

First-Principles Study of Magnetic Properties of 3d Transition Metals Doped in ZnO Nanowires

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Abstract The defect formation energies of transition metals (Cr, Fe, and Ni) doped in the pseudo-H passivated ZnO nanowires and bulk are systematically investigated using first-principles methods. The general chemical trends of the nanowires are similar to those of the bulk. We also show that the formation energy increases as the diameter of the nanowire decreases, indicating that the doping of magnetic ions in the ZnO nanowire becomes more difficult with decreasing diameter. We also systematically calculate the ferromagnetic properties of transition metals doped in the ZnO nanowire and bulk, and find that Cr ions of the nanowire favor ferromagnetic state, which is consistent with the experimental results. We also find that the ferromagnetic coupling state of Cr is more stable in the nanowire than in the bulk, which may lead to a higher T_c useful for the nano-materials design of spintronics.

Keywords First-principles · Transition-metals · Formation energies · Nanowires · Magnetism

Introduction

The utilization of the charge freedom degree of electrons in semiconductors to describe the transportation properties

and of the spin freedom degree of electrons in magnetic materials to store the information is separated. Until Ohno reports that ferromagnetism can be achieved in (Ga,Mn)As system by introducing magnetic ions Mn into GaAs matrix [1], which invokes great interests in the diluted magnetic semiconductors (DMSs) because of the utilization of both the charge and spin freedom degrees of electrons in these materials [2, 3]. Both theoretical and experimental investigations are performed extensively due to the great potential applications of DMSs in spintronic devices [4–10]. However, one difficulty for the applications is that the Curie temperatures (T_c) of most DMSs materials are below the room temperature. Many attempts have been performed to find high T_c DMSs materials [11–14]. Sato and Katayama-Yoshida [11] have systematically investigated the ferromagnetic properties of transition metals (TMs) doped in ZnO based DMSs using first principles calculations, and suggested that the Cr-doped ZnO is one candidate for high T_c ferromagnetic DMSs. Nano-scaled DMSs have also been reported recently [12–14]. The Cr-doped single-crystalline nanowires with the stable room-temperature ferromagnetism have been successfully fabricated [14]. However, the origin of the ferromagnetism is still under debate. The Zener model has been proposed to explain the interaction between the TM ions [15]. In addition, wei et al. also proposed a band coupling model based on p - d and d - d repulsions between TM ions and host elements to explain the origin of the ferromagnetism using first-principles band structure calculations [16, 17].

Recently, experimental investigations show that the doping is more difficult in the nanosized structures than in the bulk semiconductors, leading to the low solubility of the dopant [18–22]. So far, the origin of this doping difficulty in the nanosized structures is still not clear. Since the concentration of the charge carriers in the nanosized

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ZnO-based DMSs is important for their applications, it is of great interest to investigate the chemical trends of defect formation and magnetic couplings of TMs doped in the ZnO nanowire theoretically.

In this letter, we systematically calculate the defect formation energies and magnetic coupling properties of transition metals (Cr, Fe, and Ni) doped in the ZnO nanowire and bulk. We find that the two nearest Cr atoms favor ferromagnetic state, which is more stable in the nanowire than in the bulk case. We also find that Cr and Fe can be doped in the ZnO nanowire more easily than Ni due to their lower formation energies, and favor ferromagnetic states.

The paper is organized as follows. In Sect. “[Calculational Methods and Details](#)”, we describe our calculational methods and details. In Sect. “[Results and Discussion](#)”, we discuss the defect formation energies of transition metals in ZnO nanowires and bulk, and the magnetic coupling properties of the TMs in the two systems. A brief summary of the letter is given in Sect. “[Summary](#)”.

