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Investigating the ferromagnetic exchange interaction in Co-doped ZnO magnetic semiconductors

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We propose a defect-complex model to clarify the origin of ferromagnetism in Co-doped ZnO magnetic semiconductors, based on first-principles calculations. The spin-polarized defect states of oxygen vacancy (V_O) induced by the charge-transfer process are essential to the ferromagnetism. Depending on the charge state of V_O and carrier concentration, (${V_O}^{2+}$ + zinc interstitial) and (${V_O}^{0}$ + zinc vacancy) defect complexes are predicted to control the ferromagnetic exchange interaction between the Co ions for insulating and conductive samples, respectively.

Keywords: Ferromagnetic semiconductor; First-principles calculation; Exchange coupling; Defects in semiconductors

The exploration of magnetic semiconductors, which combine both charge and spin degree of freedom of electrons, is of fundamental interest for spintronics. Due to the high Curie temperature, Co-doped ZnO (CoZnO) has been widely studied as an archetypal material. Experimental studies [1,2] indicate that the defect-free single-crystal CoZnO shows antiferromagnetic (AFM) exchange interaction between the Co dopant atoms, which has been verified by theoretical results [3] and by our density field theory (DFT) calculations (C-1 in Table 1). Therefore, the existence of defects in CoZnO is considered to be a crucial factor for the ferromagnetic (FM) exchange interaction [4]. However, the magnetic behavior of CoZnO is extremely sensitive to the synthesis conditions, and consequently the results from different groups remain controversial. It means that the nature of the defects which dominates the FM exchange interaction is much more complicated.

The direct experimental approach to verify the role of defects in the FM exchange interaction has been to artificially introduce defects into samples to alter the magnetization [5–8]. Oxygen vacancies (V_O) and zinc interstitials (Zn_i) have attracted much attention since they can be conveniently introduced by a post-annealing process. Annealing the samples in an oxygen-deficient atmosphere is considered to increase the amount of V_O and consequently enhance the magnetization [5,6]. Zn_i introduced by zinc-reduction annealing can also manipulate the magnetization of CoZnO [7,8]. These experimental results reveal that the FM exchange interaction between the dopants is strongly associated with V_O or Zn_i.

However, first-principles calculations predicted that the FM exchange interaction in CoZnO can hardly be mediated V_O. In terms of the three possible charge states of V_O, the FM exchange interaction only benefits from ${V_O}^{1+}$ (C-3 in Table 1) [9]. (In the following the charged defect is denoted as D^{n+}.) However, its formation energy (E^f) is much higher than that of neutral V_O or ${V_O}^{2+}$, which cannot mediate the FM interaction (C-2 and C-4 in Table 1) [9,10]. In addition, Zn_i cannot mediate the FM exchange interaction either [3,9]. Therefore, the experimentally observed ferromagnetism cannot be attributed to only V_O or Zn_i. In order to clarify the real origin of the ferromagnetism in CoZnO, it is necessary to go beyond the single defect model, and to search for defect complexes which can mediate the FM exchange interaction.

In this paper, by performing first-principles calculations we revealed that the FM exchange interaction in CoZnO can be mediated by the spin-polarized donor defect states. We study the effect of various defects in

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Table 1. The energy difference between the AFM and FM spin orderings (δE_{AFM-FM}) of CoZnO. Positive value means Co ions prefer the FM spin order. C-2 to C-9 denote the types of defects or defect complexes in CoZnO and C-1 has no defect. See text for details. A 4 × 4 × 3 supercell with four Co ions is used for C-7, and δE_{AFM-FM} is halved so that it can be compared with the others.

	Defect type	δE_{AFM-FM} (meV)
C-1	No defect	−3.71
C-2	$V_O{}^0$	−13.07
C-3	$V_O{}^{1+}$	408.55
C-4	$V_O{}^{2+}$	−29.56
C-5	Zn_i	−4.86
C-6	$(V_O + Zn_i)^{2+}$	4.41
C-7	$(2V_O + Zn_i)^{4+}$	245.85
C-8	$(V_O{}^0 + V_{Zn}{}^0)$	298.12
C-9	V_{Zn}	−2.72

CoZnO. Depending on the charge state of V_O and the carrier concentration, the donor defect states can be induced by the $(V_O{}^{2+} + Zn_i{}^0)$ and $(V_O{}^0 + V_{Zn}{}^0)$ defect complexes. The existence of $(V_O{}^{2+} + Zn_i{}^0)$ provides a good explanation for the origin of ferromagnetism of insulating CoZnO, and $(V_O{}^0 + V_{Zn}{}^0)$ for conducting CoZnO.

In a 3 × 3 × 2 ZnO supercell (72 ions), two nearest-neighbor Zn cations are substituted by Co, and V_O is formed by removing the immediate anion between the dopants. A plane-wave basis set with a cutoff of 40 Ryd and 2 × 2 × 2 special k points are used for the first-principles calculations [11] with PBE-type exchange–correlation functional [12]. The coordinates of ions are relaxed with the theoretical lattice constants fixed until the ionic force is less than 10^{-3} Ryd/Bohr. The charged defects and defect complexes have been realized by using a compensating jellium background.

