Magnetic properties of Co-doped SnO: first-principles calculations*

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(Received 7 June 2010; revised manuscript received 11 January 2011)

Based on density functional theory calculations, the electronic and magnetic properties of Co-doped SnO are investigated. It is found that the spin-polarized state, with a magnetic moment of about 1.0 μ_B per Co-dopant, is more favorable in energy than the non-spin-polarized state. Moreover, the origin of the ferromagnetism in Co-doped SnO is found to be the double exchange mechanism. Our results indicate that Co-doped SnO is a possible candidate of the p-type spintronics material.

Keywords: dilute magnetic semiconductors, p-type SnO, first-principles calculations

PACS: 71.20.Nr, 71.20.–b, 74.25.Ha **DOI:** 10.1088/1674-1056/20/5/057101

1. Introduction

In the past three decades, dilute magnetic semiconductors (DMS) have attracted a lot of attention due to the additional spin degree of freedom and the properties needed in the new functionality of detectors, memories and light-emitting sources.[1−3] More recently, Zhang *et al.*[4] considered the TM–Si alloys (TM = V, Cr, Mn, Fe, Co and Ni) in the zinc-blende structure. It is well known that both n-type and p-type DMS are essential in spin based devices. However, most of DMS, which exist in nature or have been synthesized in the laboratory, are n-type semiconductors, such as GaN, TiO_2 and ZnO doped with Mn, Cr, Ni, Cu or Fe.[4−11] There are a few reports on p-type DMS. Majumdar and Banerji[12] reported N-doped ZnO films showing p-type conductivity at room temperature. Yi *et al.*[13] observed room temperature ferromagnetism with p-type conductivity in pulsed laser deposited ZnO:Li films with certain doping concentrations and oxygen partial pressures. However, it is quite difficult to obtain good, reliable and reproducible p-type DMS due to the presence of unintentionally introduced donor oxygen vacancies (Vo) or zinc interstitials (Zn_i). Recently, Fu *et al.*[14] fabricated p-type SnO thin films on (100) Si, c-plane Al_2O_3 and r-plane Al_2O_3 substrates. Ogo *et al.*[15] reported p-channel thin-field transistors based on epitaxial SnO films grown on yttria-stabilized zirconia substrates. Christensen *et al.*[16] examined pressure-induced changes in electronic and structural properties of tin monoxide by means of *ab initio* density-functional calculations. However, there has been no theoretical or experimental study performed on the magnetic properties of the transitional metal doped SnO. In this paper, electronic and magnetic properties of the Co-doped SnO are studied by the first-principles calculations and a possible p-type ferromagnetic semiconductor material has been found. We hope that our work would inspire further experimental researches and that the same mechanism can be explored for other transitional metal (TM) doped SnO.

2. Computational methods

In the present work, the structural optimizations, the magnetic property calculations and the electronic property calculations are all performed using the density functional theory (DFT) approach based on the pseudo-potential technology in the code CASTEP programme.[17] The local density approximation (LDA), however, fails in general in predict-

*Project supported by the National Natural Science Foundation of China (Grant Nos. 61078057 and 50702046), the Northwestern Polytechnical University "Aoxiang Star" Project, and the Northwestern Polytechnical University Foundation for Fundamental Research of China (Grant No. NPU-FFR-JC200821/JC201048).

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ing the insulating behavior of many transition metal oxides.[18] The incorporation of an effective on-site Coulomb interaction, characterized by the Hubbard U between 3d states of Sn atom, into the LDA scheme considerably improves the theoretical prediction for energy band structures.[19] We thus adopt the local density approximation Hubbard U (LDA+U) approach in this work. The ionic cores were represented by ultrasoft pseudopotentials for Sn, O and Co atoms. The stannum $5s^2$, $5p^2$ electrons, the oxygen $2s^2$, $2p^4$ electrons and the Cobalt $3d^7$, $4s^2$ electrons were treated as parts of the valence states. The plane-wave cutoff energy was 340 eV and the Brillouin zone integration was performed over the $3\times3\times3$ grid size using the Monkorst-Pack method for the Co-doped SnO structure optimization. The structural parameters of the Co-doped SnO were determined using the Broyden–Fletcher–Goldfarb–Shenno (BFGS) minimization technique. The maximum root-mean-square convergent tolerance was less than 1×10^{-6} eV per atom, which means the force imposed on each atom was not greater than 0.03 eV. All calculations were performed in the reciprocal space.