Calculational Methods and Details

Our total energy calculations are performed using the density functional theory (DFT) in the generalized gradient approximation (GGA) of PW91 functional [23] for the exchange correlation potential and the projector augmented wave (PAW) method [24] as implemented in the Vienna ab initio simulation package [25]. The electron wave function is expanded in plane waves up to a cutoff energy of 300 eV, and all the geometries are fully relaxed until the quantum mechanical forces acting on the atoms become less than 0.01 eV/Å. We used only the Γ point for the k points-sampling in the nanowire calculations. The ZnO nanowire of 1.0 nm diameter is generated from the $7 \times 7 \times 2$ supercell of bulk wurtzite (WZ) ZnO along the [0001] direction. The outside of the nanowire within the $7 \times 7 \times 2$ supercell is vacuum space to avoid the interaction between the nanowires in the neighboring supercells. The supercell selected here has a periodical length of $2c$, where c is the bulk lattice parameter along the [0001] direction. We use the pseudo-H to passivate the dangling bonds of Zn and O atoms on the surface of the nanowire [26]. Our nanowire supercell for ferromagnetic calculations contains 48 Zn, 48 O, 24 $H_{1.5}$ and 24 $H_{0.5}$ atoms, as shown in Fig. 1a.

The defect system is modeled by putting one or two defects into supercell mentioned above. To determine the defect formation energy, we calculate the total energy $E(\alpha,0)$ for the supercell containing the relaxed defect α in neutral state, and the total energy $E(\text{ZnO})$ for the host ZnO nanowire in the absence of the defect as well as the total

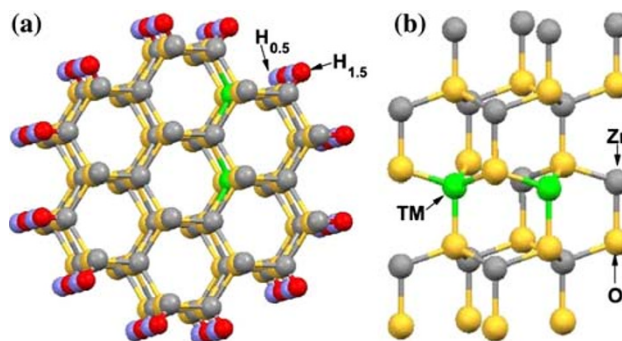


Fig. 1 **a** The ZnO nanowire unit-cell and **b** bulk unit-cell are studied here. The *grey spheres* are Zn, *yellow* are O, *red* are $H_{1.5}$, and *blue* are $H_{0.5}$. The *green spheres* are the Zn sites substituted with Cr atoms or other TM atoms. The geometry is before relaxation

energies of the elemental solids. The defect formation energy $\Delta H_f(\alpha,0)$ is defined as [27]

$$\Delta H_f(\alpha,0) = \Delta E(\alpha,0) + n_{\text{Zn}}\mu_{\text{Zn}} + n_{\text{O}}\mu_{\text{O}} + n_{\text{A}}\mu_{\text{A}}, \quad (1)$$

where

$$\Delta E(\alpha,0) = E(\alpha,0) - E(\text{ZnO}) + n_{\text{Zn}}\mu_{\text{Zn}}^0 + n_{\alpha}\mu_{\alpha}^0. \quad (2)$$

μ_i is the chemical potential of constituent i relative to element solid with chemical potential μ_i^0 [28, 29]. The n_i 's are the number of Zn and extrinsic defects α . For comparison, we also investigate bulk case doped with the same impurities with $2 \times 2 \times 2$ supercell of WZ containing 16 Zn atoms and 16 O atoms, as shown in Fig. 1b, and the Brillouin zone integration is performed with $4 \times 4 \times 4$ k -meshpoints for the bulk magnetic calculations.

In our previous work, we have systematically studied the ferromagnetic properties of Mn ions doped in the ZnO nanowire in different configurations, and found that the ferromagnetic coupling between the Mn ions exists in the ZnO nanowire with unpassivated surfaces while not in the nanowire with passivated surfaces [30]. In order to exclude the surface states locating in the band gap, which may have effects on the ferromagnetism and are not present in the passivated case, we passivate the nanowire using pseudo-H atoms. Our calculated band gaps are 2.24 and 0.8 eV for the passivated nanowire with the diameter of 1.0 nm and bulk case, respectively.

