic (FM) property have been reported, such as Cr-doped ZnTe and AlN [3,4], TMs-doped In_2O_3 [5,6], TiO_2 [7,8], SnO_2 [9], and ZnO [10,11]. However, the origin of ferromagnetism in such DMSs is still controversial because of the clustering effect of these dopants [12,13]. To solve the problem of magnetic precipitate, alternative intrinsically nonmagnetic dopants, which can induce RT ferromagnetism in DMSs, are desired. Studies on DMSs obtained by doping intrinsic nonmagnetic elements, such as carbon, nitrogen and copper, have been reported theoretically and experimentally [14–23]. In this research, zinc-doped β-Ga_2O_3 is selected to study FM properties. Compared with other cation dopant, zinc dopant can induce less distortion in the matrix because of the similar ionic radii of zinc and gallium. Monoclinic gallium oxide β-Ga_2O_3 has received significant attention for its excellent optical and electronic properties [24–26]. According to the mean field theory, RT ferromagnetism can be realized in doped wide bandgap semiconductors [27]. Therefore, β-Ga_2O_3 is prospected to be a promising candidate for a new DMS with high T_C, as confirmed by experimental and theoretical studies [28–30]. The FM properties of intrinsically nonmagnetic element-doped β-Ga_2O_3 warrant further study. In the present research, we studied the electronic structures and magnetic interactions of Zn-doped β-Ga_2O_3 through first-principles calculations. Our calculations show that Zn dopants induce very small lattice distortions of β-Ga_2O_3, and Zn-doped β-Ga_2O_3 is predicted to be FM, with a magnetic moment (MM) of 1.0 μ_B per supercell with one Zn-dopant. Our calculations indicate that no obvious clustering tendency exists in Zn-doped β-Ga_2O_3. Our model is significant for understanding the nature of magnetic interactions in promising DMS candidates.

2. Details of calculations

To construct Zn-doped Ga_2O_3 systems, a $1 \times 2 \times 1$ supercell containing two monoclinic unit cells was modeled, in which one gallium atom was substituted by a zinc atom at either octahedral Ga(A) or tetrahedral Ga(B) coordinated site, as shown in Fig. 1. In our calculations, the plane wave ultra-soft pseudo-potential was selected to describe the interaction between the electron and the ionic cores [31]. The Perdew–Burke–Ernzerhof (PBE) scheme of the generalized gradient approximation (GGA) was adopted for describing the exchange correlation interactions [32]. Basic parameters were chosen as follows: kinetic energy cut-off was 400 eV and SCF tolerance was 0.5×10^{-6} eV/atom. The maximum displacement was 0.5×10^{-3} Å and the force per atom was lower

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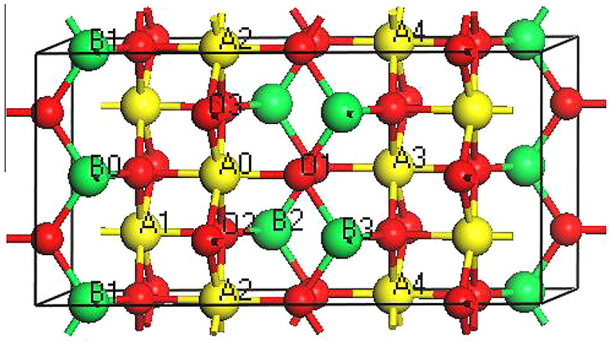

Fig. 1. The large green, yellow and small red spheres are the tetrahedral, octahedral coordinated Ga and O atoms, respectively. The Ga atoms labeled by A0–A4 and B0–B3 are the sites to be replaced by Zn atoms (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

than 0.01 eV/Å. In addition, the maximum stress was 0.02 GPa. A $3 \times 4 \times 4$ Monkhorst–Pack *k*-points grid was selected for irreducible Brillouin zone sampling. The electronic states of $2s^2 2p^4$, $3d^{10} 4s^2 4p^1$ and $3d^{10} 4s^2$ are considered as the valence states for O, Ga and Zn, respectively. All the calculations were completed by the CASTEP package in Materials Studio (MS) software [33].

3. Results and discussion

The geometrical structures and atomic coordinates were fully relaxed without any restriction by the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method [34]. The calculated lattice parameters *a* and *c* of intrinsic β-Ga_2O_3 are 12.502 Å and 5.897 Å, respectively, which are in good agreement with experimental values [35]. Thus, our calculation method is reasonably accurate. Table 1 presents the calculated lattice parameters for Zn-doped Ga_2O_3, with one Ga atom replaced by one Zn atom at either of the sites mentioned above. The lattice parameters change slightly: 0.067 Å for *a* and −0.013 Å for *c* after structural optimization. These differences originate from the minor difference in atomic radius between Zn and Ga. The fractional coordinates of Zn dopant and its nearest neighbor oxygen atoms of Zn-doped Ga_2O_3 with $Zn_{Ga(B)}$ configuration are also listed in Table 1. The minor displacements of related atoms indicate Zn dopant can induce small distortion of the structure.