The exchange interaction of ZnO-based magnetic semiconductors involves: (i) the valence or (ii) conduction band, (iii) the local defect state of the parent material and (iv) the 3*d* states of the dopants. The states hybridization of these components are controlled precisely by the band gap. However, it is well known that most DFT calculations underestimate the band gap of semiconductors. Since the DFT + U method cannot fully correct the band gap error of ZnO, following a similar scenario [13], we employed a GGA + $U_{O:p+Zn:d+Co:d}$ method in which Coulomb repulsion corrections are applied to O:2*p*, Zn:3*d* and Co:3*d* orbitals (U = 7.5, 7.5 and 1.35 eV, respectively). U_{Co} implemented in the calculation is determined by means of constrained-density-functional calculations [14]. In the current studied, U_{Co} is much larger than the previously predicted value [15] since we choose the new normalizing method of the pseudo-potential atomic wave functions in the Quantum-Espresso code. (The computational techniques have been interpreted by Lathiotakis et al. [16].) We find that both the magnitude of U_{Zn} or U_O is proportional to the predicted energy gap, and the final values implemented in our calculation are determined by the experimental energy gap of ZnO. Both the calculated band structure shown in Figure 1a and the predicted lattice parameters (a = 3.24 Å and c = 5.22 Å) are in good agreement with the experiments.

First we discuss the influence of Fermi level (E_F) on the formation energy of V_O in different charge states.

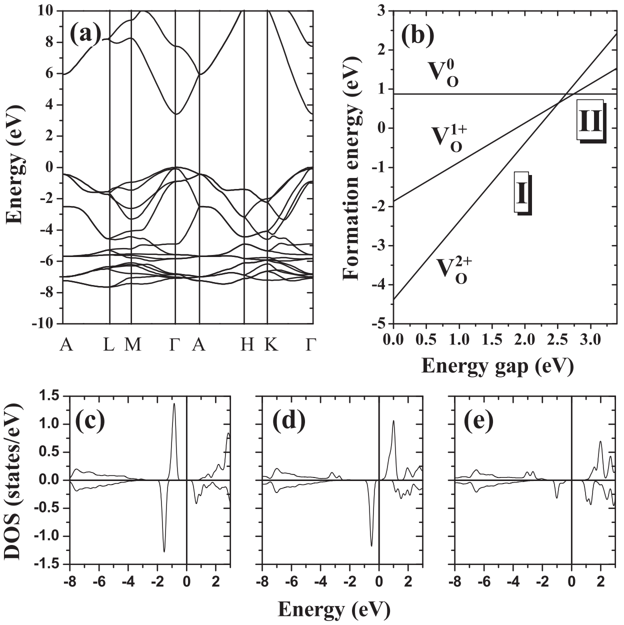

Figure 1. (a) Band structure of ZnO. (b) E^f of V_O as a function of E_F. Zinc-rich condition is imposed. Two types of charged V_O are identified. (I) $V_O{}^{2+}$ when E_F is deep in the band gap, and (II) neutral V_O when E_F is near CBM. (c)–(e) Donor defect state of V_O in the 0, 1+, or 2+ charge state, respectively.

For n-type semiconductors, E_F ranges from the middle of the energy gap to the conduction band minimum (CBM). When E_F is located in the middle of the energy gap, the carrier concentration is low, corresponding to the intrinsic ZnO or the insulating CoZnO semiconductors. One the other hand, when E_F is close to the CBM, the sample possesses a high carrier concentration. Our results (Fig. 1b) show that for the insulating CoZnO sample ($E_F \approx 1.7$ eV), V_O prefer the 2+ charge state. On the other hand, V_O strongly prefer the neutral state when the sample has a higher carrier concentration (E_F around CBM). In the following discussion, we focus on two typical cases corresponding to the insulating and conductive CoZnO semiconductors: $V_O{}^{2+}$ in region I and neutral V_O in region II, respectively (see Fig. 1b). One may note that around the energy of 2.5 eV relative to the valence band maximum, V_O at different charge states have the equivalent E^f. We do not discuss this complicated case. In Figure 1b, the intersection of the lines indicates the transition level between the charge states of q/q'. It is surprising and also interesting that the calculated transition level 2+/0 of V_O is in good agreement with the hybrid functional results [17]. It should be noted that the GGA + $U_{O:p+Zn:d+Co:d}$ method as implemented in the current studies significantly reduces the computation cost as compared with the hybrid functional method.

The zinc annealing process has been believed to enhance the magnetization of CoZnO [7,8]. Therefore we checked if Zn_i could enforce the FM exchange interaction without other defect (C-5 in Table 1). We find that Zn_i:4*s* electrons are delocalized to the whole supercell due to their strong reducing nature. Therefore the neutral Zn_i can hardly benefit the FM exchange interaction, which is in agreement with the precious results [3,9].