Magnetic coupling properties of rare-earth metals (Gd, Nd) doped ZnO: first-principles calculations

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The electronic structure and magnetic coupling properties of rare-earth metals (Gd, Nd) doped ZnO have been investigated using first-principles methods. We show that the magnetic coupling between Gd or Nd ions in the nearest neighbor sites is ferromagnetic. The stability of the ferromagnetic coupling between Gd ions can be enhanced by appropriate electron doping into ZnO:Gd system and the room-temperature ferromagnetism can be achieved. However, for ZnO:Nd system, the ferromagnetism between Nd ions can be enhanced by appropriate holes doping into the sample. The room-temperature ferromagnetism can also be achieved in the n-conducting ZnO:Nd sample. Our calculated results are in good agreement with the conclusions of the recent experiments. The effect of native defects ($V_{Zn}, V_{O}$) on the ferromagnetism is also discussed.

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I. INTRODUCTION

The diluted magnetics semiconductors (DMSs) such as 3$d$ transition metals (TMs) doped ZnO have attracted a lot of attention due to their great potential applications in the spintronic devices [1–11]. Recently, rare earth (RE) ions doped DMSs have also invoked great interests since the colossal magnetic moment of Gd in GaN was reported by Dhar et al. [12]. They reported that the average value of the moment per Gd is as high as 4000 $\mu_B$ which can be explained in terms of a long-range spin polarization of the GaN matrix by Gd [12]. First principles studies have been carried out by different teams to explain ferromagnetism in GaN:Gd [13, 14]. Dalpian and Wei [13] reported that the coupling between Gd atoms is antiferromagnetic and the electrons can stabilize the ferromagnetic phase because of the coupling between the Gd $f$ and host $s$ states introduced by the same symmetry. However, Liu et al. [14] argued that the room-temperature ferromagnetism in GaN:Gd can be explained by the interaction of Gd $4f$ spins via $p-d$ coupling involving holes introduced by intrinsic defects and holes are more effective than electrons in contributing to the observed colossal magnetic moment of Gd ions.

Experimental studies for the ferromagnetism of ZnO:Gd systems have also produced controversial conclusions [15, 16]. Potzger et al. [15] found ferromagnetism in Gd-implanted ZnO single crystals. They noted that when sufficient density of Gd ions is present, then annealing is necessary to release enough charge carriers to establish the ferromagnetic coupling of the diluted Gd ions. However, Ungureanu et al. [16] reported that there are no exchange interaction between the RE ions and a large negative magnetoresistance is obtained which can be interpreted as a paramagnetic response of the system to the applied magnetic field.

Compared with 3$d$ transition metals (TMs), 4$f$ rare earth (RE) metals have larger magnetic moments. Furthermore, the electrons may mediate the ferromagnetic coupling between the RE ions, due to the coupling between $f$ electrons (with $a_1$ symmetry) and host $s$ electrons [13]. This conclusion may be good for ZnO based DMSs, because grown ZnO films or single crystals always exhibit $n$-type conductivity. Until now, no theoretical studies about RE ions doped ZnO systems are found. Therefore, it is interesting to investigate the electronic structures and magnetic couplings properties of ZnO:RE.

In this work, we have systematically studied the magnetic coupling between the RE ions with different electron and hole concentrations doped into the ZnO:RE samples. We find that the coupling between Gd ions in ZnO is ferromagnetic. Furthermore, the electrons of appropriate concentration can enhance the ferromagnetic coupling between them. However, for Nd ions, the holes of appropriate concentration can enhance the ferromagnetic coupling between them. The effect of native defects ($V_{Zn}, V_{O}$) on the ferromagnetism is also discussed. We note that although the oxygen vacancy can contribute electrons to the system, the coupling between Gd ions is anti-ferromagnetic. Maybe this is because the concentration of electrons introduced by oxygen vacancy is too high in our studied supercell.