3. Results and discussion

The SnO has a tetragonal structure with $a = b =$ 0.380295 nm, $c = 0.483828$ nm and $c/a = 1.27$[20] in its most common variety (black SnO). The unit cell contains two formula units with the oxygen atoms placed at (0; 0; 0) and (1/2; 1/2; 0) and the tin atoms placed at (0; 1/2; v) and (1/2; 0; $-v$), with $v = 0.2369$. The structure of SnO is of layers and each Sn atom is at the apex of a square pyramid, whose base is formed by four oxygen atoms. Each oxygen ion is surrounded by four Sn ions. All the nearest neighbor Sn-oxygen distances are equal to 2.22 Å. In this work, a supercell consisting of $2 \times 2 \times 2$ SnO unit-cells is modeled, in which one Sn atom is replaced by a Co atom. This corresponds to a doping concentration of 6.25 at%. In Fig. 1 we show a portion of the crystal structure of the tetragonal SnO and the $2 \times 2 \times 2$ super-cell.

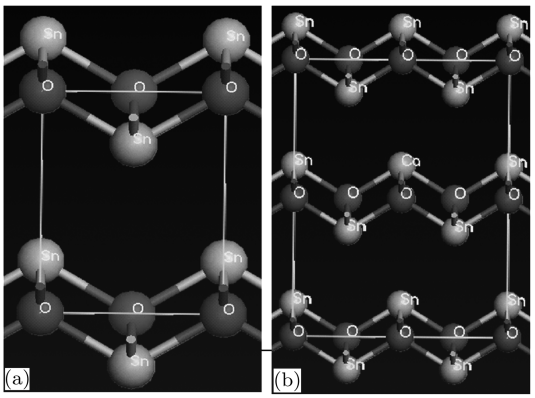


Fig. 1. The crystal structures of (a) the tetragonal SnO and (b) the $2 \times 2 \times 2$ super-cell.

First, we calculate the final energy of the supercell with and without spin-polarization. The Hubbard U is set to be 0, 0.5 and 2.5 eV for the spin-polarized cases. The results are listed in Table 1. It is clear that the spin-polarized state with the Hubbard $U = 0$ eV has the lowest final energy. According to the principle of the lowest energy, the spin-polarized state with the Hubbard $U = 0$ eV is the most stable state. We thus chose the Hubbard $U = 0$ eV in this work.

Table 1. Final energies for the $2 \times 2 \times 2$ super-cell with and without spin-polarization.

States	Non-spin polarized	$U = 0$ eV	$U = 0.5$ eV	$U = 2.5$ eV
Final energy /eV	–9498.7031	–9498.7505	–9497.9852	–9497.0769

To evaluate the stability of the Co-doped SnO structure, the formation energy $E_{\rm form}$ of $Sn_{15}CoO_{16}$ is calculated as[21]

$$E_{\rm form} = E(Sn_{15}CoO_{16}) - E(Sn_{16}O_{16}) - E(Co) + E(Sn),$$

where $E(Sn_{15}CoO_{16})$ and $E(Sn_{16}O_{16})$ are the total energies of Co-doped and pure SnO super-cell respectively, $E(Co)$ and $E(Sn)$ are the energies of an isolated Co and an isolated Sn atom, respectively. The formation energy obtained is 2.38 eV. This result indicates that the Sn–O–Co structure is preferred in the Co-incorporated SnO. Thus the $2 \times 2 \times 2$ super-cell is suitable for our study.

