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First-principles study of single intrinsic vacancy formation and its effect on the electronic density states and magnetic moment of V-doped ZnO

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ABSTRACT

We calculated the formation energy of single vacancy in V-doped ZnO in different conditions (oxygen or zinc rich) by first principles. Effect of an intrinsic vacancy on the electronic density of states and magnetic moment of V-doped ZnO ($\text{Zn}_{15}\text{VO}_{16}$) with and without single vacancy was also calculated. Our calculation was performed by the CASTEP program within spin-polarized GGA approximation implemented in materials studio software. The formation energy showed that oxygen vacancy inclined to stay far from vanadium (V) and zinc vacancy preferred to stay at a position near V. The calculated formation energy also showed that a zinc vacancy may automatically occur but an oxygen vacancy may not appear automatically. Vanadium doping introduced spin-polarization around Fermi level. For an energy favorable vacancy, an oxygen vacancy had little effect on the electronic density of states. A zinc vacancy made the spin-polarization peaks around Fermi level broaden and decreased their magnitude. For the magnetic moment in energy favorable configurations, an oxygen vacancy had little effect on the magnetic moment; a zinc vacancy significantly decreased the magnetic moment (as high as 63.7%). Changes in magnetic moments were consistent with electronic density of states. Our calculation may interpret various experimental magnetic moment values. Our work also provided a reference for preparing V-doped ZnO-based dilute magnetic semiconductors.

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1. Introduction

ZnO is a wide-direct bandgap semiconductor (3.4 eV at room temperature) and widely used in practical devices [1–4]. Transition metal doped ZnO has attracted many researchers in recent years for its potential use in future spintronic devices [5–7]. There has been some work that studied ferromagnetism under room temperature in V-doped ZnO. Zhou et al. have experimentally studied the reason for the absence of ferromagnetism in V-doped ZnO [8]. Wang et al. theoretically found that magnetism was related to V content and configuration [9]. Naydenova et al. has experimentally reported that room temperature ferromagnetism was related to contents and defects in V-doped ZnO [10]. It is known that ZnO-based semiconductors are likely to form intrinsic vacancy during preparing [11]. Xu et al. believed that vacancy played an important role in the magnetic properties of ZnO [12]. The magnetic moment of isolated V^{2+} ion is $3 \mu_{\text{B}}$ /V and that of V^{3+} ion is $2 \mu_{\text{B}}$ /V. But the experimental result has been only $0.5 \mu_{\text{B}}$ [13,14] and even $0.002 \mu_{\text{B}}$ /V has been recently found [15].

He et al. explored the effect of single oxygen vacancy on the magnetic moment of TiO_2 [16]. We could expect that intrinsic vacancy in V-doped ZnO will affect its magnetic moment. It is also known that the V content is based on the formation energy, and its magnetic moment relates closely to electronic density of states. In this paper, we first calculated the formation energy of single vacancy in different conditions (oxygen or zinc rich). After that, we computed the effect of single vacancy on electronic density of states and magnetic moment in V-doped ZnO.

2. Computational methods

Our first-principles calculations were performed by CASTEP program within spin-polarized GGA approximation [17] implemented using materials studios software. To ensure speed and accuracy, we used 400 eV as cutoff energy after extensive tests. Valence electronic configurations used for vanadium (V), zinc and oxygen atoms were $3d^34s^2$, $3d^{10}4s^2$ and $2s^22p^4$, respectively. We used $9 \times 9 \times 6$, $4 \times 4 \times 2$ and $4 \times 4 \times 2$ k -points [18] to sample the First Brillouin zone of pristine ZnO, V-doped ZnO and V-doped ZnO with single intrinsic vacancy (oxygen or zinc vacancy), respectively. Ultrasoft pseudopotentials were used in our calculations and

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the calculations were carried out in reciprocal space. A used SCF tolerance was 1×10^{-6} eV/atom.

3. Result and discussion

3.1. Formation energy

There were four possible sites for oxygen and zinc vacancy to form. The possible sites are shown in Fig. 1a. Sites 1 (near) and 2 (far) were the possible sites for oxygen vacancy. Sites 3 (near) and 4 (far) represented the possible sites for zinc vacancy. We used configurations I, II, III and IV to represent a vacancy formed in sites 1, 2, 3 and 4, respectively. We can know which type of vacancy occurred in the formed site.

It is known that the content of vacancy is according to its formation energy (E_f). The formation energy of different configurations was calculated using the equation: $E_f = E_{\text{tot}} - n_{\text{Zn}}\mu_{\text{Zn}} - \mu_{\text{V}} - n_{\text{O}}\mu_{\text{O}}$ (1). In Eq. (1), μ represented chemical potential and its subscript index represented the element. E_{tot} was the total energy of different configurations. The relationship between chemical potential of zinc and oxygen atoms in (Zn,V)O system was $\mu_{\text{ZnO}} = \mu_{\text{Zn}} + \mu_{\text{O}}$ [19]. In zinc rich condition, μ_{Zn} was given by $\mu_{\text{Zn}}^{\text{metal}}$. On the other hand, μ_{O} was decided by $(1/2)\mu_{\text{O}_2}^{\text{gas}}$ in oxygen rich condition. In other experimental condition, the relationships were $\mu_{\text{Zn}} < \mu_{\text{Zn}}^{\text{metal}}$ and $\mu_{\text{O}} < (1/2)\mu_{\text{O}_2}^{\text{gas}}$. The chemical potential μ_{V} came from $\mu_{\text{V}}^{\text{metal}}$. The calculated relative formation energy of different configurations was shown in Fig. 1b. In Fig. 1b, we set the relative chemical potential of zinc to zero in an oxygen rich situation. We also set the relative formation energy (E_f) of V-doped ZnO ($\text{Zn}_{15}\text{VO}_{16}$) to zero and the other configurations were relative to the E_f of $\text{Zn}_{15}\text{VO}_{16}$. From Fig. 1b, we saw that a zinc vacancy was easier to form than an oxygen vacancy. An oxygen vacancy could not be formed automatically and it could only appear under certain experiment conditions. On the other hand, a zinc vacancy could be formed automatically under a wide experimental condition. As relative formation energy shown in Fig. 1b, configurations II and III were energy favorable. The energy between the formation energy of configurations I and II was about 177.8 meV. The energy gap between them was little, which meant that an oxygen vacancy can form at a position near V in certain experiment. The energy between the formation energy of configurations III and IV was about 963.2 meV. The energy gap between them was much, which meant that a zinc vacancy was difficult to