Results and Discussion

Formation Energies of the Defects in ZnO Nanowires and Bulk

The defect formation energy $\Delta H_f(\alpha,0)$ of defect α in neutral state determines the dopant solubility in a host at given growth conditions. Generally, high formation energy leads to low solubility. The defect formation energy $\Delta H_f(\alpha,0)$ of

TMs doped in the ZnO nanowires and bulk is calculated using Eq. 1 in the defect rich condition, i.e., $\mu_i = 0$. The calculated relative formation energy $\Delta H_f(\alpha, 0)$ of the neutral transition metal impurities doped in nanowires and bulk are shown in Fig. 2, indicating that the chemical trends of defect energy are similar in the two cases. For the nanowire, the formation energies for Cr and Fe are lower, leading to the higher doping concentration. For the case of Cr, the formation energy difference between nanowire and bulk is 0.131 eV. The diameter of the nanowire we studied here is 1.0 nm. In order to investigate, the nanosize effect on the formation energy, we also calculate the formation energies of TMs doped in the smallest nanowire with diameter of 0.65 nm (see Fig. 2). The formation energies increase as the size of the nanowire decreases. Therefore, the doping in the nanowires with the smaller diameter becomes more difficult, which is similar to the case of nanocrystals (in our calculation, we ignored the spin-orbit (S-O) coupling interaction, thus only the states with the same spin can couple with each other. To the first order, including the S-O coupling will not change the quantity much. Further reference can be found in [31]). The variations of formation energies could be explained by the shift of the single electron energy levels of $3d$ relative to the conduction band minimum (CBM) and valence band maximum (VBM) due to the quantum confinement effect.

Magnetic Couplings between the Transition Metals in ZnO Nanowire and Bulk

In order to find whether ferromagnetic (FM) coupling between TM atoms exists in the nanowire with the diameter of 1 nm, we substitute two Zn atoms with two TM atoms with the nearest distance (the two TM atoms are the

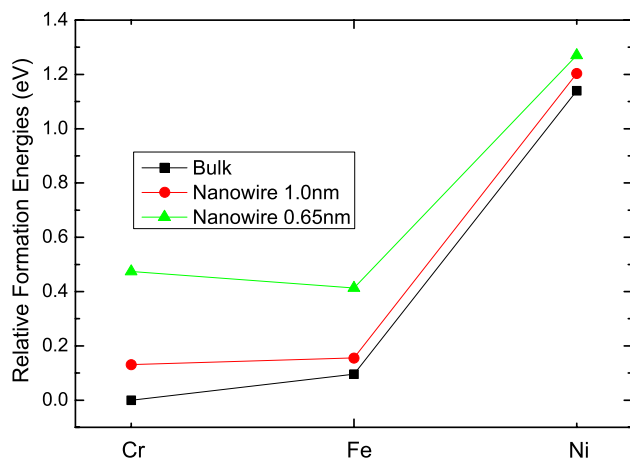


Fig. 2 The calculated relative defect formation energies $\Delta H_f(\alpha, 0)$ of the neutral transition metal impurities in ZnO nanowires of different diameters and bulk case. (All the formation energies take reference to the formation energy of Cr doped in the bulk ZnO)

in-plane nearest neighbors and the plane is perpendicular to the c axis). Therefore, the transition metal concentration is 4.2%. For comparison, we also study the bulk case with the TMs concentration of 12.5%. Figure 1 shows the supercells and the TMs substitutional sites. For each configuration, both ferromagnetic and anti-ferromagnetic (AFM) states are calculated. According to the energy difference ΔE between the total energy of AFM and FM states, we can find which state is more favored. The positive (negative) ΔE means that the FM (AFM) state is more stable. The calculated results are listed in Table 1. In the nanowire, Cr and Fe favor ferromagnetic states energetically, and Co and Ni prefer anti-ferromagnetic states, whereas the opposite is only true for the cases of Fe and Ni in the bulk.

Based on the band coupling model, Walsh et al. investigated the ferromagnetism of Co-doped ZnO using DFT+ $U_{d/s}$ to correct the band gap error by applying a Coulomb U on both the s and d orbitals to further raise the CBM level [9]. The correct picture of TMs $3d$ levels in the nanowire at the Γ point can be obtained due to the enlarged band gap resulting from the quantum confinement effect, even if the gap is not accurate enough. Note that our calculated band gap of the pure passivated nanowire is 2.24 eV. Based on the crystal field theory, the TMs $3d$ states split into one triply degenerate t_2 state and one doubly degenerate e state in zinc-blende (ZB) structures. The t_2 states further split into one doubly degenerate e state and one singly a_1 state due to the lower point group C_{3v} in the WZ. The O $2p$ levels also split into e and a_1 states. Figure 3 shows the schematic plot of the Cr $3d$ levels in majority spin at Γ point in the bulk and nanowire band structures.

