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Ab initio prediction of half-metallic ferromagnetism in $Zn(TM)O_2$ (TM = Cr, Mn, Fe, Co, Ni) compounds

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Abstract

From the results of first principles tight-binding linear muffin-tin orbital (TB-LMTO) calculations, half-metallic ferromagnetism is proposed in $Zn(TM)O_2$ with a chalcopyrite structure. The calculated electronic and magnetic property shows that consistent with the integer value for the total magnetic moment, half metallicity is obtained for $ZnCrO_2$, $ZnMnO_2$, $ZnFeO_2$, $ZnCoO_2$ and $ZnNiO_2$. A careful analysis of the spin density reveals the ferromagnetic coupling between the p–d states and the cation dangling-bond p states, which is believed to be responsible for the stabilization of the ferromagnetic phase. The calculated heat of formation, bulk modulus and cohesive energy are reported.

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1. Introduction

Spintronics, namely spin-based electronics, is a new generation of microelectronics, which utilizes both, charge and spin degrees of freedom of carriers. Half-metals and diluted magnetic semiconductors (DMSs) are expected to be promising materials for spin-based multifunctional devices [1]. In half-metals, the conduction electrons at the Fermi energy E_F are 100% spin polarized. As a wide band gap (3.35 eV), semiconductor with a high exciton binding energy (60 meV), ZnO attracts great attention for its potential use in UV laser diodes and UV-blue light emitters [2]. Very recently, ZnO has also been identified as a promising host material for the realization of DMSs due to the prediction of possible ferromagnetism in p-type $Zn_{1-x}Mn_xO$ [3]. By combining the two interesting properties: namely semi-conductivity and ferromagnetism, DMS provides an opportunity to integrate new functionality into the existing semiconductor devices. First principles calculations [4] based on local density approximation (LDA) also predict ferromagnetism in most 3d transition metal (TM) doped ZnO through a double-exchange mechanism, without requiring additional carrier incorporation. $Zn_{1-x}Co_xO$ and $Zn_{1-x}Mn_xO$ are the most widely investigated among TM-doped ZnO. Room-temperature ferromagnetism [5–8] has been reported for them, while there still exist discrepancies whether the ferromagnetism is intrinsic or not [9–13].

Very few reports have been available on Ni-doped ZnO when compared to other transition-doped ZnO. In an earlier work, ferromagnetism was reported in $Zn_{1-x}Ni_xO$ at 2 K [14] at $x>3\%$. While above 30 K, super paramagnetic behaviour was observed, which may be an indication of the occurrence of NiO [15] or Ni precipitates. Jin et al. [18] reported no indication of ferromagnetism in $Zn_{1-x}Ni_xO$ down to 2 K. Very recently, Ni^{2+}:ZnO nanocrystals were reported to have robust ferromagnetism with Curie temperature above 350 K [16,17]. Considering these discrepancies, a debate is still going on whether

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$Zn_{1-x}Cr_xO$, $Zn_{1-x}Fe_xO$ and $Zn_{1-x}Ni_xO$ could exhibit intrinsic ferromagnetism and so further investigations are needed.

In this work, we report our results of a systematic computational study of $ZnCrO_2$, $ZnMnO_2$, $ZnFeO_2$, $ZnCoO_2$, and $ZnNiO_2$ with the goal of understanding the nature and origin of the magnetic interactions. Our emphasis is on the trends exhibited by the 3d TM atom, and so we first explore the effects of substitution of a number of TM (Cr, Mn, Fe, Co and Ni) in ZnO and find out how the magnetic moment and the properties change along the series.

