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# Magnetism and electronic structure in Zn and Ti doped CoO: A first-principles study

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ABSTRACT

Electronic structure and magnetism in CoO systems doped with Zn and Ti have been studied by the first-principles calculations. The ground state is an antiferromagnetic insulator in CoO. The Zn-doped CoO becomes ferromagnetic insulators, but the $Co^{2+}$ magnetic moment is enhanced due to the Zn incorporation. By introducing one Ti atom into CoO, the conductivity is enhanced by comparing with pure CoO. The system of CoO doped with two Ti atoms on 9 and 11 substitution positions shows a half-metallic character due to the strong hybridization between Ti and Co atoms. $Ti_2Co_{14}O_{16}$ systems with Ti atoms at 9, 10 and 9, 16 and 1, 9 positions show the metallic characteristics with a large spin polarization, which can enhance the conductivity of CoO systems.



## 1. Introduction

The ferromagnetism in the transitional element doped oxides has attracted much attention due to the prediction of high-temperature ferromagnetism [1]. The successful fabrication of high Curie temperature diluted magnetic semiconductors doped with different elements has been reported, and the ferromagnetism is often related to the vacancies, magnetic contamination, and magnetic secondary phase, etc. [2–8]. The observed high-temperature ferromagnetism is sensitive to the fabrication conditions of the samples [2–8]. Meanwhile, the electrical transport and magnetoresistance (MR) in the doped oxides have also been extensively studied because of their significant importance in the fundamental physics and practical applications in the fields of spintronics and nanoelectronics devices [9–23]. Furthermore, the transition metal–oxide nanocrystals often exhibit unconventional physical properties that cannot appear in bulk [20–23]. Among them, CoO is one of the examples. CoO has a wurtzite (WZ) structure, just like ZnO, instead of rock-salt-type structure [21,22]. Recently, the large negative magnetoresistance (MR) has been observed in the $Ti_{1-x}Fe_xO_\delta$ [16], $Zn_{1-x}Co_xO$ [24,25] and $Ti_{1-x}Co_xO_2$ [17,26] inhomogeneous magnetic semiconductor films, where the physical mechanisms of MR have been ascribed to the spin-dependent hopping that comes from the spin–spin interaction between the conducting electron and local magnetic moments [26,27] or disordered moments at low temperatures [16,17,28]. Up to now, different elements have been doped into the oxide semiconductors to study the magnetic, spin-dependent transport properties and MR, where some interesting results have been observed [16,17,24–28]. However, the physical mechanisms of the transport properties in the Co-doped oxide semiconductors with a large Co atomic fraction are not clarified yet, where the system can also be treated as the nonmagnetic element doped CoO. In order to further clarify the mechanism of spin-dependent electrical transport properties in these oxides systems, the electronic structure and magnetism of the nonmagnetic element doped CoO should be investigated systematically. In this paper, the band structure and density of states (DOS) of WZ CoO systems doped with Zn and Ti atoms are calculated by using first-principles calculations. For the CoO doped with two Zn or Ti atoms, the distances of Zn–Zn and Ti–Ti have been adjusted to affect the electronic structure and magnetism.

## 2. Calculation methods

All the spin-polarized calculations are performed with the projector augmented wave method [29,30] as implemented in the computational code of Vienna ab initio simulation package [31] based on the density-functional theory. Exchange–correlation potential is treated by local density approximation (LDA + *U*). The

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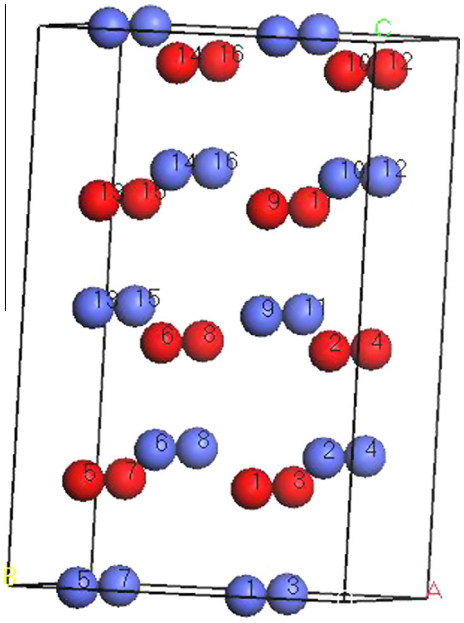

**Fig. 1.** A $2 \times 2 \times 2$ supercell of WZ CoO. The red spheres stand for O atoms, the blue spheres stand for Co atoms and the numbers marked on the atoms stand for the different positions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

effective Coulomb interaction parameter $U_{eff} = U–J$ is taken as 6.0 eV for Co $d$ orbitals, $U = 3.2$ eV and $J = 0.9$ eV ($U_{eff} = 2.3$ eV) [32] are selected and assigned for Ti $d$ orbitals. The valence-electron configurations of each element are Ti $3d^2 4s^2$, Zn $3d^{10} 4s^2$, Co $3d^7 4s^2$, O $2s^2 2p^4$, respectively. To find the theoretical equilibrium static geometries, a $\Gamma$-centered $6 \times 6 \times 6$ $k$ mesh together with an energy cutoff of 500 eV is set. The convergence criteria for total energy and force are $10^{-5}$ eV and 0.01 eV/Å. During the calculations for band structure, a series of high symmetry points are used in Brillouin zone. Fig. 1 shows the lattice structure of WZ CoO. Herewith, we choose the lattice constants of CoO as $a = b = 3.249$ Å and $c = 5.206$ Å [23] as a starting point. The geometric optimized lattice constants are $a = b = 3.200$ Å and $c = 5.117$ Å, which are well consistent with the previously reported values [21].