Based on the band coupling model, the d - d -coupling of ZnO or GaN based DMSs dominates the ferromagnetism

Table 1 The total energy difference ΔE ($\Delta E = E_{AFM} - E_{FM}$) between AFM and FM states for each configuration is showed in the second column

| Configuration | ΔE (eV) | Coupling | Mag(TM ₁) | Mag(TM ₂) |
|---------------|-----------------|----------|-----------------------|-----------------------|
| Nanowire | | | | |
| ZnCrO | 0.275 | FM | 2.779 | 2.914 |
| ZnFeO | 0.031 | FM | 3.494 | 3.532 |
| ZnCoO | -0.239 | AFM | 2.238 | -2.241 |
| ZnNiO | -0.041 | AFM | 1.229 | -1.219 |
| Bulk | | | | |
| ZnCrO | 0.243 | FM | 3.112 | 3.105 |
| ZnFeO | -0.163 | AFM | 3.488 | -3.510 |
| ZnCoO | -0.090 | AFM | 2.404 | -2.392 |
| ZnNiO | 0.188 | FM | 1.552 | 1.548 |

The third column gives the preferred magnetic coupling between the TM atoms. The fourth and fifth columns give the magnetic moments (μ_B) of two TM atoms. The minus magnetic moments indicate that the two TMs have opposite spin

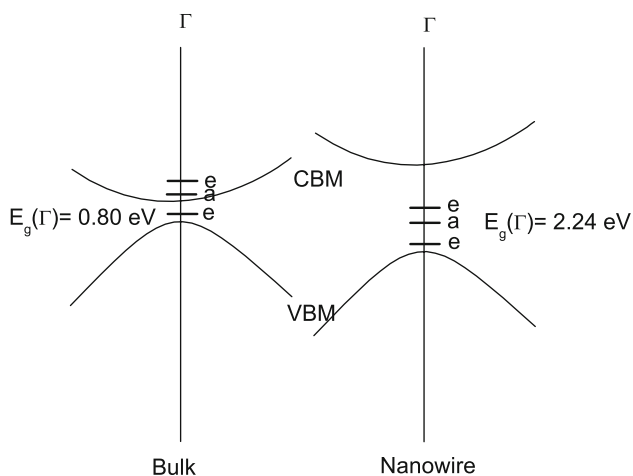


Fig. 3 The schematic plot for the the Cr 3d levels in majority spins at Γ point in the bulk and nanowires band structures

behavior due to the fact that the 3d levels are above the VBM [17]. Figure 4 shows two kinds of magnetic coupling between two Cr atoms in the nanowire. Since the energy levels have included the p – d interaction, the d levels contain the p character, and vice versa. For the FM coupling between the two Cr atoms in Fig. 4a, there is an energy gained because the highest e levels in the majority spin channels are half occupied. In minority spin channels, one e level is pushed up and the other is pushed down by the same amount (denoted as the double exchange Δ_{dd}^1). Therefore, there is no energy gained due to the empty

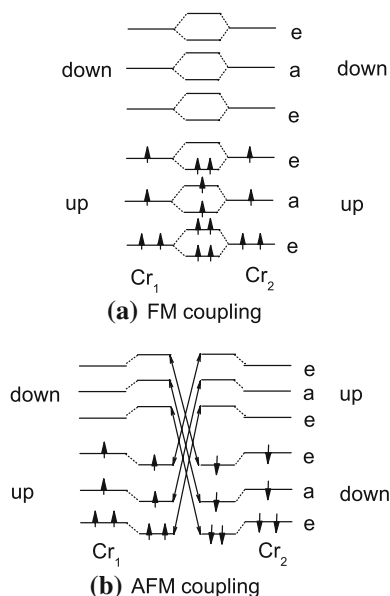


Fig. 4 The schematic view of the ferromagnetic coupling and anti-ferromagnetic coupling between the two Cr atoms doped in ZnO nanowires. The 3d levels are showed and the energy levels include the p – d interaction. The line with the double-headed arrow indicates that the two states with the same spin channel couple with each other