II. DETAILS OF CALCULATION

Our first-principles calculations are based on the density functional theory (DFT) and the Vienna ab initio simulation package [17] using the generalized gradient approximation (GGA) of PBE functional [18] for the exchange correlation potential. The electron and core interactions are included using the frozen-core projected augmented wave (PAW) approach [19]. The Zn 3$d$ and
rare earth metals 5p4f electrons are explicitly treated as valence electrons. The electron wave function is expanded in plane waves up to a cutoff energy of 400 eV. For the Brillouin zone integration, a 2×2×4 Monkhorst-Pack k-point mesh is used for the supercell containing 32 atoms and a good convergence is obtained. All the geometries are optimized until the quantum mechanical forces acting on the atoms are smaller than 0.01 eV/Å.

In our present work, we calculate the ferromagnetic properties for the RE ions doped in the zinc-blende structure ZnO and we expect our conclusions are similar to those for RE ions doped in ground phase ZnO with wurtzite structure since the band structures of the ZB and WZ alloy are very similar near the band edge at Γ [20]. In our magnetic calculations, we substitute two Zn atoms with two RE ions in the nearest neighbor (NN) sites, corresponding to a concentration of 12.5% for RE ions.

III. RESULTS AND DISCUSSIONS

A. Electronic structure of hypothetical zinc-blende phase GdO and NdO

In order to obtain a clear understanding of the magnetic coupling of the RE ions, we first study the electronic structures of the hypothetical zinc-blende (ZB) phase GdO and NdO binary alloys. The present calculated lattice constants for ZB structure ZnO, GdO, and NdO are 4.626, 5.375, and 5.444 Å, respectively. Our calculated results show that both GdO and NdO are more stable in the ferromagnetic phases and the energy differences between anti-ferromagnetic (AFM) and ferromagnetic (FM) coupling states are 16 meV and 291 meV, respectively.

Based on the crystal field theory, in a tetragonal substitutional site of ZB structure, the d orbitals are split into one triply degenerate t2g state and one doubly degenerate eg state; the f orbitals are split into two triply degenerate t2g, t1g states and one singly ag1 state. The spin-resolved band structures of GdO and NdO are plotted in Fig. 1 and Fig. 2, respectively. The labels in these two figures represent the characters of Bloch wave functions at Γ point.

In Fig. 1, due to the large electronegativity of oxygen, the 4f majority spin channels are above the oxygen p states, unlike the GdN in which the 4f majority spin channels are below the nitrogen p states [13]. At Γ point, the O p states with t2g symmetry in spin up channels are below those in spin down channels. This is because at Γ point the coupling between the Gd t2g and O t2g states is larger in the spin up channel, which pushes down the O p states. We also notice that at Γ point, the Gd s state is located below the Fermi energy in both spin up and spin down channels. Furthermore, for GdN, Gd is isovalent with Ga because of the 4f5d6s valence configuration, therefore, GdN is semiconducting [13]. For GdO, however, Gd is not isovalent with Zn, thus GdO is not semiconducting. From the density of states (DOS) of GdO plotted in Fig. 3(a), we can also conclude that GdO is not semiconducting because there are majority spin states at the Fermi-energy position and the density of states are not symmetrical for the majority and minority spins.

In Fig. 2, the band structure of the ferromagnetic phase NdO with ZB structure is showed. At Γ point, part of the 4f states are occupied in the spin up channel below the Fermi energy, while the 4f states in the spin down channel are fully empty. According to the DOS plotted in Fig. 3(b), we see that the 4f bands of majority spin are located between -0.5 eV and 0.4 eV, and the peak in the DOS of 4f states of minority spin occurs around 2.3 eV. Overall, the DOS of 4f states are broadened due to the f-s hybridization.