2. Method of calculation

The calculation of the spin-polarized band structure for $Zn(TM)O_2$ was performed by the tight-binding linear muffin-tin orbital method (TB-LMTO) within the atomic sphere approximation (ASA) [19] using the local-spin-density approximation (LSDA) [20]. In this investigation, the von Barth and Hedin exchange correlation potential is used. For simplicity of calculation, we consider $Zn(TM)O_2$ to be an ideal chalcopyrite structure. The following orbital for Cr, Mn, Fe, Co and Ni ($4s^13d^5$, $4s^23d^6$, $4s^23d^7$, $4s^23d^5$ and $4s^23d^8$), O 2s and 2p and Zn 4s, 4p and 3d are used. The accuracy of the total energies obtained within the density functional theory, using LSDA, in many cases is sufficient to predict which structure at a given pressure has the lowest free energy. Empty sphere were introduced in all cases in order to keep the overlap of atomic spheres within 16%. Band dispersions and density of states (DOSs) are obtained in each case. We have additionally analysed the orbital character of the band eigenstates and present them in terms of the so-called ''fat band'' representation of the band dispersions. However, such analysis does not provide an insight on the range of interactions important for the system. The range of interaction is one of the most important ingredients to determine the suitable tight-binding model, as it indicates whether a nearest neighbour is sufficient or there is a need to include further neighbour interactions. The Wigner–Seitz sphere radii are chosen in such a way that the sphere boundary potential was the minimum and the charge flow is in accordance with the electro negativity criteria. E and $\vec{k}$ convergence are checked.

3. Results and discussion

3.1. Structural properties

Since no experimental X-ray diffraction study is reported for $Zn(TM)O_2$ compounds to our knowledge, as a first step, one would like to calculate the lattice parameter for the above compound in the chalcopyrite structure. This is achieved by using Vegard's law [21], which is

$$a(A_{1-x}B_xC)_{alloy} = (1-x)a_{AC} + xa_{BC},$$

where AC and BC stands for ZnO and MnO. The lattice parameters of ZnO, MnO, NiO, and CoO in wurtzite structure and CrO in the cubic structure are taken from the literature (JCPDS data) and using Vegard's law, the lattice parameters of ternary compounds are calculated in the chalcopyrite structure. From the literature, we find that most of the ABC_2 compounds crystallize in the chalcopyrite structure [22] and hence we have calculated the total energy only in this structure. Moreover, we have also tried in some other structures, namely cubic, wurtzite and zincblende but we were unable to detect half metallicity in these compounds in those structures. Total energy as a function of reduced volume is calculated for the compounds in the chalcopyrite structure in a manner similar to our earlier work [23] and fitted to the equation of state. And, hence, the theoretically calculated equilibrium lattice parameter is obtained. Since it is not possible to optimize the c/a ratio using TB-LMTO, we have not done this exercise and the c/a ratio is taken as 2. In addition, the ground state properties like bulk modulus are calculated for the above-mentioned compounds. The cohesive energies are calculated using the expressions

$$E_{cohesive} = E_{total\ energy\ of\ solid} - E_{free\ atom}. \quad (1)$$

Heat of formation of these compound per atom are calculated by using the expression

$$H = \frac{1}{x+y+z}\left(E_{total} - xE^{A}_{solid} - yE^{B}_{solid} - zE^{C}_{solid}\right), \quad (2)$$

where E_{total} refers to the total energy of crystal or primitive cell used in the present calculation, x, y and z refer to the number of atoms of A, B and C, respectively. E^{A}_{solid}, E^{B}_{solid} and E^{C}_{solid} are taken from the present calculation of total energy of the solids and are calculated in Table 1.

3.2. Electronic properties

Fig. 1a and b shows electronic structure of $ZnMnO_2$ in chalcopyrite structure in both the spins. The DOS are calculated for $Zn(TM)O_2$ and are as shown in Fig. 2a–e. The total and partial DOS of 3d-states of TM atom are shown for the ferromagnetic state. The host valence band consists of two parts. One is the low-lying Zn-3d band, which appears at approximately 0.5 Ry below E_F with a peak whose width is 0.15 Ry. The other is the broad O-2p band whose energy varies from −0.4 to −0.2 Ry. Between the valence band and the conduction band, which consists of Zn-4s states, there are 3d bands of the TM atom. These bands show large exchange splitting, and they are gradually occupied as the atomic number of TM atom increases. Since the exchange splitting is larger than the crystal field splitting, all TMs are in the high-spin states. In particular, the half-metallic DOS are realized in $ZnCrO_2$, $ZnMnO_2$, $ZnFeO_2$, $ZnCoO_2$ and $ZnNiO_2$. This kind of asymmetry in the DOS at E_F can be achieved by TM atom substitution in the II–VI-compounds which exhibits half-metallic ferromagnetism, and it is proposed that these II–VI compounds