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Ab initio calculation of $Zn_{0.8}Mn_{0.2}O_{1-y}N_y$

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ABSTRACT

Based on first-principles spin-density functional calculations, using the Korringa–Kohn–Rostoker method (KKR) combined with the coherent potential approximation (CPA), we investigated the magnetic and half-metallic properties of Mn-doped p-type ZnO and the mechanism which control these properties. Mn-doped ZnO is anti-ferromagnetic spin-glass state, but it becomes half-metallic ferromagnetic upon holes doping. The electronic structure, total magnetic moment of $Zn_{0.8}Mn_{0.2}O_{1-y}N_y$ and magnetic moments of Mn and N in $Zn_{0.8}Mn_{0.2}O_{1-y}N_y$ are calculated for different holes (y) concentrations. In this paper we address the origin of half-metallic and ferromagnetic properties as controlled and oriented by the nature of hybridization of the Mn (3d) state and host p(N) states. The band structure has been used to explain the strong ferromagnetism observed in $Zn_{0.8}Mn_{0.2}O_{0.1}N_{0.9}$.

We applied magnetic fields to Mn and we calculated the spin magnetic moments of Mn and N. We show that the spin alignments of Mn atoms and the interlocking N atoms can be shown as Mn(↑)–N(↓)–Mn(↑), indicating that ferromagnetism is mediated through the RKKY or double exchange interaction between the carriers and Mn atoms. We show that for weak holes concentrations the ferromagnetism is due to the double exchange interaction, and for higher holes concentrations the RKKY exchange interaction, mediated by mobile holes, strongly oscillates with distance. Finally, we propose a damped or undamped RKKY interaction model to describe the exchange coupling constants J_{ij} between the local moments Mn_i and Mn_j.

1. Introduction

Recently, ZnO attracted much attention because of its low cost, abundance and being environmentally friendly. Besides, ZnO has a band gap energy of 3.3 eV at 300 K and a large exaction binding energy of 60 meV. So it is one of the most promising substances for optoelectronics. As was shown by Fukumura et al. [1] solubility of Mn was incorporated into the ZnO matrix is relatively high ($x \leqslant 0.35$) by pulsed laser deposition (PLD). In this particular work up to 35% Mn in ZnO without affecting much the crystallographic quality of the diluted magnetic semiconductors (DMSs), whereas about 5% is tolerable for III–V-based hosts. Moreover, Joseph et al. [2] prepared successfully p-type ZnO thin films by using the co-doping method. Indeed, this result could be confirmed if the hole mediated ferromagnetism is the dominant mechanism, attainment of p-type ZnO could pave the way for a promising potential of Mn-doped ZnO. Therefore, it is worth investigating the carrier-induced ferromagnetism in the ZnO-based DMSs.

The various experimental and theoretical investigations of the magnetic order in $Zn_{1-x}Mn_xO$ give contradictory results. However, some groups have reported ferromagnetism in (Zn, Mn)O systems [3], while others observed anti-ferromagnetic or spin-glass behavior [4]. The very latest experimental study finds no evidence for magnetic order, down to $T = 2$ K [5]. These conflicting results also exist concerning the distribution of Mn in ZnO. In the experimental results of Cheng et al. [6] we are aware of that Mn is distributed homogeneously. Yet Jin et al. [7] report clustering of Mn atoms. ZnO-based DMSs have been described within the framework of the coherent potential approximation (CPA), to take disorder into account [8]. Owing to this treatment, it is possible to simulate the random distribution of the TM (transition metal) impurities in ab initio manner. There are two directions of the magnetic moment along the quantization axis, i.e. up and down directions; consequently, there are two self-consistent solutions for the electronic structure of the ZnO-based DMS. One is the ferromagnetic (FM) state in which all of the magnetic moments are parallel with each other. This is written as $(Zn_{1-x}, TM_x^{up})O$, where x is the TM concentration. The other is the spin-glass state

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in which the magnetic moments are pointed randomly at each other. Therefore, the system has no magnetization. This is written as (Zn_{1-x}, $TM^{up}_{x/2}$, $TM^{down}_{x/2}$)O. Comparing the total energy of the FM state with that of the spin-glass state, DE = TE (spin-glass state)−TE (ferromagnetic state) it is possible to judge which state is more stable. Sato and Katayama-Yoshida [8] had carried out the Korringa–Kohn–Rostoker coherent-potential approximation (KKR-CPA) calculations in randomly substituted 3d TM impurities in ZnO and found FM state to be stable for half-filled or more than half-filled impurities such as V, Cr, Fe, Co and Ni, while a spin-glass like state is found to be stable for ZnO containing 5% of Mn impurities. Mn impurities are introduced randomly into cation sites of the ZnO semiconductor. This disordered substitution in DMS is well described by the KKR-CPA method. With respect to previous theoretical studies, $Zn_{1-x}Mn_xO$ is not FM without additional carriers. In order to stabilize the FM phase, it is necessary to insert carriers into the system. According to the Zener model approach by Dietel et al. [9] ferromagnetism in DMS originates from the RKKY-like interaction between the localized TM moments and delocalized holes carriers. ZnO is n-type doped with free electrons in the conduction band or p-type with free holes carriers in the valance band. The stabilization of ferromagnetism will be more efficient when the carriers are holes instead of electrons.