B. Ferromagnetic coupling of Gd and Nd ions doped in ZnO

In the following, we systematically study the properties of ferromagnetic coupling between Gd (Nd) ions in different charged states. Experimentally, Potzger et al. [15] found ferromagnetism in Gd-implanted ZnO single crystals. They further reported that when sufficient density of Gd ions is present, then annealing is necessary to release enough charge carriers to establish the ferromagnetic coupling of the diluted Gd ions. In our present study, we substitute two Zn atoms with two RE ions (Gd or Nd) in the nearest neighbor sites. We simulate the effect of donors (acceptors) by introducing electrons (holes) into the ZnO:RE systems. We want to know how
the electrons and holes with different concentrations mediate the ferromagnetism in the ZnO:RE systems. We have also investigated whether the intrinsic defects (V_{Zn}, V_{O}) play an important role in the magnetic properties of ZnO:RE systems. Our results show that the ground states of Gd and Nd doped ZnO systems are all ferromagnetic coupling states in the neutral state, and the energy differences \( \Delta E \) between the anti-ferromagnetic coupling state (AFM) and the ferromagnetic coupling state (FM) are 7 and 94 meV, respectively. The direct coupling between 4\( f \) electrons is very weak compared with the energy difference \( \Delta E \) for 3\( d \) transition metals doped in ZnO [10, 11, 21]. This is because the orbitals of 4\( f \) electrons are very localized [13]. The band structure of FM phase for ZnO:Gd and ZnO:Nd systems are plotted in Fig. 4 and Fig. 5, respectively. In Fig. 4 for ZnO:Gd system, the 4\( f \) bands of the majority spin (lying at about \(-20\) eV) are not plotted because they are far from the Fermi energy. However, in Fig. 5 for ZnO:Nd system, the 4\( f \) bands of the majority spin are located near the Fermi energy due to the partially occupied 4\( f \) orbitals.

Due to the \( s-f \) coupling, electrons may mediate the fer-
TABLE I: Calculated energy differences \( \Delta E \) (\( \Delta E = E_{\text{AFM}} - E_{\text{FM}} \)) between anti-ferromagnetic and ferromagnetic configurations for ZnO:Gd and ZnO:Nd in different charged states.

| RE     | charge state | \( \Delta E \) (meV) |
|--------|--------------|-----------------------|
| Gd     | neutral      | 7                     |
|        | 0.15e/Gd     | 44                    |
|        | 0.25e/Gd     | 67                    |
|        | 0.50e/Gd     | 61                    |
|        | 0.75e/Gd     | -8                    |
|        | 1.00e/Gd     | -37                   |
|        | 0.50h/Gd     | 4                     |
|        | 1.00h/Gd     | 0                     |
|        | \( V_{\text{Zn}} \) | 0                     |
|        | \( V_{\text{O}} \) | -8                    |
| Nd     | neutral      | 94                    |
|        | 0.25h/Nd     | 128                   |
|        | 0.50h/Nd     | 134                   |
|        | 0.75h/Nd     | 69                    |
|        | 1.00h/Nd     | 20                    |
|        | 0.25e/Nd     | 46                    |
|        | 0.50e/Nd     | 16                    |
|        | \( V_{\text{Zn}} \) | 52                     |
|        | \( V_{\text{O}} \) | 67                     |

Ferromagnetism in n-type samples [21][22]. Experimentally, Ungureanu et al. [24] also reported that the presence of ferromagnetism in ZnO:Gd films might indicate electron mediated interion exchange. In order to test this speculation, we insert different amounts of electrons into the ZnO:Gd supercell. Remarkably, we find that even when 0.15 electron per Gd is inserted into the ZnO:Gd system, the stability of the FM phase is enhanced with \( \Delta E = 44 \) meV (\( \Delta E = E_{\text{AFM}} - E_{\text{FM}} \)), much larger than the neutral case of \( \Delta E = 7 \) meV. We also calculate the cases of 0.25, 0.50, 0.75, and 1.0 electron per Gd. The corresponding \( \Delta E \) are 67, 61, -8, and -37 meV. We note that the ZnO:Gd system will favor AFM phase if 0.75 or 1.0 electron per Gd is inserted into the system. In practice, however, even for 0.5 electron per Gd, such high doping corresponding to \( 1.314 \times 10^{21} \, \text{cm}^{-3} \) is hard to achieve experimentally. For hole doping, the calculated \( \Delta E \) is 4 meV after creating 0.5 hole per Gd in the system, thus indicating that the stability of the FM phase is weakened by the hole doping. In particular, when the hole doping is as high as 1.0 hole per Gd, we find that the energies of FM and AFM phases of ZnO:Gd are degenerate and thus the system favors paramagnetic phase. Since the intrinsic defects are important as well for the magnetic properties, we have also investigated how the zinc and oxygen vacancies affect Gd-Gd magnetic interaction. For zinc vacancies \( V_{\text{Zn}} \), in our studied supercell one \( V_{\text{Zn}} \) contributes 2 holes to the system, and our calculated \( \Delta E \) is 0 meV, i.e., the ZnO:Gd system favors paramagnetic phase. This is consistent with the case of 1.0 hole/Gd, both can lead the ZnO:Gd system to favor paramagnetic phase. However, one \( V_{\text{O}} \) introduces two electrons to the system and leads the system to anti-ferromagnetic phase with \( \Delta E = -8 \) meV. The effect of one \( V_{\text{O}} \) on the system is similar to that of the case of 1.0 electron per Gd.