form in a position far from V. From the discussion about formation energy, V-doped ZnO with a zinc vacancy (configuration III) may form under many experiments.

3.2. Electronic properties

In the first section, we computed the formation energy of various configurations of V-doped ZnO containing single intrinsic vacancy. We know that an oxygen vacancy inclines to stay at a position far from V and a zinc vacancy prefers to locate at a position near vanadium (V) atom. It is known that a magnetic moment related closely to electronic density of states (DOS). So we calculated their electronic DOS before their magnetic moment. Calculated electronic DOS are shown in Fig. 2. We calculated the DOS of pristine ZnO and V-doped ZnO without vacancy. For V-doped ZnO with single vacancy, we only gave the DOS of energy favorable configurations (II and III). Electrons provided by V moved the electronic density of states (DOS) of pristine ZnO to lower energy (Fig. 2a). As shown in Fig. 2a, V doping introduced spin-polarization around the Fermi level, which meant to introduce net magnetic moment in pristine ZnO. Our calculated electronic DOS agreed with another report [10]. From Fig. 2a, we can see that spin-polarization mainly come from V_{3d} orbit. The contribution of O_{2s} , O_{2p} , V_{4s} and V_{3p} to the polarization can be neglected. After one oxygen vacancy appeared (Fig. 2b), the spin-polarization of V_{3d} around Fermi level was similar to that of V-doped ZnO ($\text{Zn}_{15}\text{VO}_{16}$). An oxygen vacancy had little effect on the electronic DOS of V-doped ZnO, which meant that electrons released by oxygen vacancy may localize at the vacancy. Accordingly, the magnetic moment had little change. In the case of a zinc vacancy (Fig. 2c), the electronic DOS moved to higher energy than that of V-doped ZnO. The peaks of V_{3d} became broader and their magnitude decreased. The changes in electronic DOS may mean a decreasing magnetic moment would be found. The changes in electronic DOS and decreased peaks may mean that holes provided by zinc vacancy partly compensated the spin-polarization around Fermi level.

3.3. Magnetic moment calculation

In the first and second sections, we calculated formation energy and electronic DOS of various configurations. We also anticipated changes in magnetic moment from electronic density

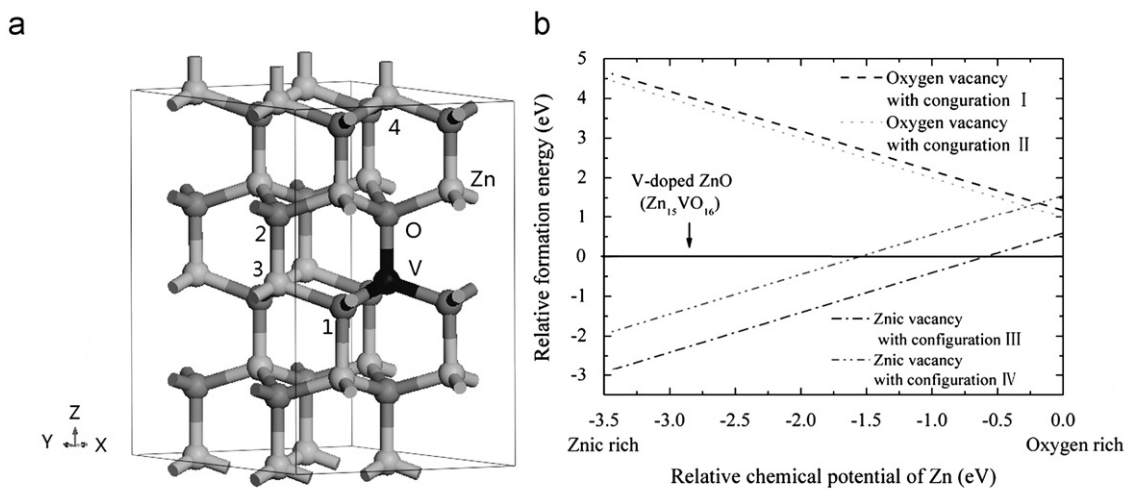


Fig. 1. (a) A scheme of $2 \times 2 \times 2$ supercell for various configurations based on V-doped ZnO (the black, dark-gray and gray ball represented V, oxygen and zinc atom, respectively). (b) Relative formation energy (E_f) of different configurations. The line equal to zero was the E_f of $\text{Zn}_{15}\text{VO}_{16}$ and the E_f of other configurations was relative to the E_f of $\text{Zn}_{15}\text{VO}_{16}$.

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