The calculated energy results show that the spin-polarized state for any case mentioned above has lower energy than the nonspin-polarized counterpart. Therefore, the spin-polarized state in any of the cases is ground state, which is necessary for FM semiconductors. The spin-polarized state for $Zn_{Ga(B)}$ configuration has a lower total energy by 59 meV per supercell compared with $Zn_{Ga(A)}$ configuration, which means the Zn atom tends to substitute the Ga atom at the tetrahedral coordinated site in Zn-doped Ga_2O_3. So, we focus on the properties of the spin-polarized state for $Zn_{Ga(B)}$ configuration in this paper.

The formation energy of a defect or impurity Zn in charge state $q = 0$ is defined as

$$E_{\text{form}} = E_{\text{Zn-Ga}_2\text{O}_3} - E_{\text{Ga}_2\text{O}_3} - \mu_{\text{Zn}} + \mu_{\text{Ga}}, \quad (1)$$

where $E_{\text{Zn-Ga}_2\text{O}_3}$ and $E_{\text{Ga}_2\text{O}_3}$ are the total energies of Zn-doped β-Ga_2O_3 and equivalent intrinsic β-Ga_2O_3, respectively; μ_{Zn} and μ_{Ga} are the corresponding chemical potentials of zinc atom and gallium atom, respectively. The calculated values of E_{form} for $Zn_{Ga(B)}$ and $Zn_{Ga(A)}$ configurations are 0.89 and 0.95 eV, respectively. These moderate formation energies indicate Zn substituting Ga atom is stable. So, Zn-doped β-Ga_2O_3 can be fabricated in experiments with certain conditions. As a matter of fact, Zn-doped β-Ga_2O_3 had been prepared by many experimental methods [36,37].

The electronic properties of Zn-doped β-Ga_2O_3 have been studied in our research. As listed in Table 1, the calculated band gap of intrinsic β-Ga_2O_3 is 1.96 eV, which is lower than the experimental result. This result is attributed to the underestimation of the interaction among electrons in the DFT method. The band structure of Zn-doped β-Ga_2O_3 is shown in Fig. 2. An interesting feature of the band structure is the spin splitting of impurity bands induced by Zn dopant. The up-spin bands (Fig. 2a) present metallic character, in which two bands cross the Fermi level. The down-spin bands (Fig. 2b) show semiconductor behavior with band gap of 1.90 eV. Therefore, Zn-doped β-Ga_2O_3 shows half-metallic characters with 100% spin polarization, indicating that Zn-doped β-Ga_2O_3 can be considered as an ideal material for spin-injection applications. It can be seen that the Zn-induced impurity bands are located above the valence band maximum in Fig. 2a. Thus, the Zn dopant can act as a shallow acceptor, and p-type conduction can be realized in Zn-doped β-Ga_2O_3, which has been confirmed by experimental results reported [36].

To investigate the origin of FM properties of Zn-doped β-Ga_2O_3, we present the total density of state (DOS) and partial DOS for the Zn-doped β-Ga_2O_3 system in Fig. 3. The down-spin states are fully occupied, whereas the up-spin states are partially filled in total DOS. The asymmetrical DOS near the Fermi level suggests the magnetic property of such doped system, resulting in a MM of 1.0 μ_B per supercell. In partial DOS, it can be clearly found that the Zn 3d states overlap obviously with those of O 2p near the Fermi level, suggesting a strong exchange interaction between them. From Table 2, FM coupling strength is sensitive to the distance between Zn dopants, suggesting that the splitting of the energy levels near

Table 1
The calculated lattice parameters and the formation energies of intrinsic β-Ga_2O_3 and Zn-doped β-Ga_2O_3.

		a (Å)	*b* (Å)	*c* (Å)	*β*	E_{form} (eV)	E_g (eV)
β-Ga_2O_3 Ref. [36]		12.23	3.04	5.80	103.7		4.40
Intrinsic β-Ga_2O_3		12.502	3.093	5.897	103.688		1.96
$Zn_{Ga(A)}$ (nonspin-polarized state)		12.570	3.097	5.891	103.504	0.99	
$Zn_{Ga(A)}$ (spin-polarized state)		12.569	3.096	5.891	103.491	0.95	
$Zn_{Ga(B)}$ (nonspin-polarized state)		12.561	3.100	5.884	103.652	0.95	
$Zn_{Ga(B)}$ (spin-polarized state)		12.569	3.097	5.884	103.630	0.89	
			Ga (Zn)	O1-I	O1-II	O2	O3
The fractional coordinates of Zn dopant and its nearest neighbor oxygen atoms							
x	Undoped		0.4101	0.4960	0.4960	0.3262	0.3367
	Doped		0.4096	0.5010	0.5010	0.3221	0.3354
y	Undoped		0.2500	0.5000	0	0.2500	0.2500
	Doped		0.2500	0.5065	0.9935	0.2500	0.2500
z	Undoped		0.2052	0.2568	0.2568	0.4357	0.8906
	Doped		0.2080	0.2647	0.2647	0.4420	0.8838