## 3. Results and discussion

Fig. 2(a) shows the calculated band structure of pure CoO. It is clearly seen from Fig. 2(a) that the calculated band gap $E_g$ is 1.55 eV. Meanwhile, the majority and minority spin channels have the same band structure, where each $Co^{2+}$ ion has a moment of 2.72 $\mu_B$, revealing that pure CoO is antiferromagnetic (AFM). The AFM is also consistent with the experimental results of antiferromagnetic CoO with a Néel temperature of 291 K. In a high-spin $t_{2g}^5 e_g^2$ configuration, a $Co^{2+}$ ion has three unpaired electrons, which should contribute the spin moment of 2.72 $\mu_B$. The experimentally measured spin moments of $Co^{2+}$ ion are in the range of 3.38–3.80 $\mu_B$, but the about 1.0 $\mu_B$ orbital moment is included [33–37]. In this work, the spin–orbital interactions are not considered, so the experimental spin moment of $Co^{2+}$ ion should be in the range of 2.38–2.80 $\mu_B$. Therefore, both the calculation methods and calculated results are reliable. Fig. 2(b) shows the total density of states (TDOS) and partial density of states (PDOS). In Fig. 2(b), it is also clear that the ground state of pure CoO is an AFM insulator. Meanwhile, the valence band (VB) maximum of pure CoO comes from O $2p$ and Co $3d$ states; while the conduction band (CB) minimum is from Co $3d$ states. The O $2p$ states overlap with Co $3d$ near Fermi level, suggesting the strong exchange interaction. The strong exchange interaction between Co and O is the superexchange coupling, which can contribute to the AFM ordering of CoO [38,39].

Fig. 3 shows the band structure, TDOS and PDOS of $Zn_1Co_{15}O_{16}$ with one Zn atom at 9 position. In Fig. 3(a), a band gap of 1.46 eV is clearly seen in the band structure of the majority and minority spins, which also shows an insulating characteristic. The same character can also be seen from the DOS in Fig. 3(b). In view of PDOS, we give the results of the neighbor O and Co atoms, which are O at 9 position and Co at 10 position. It shows that the CB minimum is mainly from Co $3d$ states; while the VB maximum comes

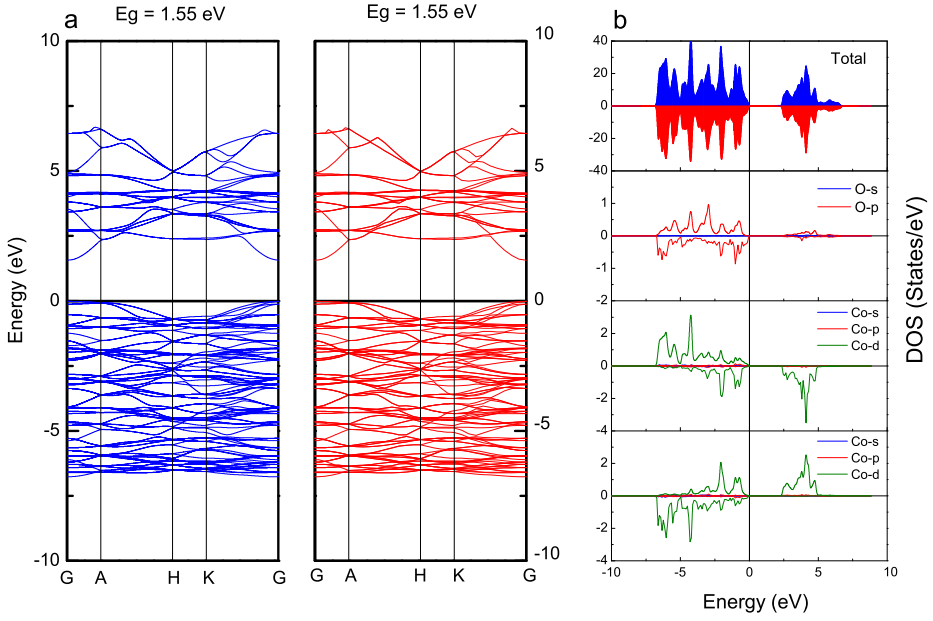


**Fig. 2.** The calculated band structure, total density of states (TDOS) and partial density of states (PDOS) of pure CoO. The blue lines refer to majority spin states, while the red ones refer to the minority spin states. The Fermi level is set to 0 eV on the energy axis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)