occupation. For the AFM coupling in Fig. 4b, the e level of one Cr ion with majority spin couples with that of the other Cr ion with the same spin (denoted as the super-exchange $\Delta_{dd}^{1,2}$) [31], and there is also energy gained due to the half occupation of the e levels. Since the energy gained from the double exchange interaction is larger than that from the super-exchange interaction due to the existence of large exchange splitting ϵ_{ddb} , the FM states are favored in the Cr-doped ZnO nanowire, which is also true for the Fe doped in ZnO nanowire. However, for the case of Co, the highest occupied e is fully occupied and there is energy gained from the super-exchange interaction, as a result, the AFM state is favored. Note that our calculated results of TMs doped in the nanowire are consistent with the theoretical analysis. To further understand the origin of ferromagnetism of TMs in the ZnO nanowire, we also plot the density of states (DOS) of 3d levels of the FM and AFM states in Fig. 5 for the two Cr and two Co ions, respectively.

Furthermore, we also show that the FM state of Cr is more stable in the nanowire than that in the bulk, which can be interpreted by the fact that compared with the case of Cr doped in the bulk, in the nanowire, the p – d repulsion in the

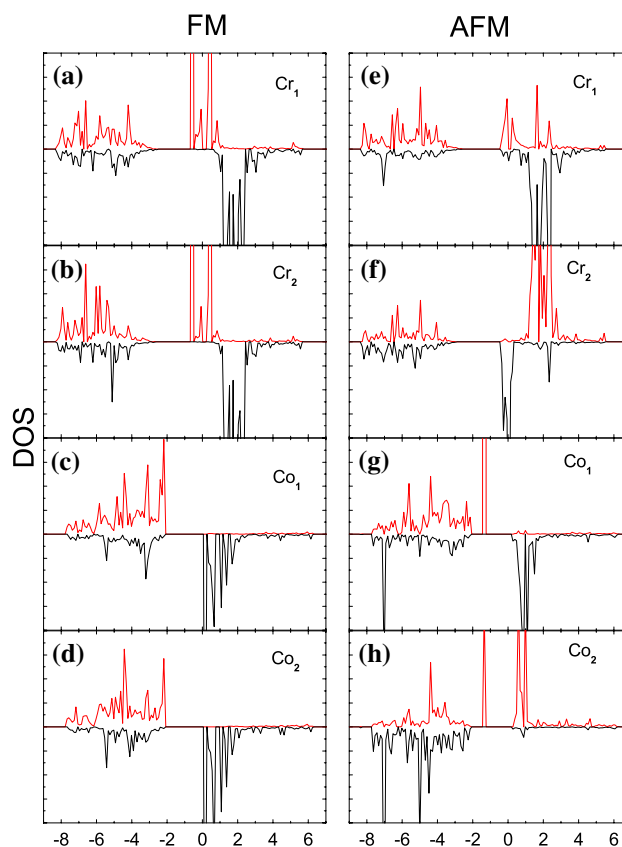


Fig. 5 The DOS of 3d levels for a, b two Cr ions in their FM coupling state, c, d two Co ions in their FM coupling state, e, f two Cr ions in their AFM coupling state, g, h two Co ions in their AFM coupling state

nanowire becomes weaker and the exchange splitting ε_{dd} increases due to low concentration of Cr and the VBM moving down. Since the superexchange $\Delta_{dd}^{1,2}$ term decreases, which favors to the anti-ferromagnetic state, and the FM stabilization energy Δ_{dd}^1 does not significantly change, the ferromagnetic state is more stable in the nanowire. The total energy difference ΔE ($\Delta E = E_{AFM} - E_{FM}$) of 0.275 eV for the Cr-doped nanowire is bigger than that of 0.243 eV for the Cr-doped bulk, suggesting that the former has a higher T_c . Since the high T_c is crucial to the spintronic devices, our calculated results could be useful in nano-materials design for spintronics.

Summary

In summary, we have investigated the formation energies of TMs (Cr, Fe, and Ni) doped in the ZnO nanowires and bulk using first-principles total energy methods. The chemical trends are similar in the two systems. We also find that the formation energies increase as the diameter of the nanowire decreases, indicating that the doping becomes more difficult with decreasing diameter. Finally, it is found that the ferromagnetic state of Cr doped is more stable in nanowires than in the bulk, leading to a higher T_c indispensable to the spintronic devices.

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