The band structure and the total electronic density of states (DOS) for spin-up and spin-down electrons in pure SnO are plotted in Figs. 2(a) and 2(b), respectively. Clearly, it is found that the undoped SnO has an indirect gap of 0.421 eV from G to M, while the minimum direct gap is 2.48 eV at G point, which

is –3.0 eV.[19] It is well known that a shortcoming of D smaller than the experimental value of 2.5FT calculation is the underestimation of band gap values. The spin-up and the spin-down bands are almost symmetrical and the DOS curves for spin-up and spin-down are completely symmetric, which suggest that pure SnO is not a spontaneous magnetic semiconductor.

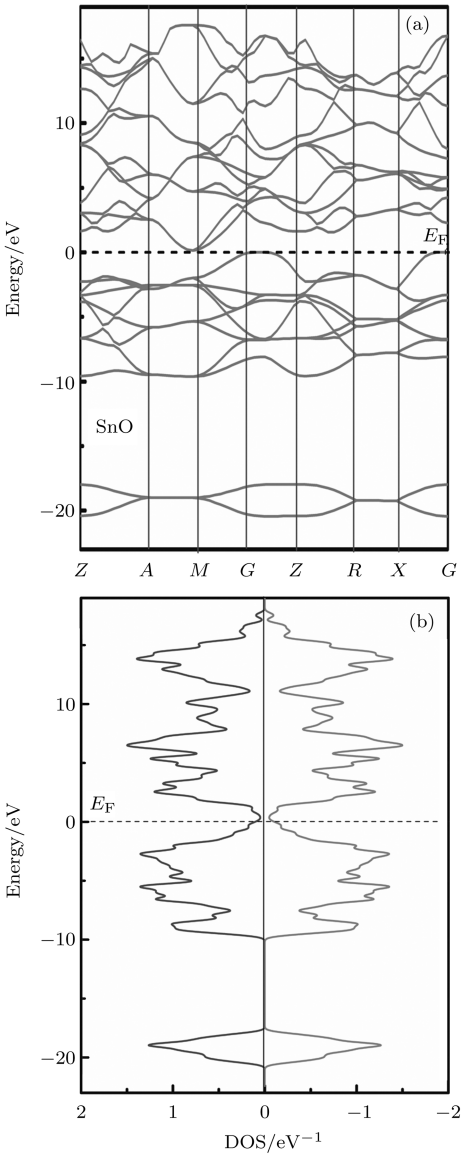


Fig. 2. Calculated band structure and density of states of the pure SnO. (a) Band structure, (b) density of states.

In order to investigate the magnetic properties of the Co-doped SnO, we calculate the band structures of spin-up and spin-down electrons. The results are shown in Fig. 3. It is obvious that a spontaneous magnetization is ideal for the injection of spin into nonmagnetic SnO and the d states of Co atoms appearing near the Fermi level. The system shows half-metallic behaviour with the minority spin being metallic and the majority spin being semiconducting.