Our above calculated results are listed in table I. According these results we can conclude that electrons can effectively mediate the ferromagnetism through the concentration of its concentrations. Ungureanu et al. [24] also reported that the presence of ferromagnetism at 300 K in ZnO:Gd films with around 1% Gd co-doped with 0.2% Al might indicate electron mediated exchange in ZnO:Gd systems. In their samples, Al servers as n-type dopant. The concentration of electrons introduced by Al (1% Gd co-doped with 0.2% Al) is in the range of our studied cases of 0.15~0.25 electron per Gd, which, as predicted from Table I, also leads the ZnO:Gd system to favor ferromagnetic phase. As for the Curie temperature \( T_c \), our calculated energy differences \( \Delta E \) in Table I suggest that for the present calculated ZnO:Gd system with the electron concentration comparable with that in attainable experiment [24], the derived \( T_c \) is higher than room temperature (RT). This prediction, which is really consistent with the experiment [24], is based on the established fact [25] that RT ferromagnetism can only be achieved when \( \Delta E \) is larger than about 30 meV. Note again that for the ZnO:Gd system, the s-f coupling is much larger than the f-f and f-p couplings, which makes it be the main factor for the electron-mediated ferromagnetism in ZnO:Gd system.

For ZnO:Nd system, the holes can also mediate the ferromagnetism according to our calculated results listed in table I. In the neutral case, the calculated energy difference \( \Delta E \) for the ZnO:Nd system is 94 meV. In the hole-doped cases, the energy differences \( \Delta E \) are 128 and 134 meV for 0.25 and 0.50 hole per Nd, respectively. Thus the FM coupling with low or intermediate hole concentration is more stable than that of the neutral system. However, when the concentration of holes is as high as 0.75 (1.0) hole per Nd, the energy difference \( \Delta E \) is 69 (20) meV, which indicates that overdoping of holes to the ZnO:Nd system will lower \( \Delta E \) and the subsequent stability of the FM phase. For electron doping, according to our calculated \( \Delta E \) in Table I, the stability of FM ordering of ZnO:Nd system is weakened. In general, grown ZnO sample is always n-type conducting. Based on our calculated results, if the electron concentration is relatively low (0.25 electron/Nd for example shown in Table I), the RT ferromagnetism can also be achieved for ZnO:Nd system. Ungureanu et al. [24] also reported that the ferromagnetism is present in ZnO:Nd system similar to that of ZnO:Gd system at the same doping level. For vacancies, both \( V_{\text{Zn}} \) and \( V_{\text{O}} \) in ZnO:Nd system result in the FM phase with \( \Delta E = 52 \) and 67 meV, respectively.

Due to the strong on-site Coulomb repulsion among the localized 4f electrons, the traditional DFT with GGA (PBE) or LDA scheme can not accurately describe the strong correlation. Therefore, several methods are adopted to overcome the drawback mentioned above, such as LDA+U [20], and Heyd-Scuseria-Ernzerhof (HSE) hybrid-functional [27][28]. For GaN:Gd
In summary, we have systematically investigated the magnetic properties of ZnO:RE (RE=Gd, Nd) systems in different charged states. Because of the s-f coupling between the Gd ions f and the host s states, the electrons can mediate the ferromagnetism in the ZnO:Gd system. We present that the RT ferromagnetism can be achieved in ZnO:Gd system if electrons of appropriate concentration are doped in the sample. However, for ZnO:Nd system, the holes can enhance the stability of the FM ordering, and the RT ferromagnetism can also be achieved in the n-type ZnO:Nd. Our calculated results agree well with the recent experimental observation.

V. ACKNOWLEDGMENTS

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