Gopal and Spaldin [10] performed a systematic study of the magnetic behavior of TM-doped ZnO for a range of TM ions and defects: Zn vacancies, octahedral Zn interstitials, TM interstitials and Li interstitials. They study the possible p-type dopants, Cu and Li with TM in ZnO. Their main result is the absence, in general, of a tendency for pairs of TM ions substituted for Zn to order ferromagnetically; in most cases AFM ordering is more favorable. FM ordering of TM ions is not induced by the addition of substitutional Cu impurities or by oxygen vacancies. Incorporation of interstitial or substitutional Li is favorable for ferromagnetism, as are Zn vacancies. Maouche et al. [11] reported a theoretical study of (Zn, Mn)O system co-doped with N, and show that this co-doping can change the ground state from anti-ferromagnetic to FM.

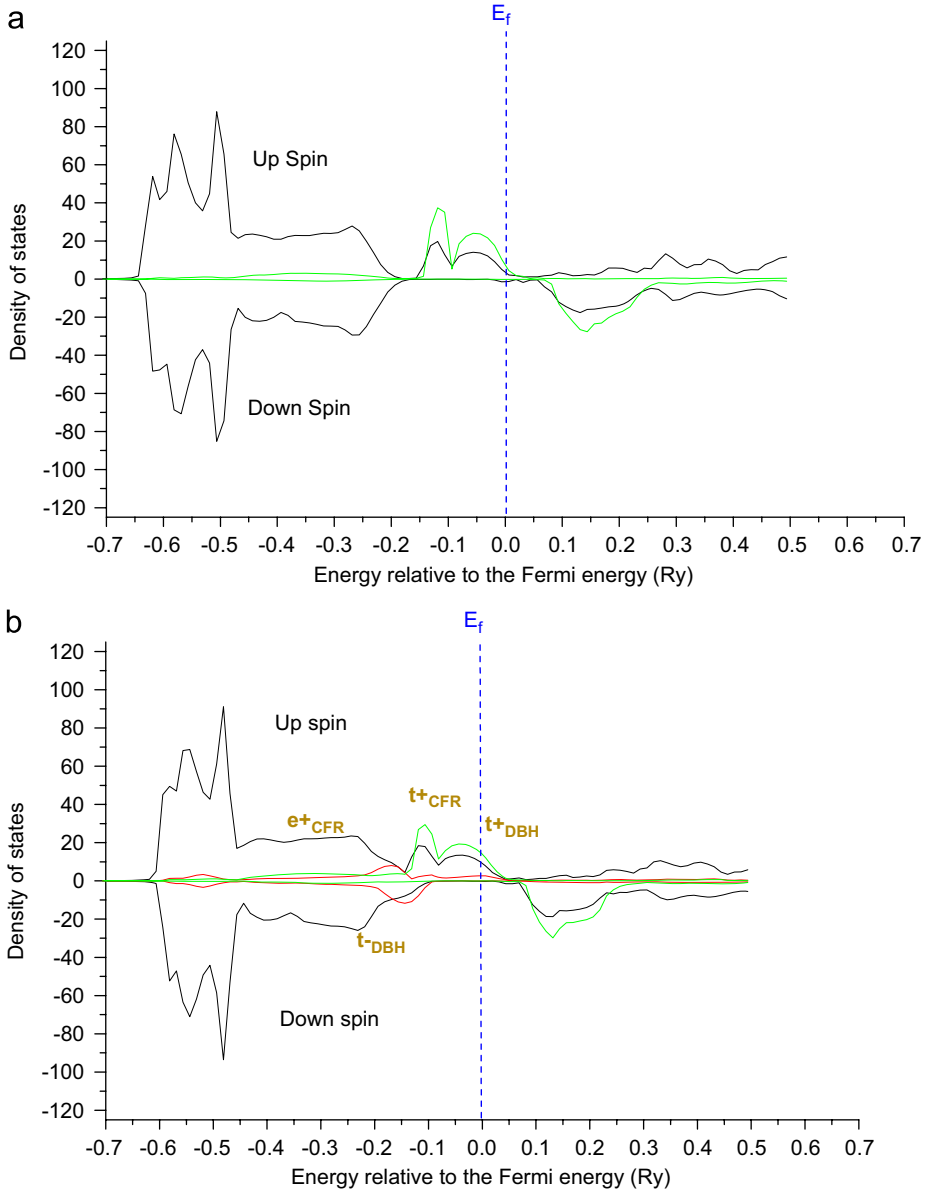

Fig. 1. Density of state: total, d and p states projected density of state (DOS) of Mn, N-doped and co-doped ZnO, $Zn_{1-x}Mn_xO_{1-y}N_y$: (a) $x = 0.2$ and $y = 0$, (b) $x = 0.2$ and $y = 0.1$, (c) $x = 0.2$ and $y = 0.2$ and (d) $x = 0.2$ and $y = 0.25$. Black, green and red solid lines correspond to total, d-Mn and p-N projected DOS, respectively.