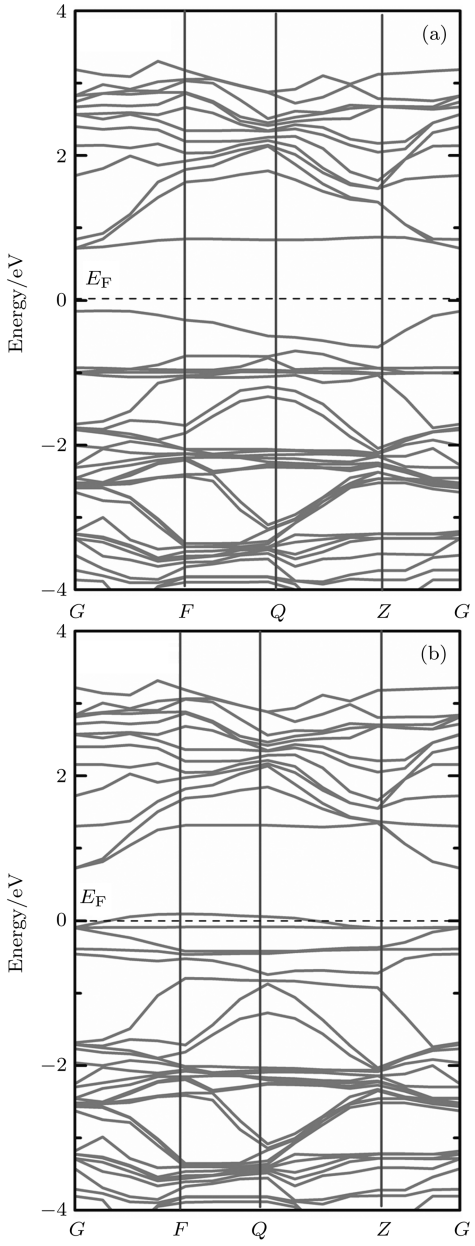


Fig. 3. Calculated band structures in the Co-doped SnO. (a) The bands of spin-up electrons, (b) the bands of spin-down electrons.

To further investigate the spin polarization, we calculate the total DOS and the partial density of states (PDOS) of the Co-doped SnO. The corresponding plots of the projected DOS and PDOS are shown in Figs. 4(a)–4(f), respectively. It is clear that the Fermi energy passes through the gap in the spin-down DOS and the system exhibits half-metallic character. The Co 3d states dominate the DOS at the Fermi level, which means that most of the magnetic moment comes from the Co 3d electrons. The magnetic moment is 1.0 μ_B per super-cell with one Co atom. The role of O in mediating the magnetic coupling between Co atoms can be seen from Figs. 4(b) and 4(d).

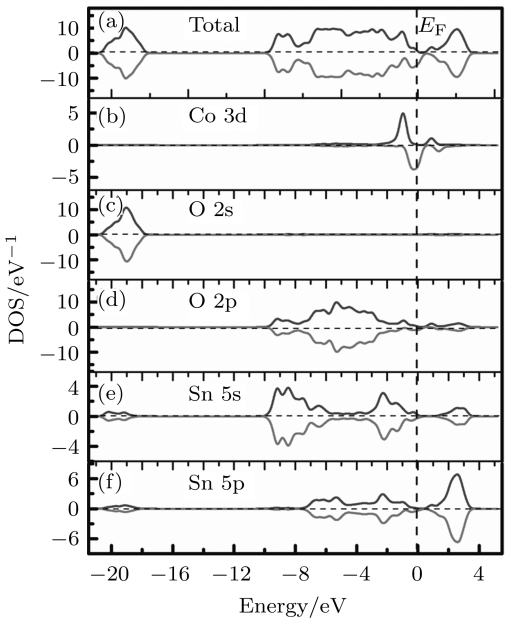


Fig. 4. Calculated density of states. (a) The total DOS of Co-doped SnO, (b) the partial spin DOS of Co 3d, (c) the partial spin DOS of O 2s, (d) the partial spin DOS of O 2p, (e) the partial spin DOS of Sn 5s, (f) the partial spin DOS of Sn 5p.

It is obvious that the spontaneous magnetization is induced by the Co 3d states hybridization with the 2p states of O atoms, which leads to the double exchange interaction.[7,22−26] In addition, these impurity states of Co atom clearly show large exchange splitting, which induce the high spin configuration of 3d electrons in Co atoms. The impurity bands are partially filled and the widths of the d bands are smaller than the exchange splitting. These behaviours indicate that the origin of the ferromagnetism in the Co-doped SnO is the double exchange mechanism. These magnetic properties will be beneficial for exploiting more attractive electron spin devices with new functionality in SnO-based DMS.

4. Conclusion

In conclusion, we investigate the electronic and magnetic properties of the Co-doped SnO using first-principles calculations of plane wave ultra-soft pseudopotential technology based on the density functional theory. The results imply that the Co-doped SnO is a ferromagnetic half-metal material. The ferromagnetic coupling results from the hybridization between the O 2p and Co 3d states. We hope that these calculation results can motivate some experimentalists to work on TM-doped SnO systems.

Acknowledgement

The calculations were performed at the Center for High Performance Computing of Northwestern Polytechnical University.

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