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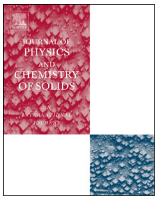

Magnetic and electronic properties of Cr- and Mn-doped SnO_2: *ab initio* calculations

Y. Ziat [a], A. Benyoussef [a,b,c], A. El Kenz [a,*]

[a] LMPHE (URAC 12), Faculté des Sciences, Université Mohammed V-Agdal, Rabat, Morocco
[b] Institute of Nanomaterials and Nanotechnology, MAScIR, Rabat, Morocco
[c] Hassan II Academy of Science and Technology, Rabat, Morocco

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ABSTRACT

The *ab initio* calculations, based on the Korringa–Kohn–Rostoker (KKR) approximation method combined with the coherent potential approximation (CPA), indicated as KKR–CPA, have been used to study the stability of ferromagnetic and ferrimagnetic states, for systems that are SnO_2 doped and co-doped with two transition metals, that is, chromium and manganese. Our results indicate that the ferromagnetic state is more stable than the spin-glass state for the ($Sn_{1-x}Cr_xO_2$; $x = 0.07$, 0.09, 0.12 and 0.15)-doped system, while the spin-glass state is more stable than the ferromagnetic state for the ($Sn_{1-x}Mn_xO_2$; $x =$ 0.02 and 0.05)-doped system. However, the ferromagnetic and/or the ferrimagnetic states are stable for the ($Sn_{0.98-x}Mn_{0.02}Cr_xO_2$; $x = 0.05$, 0.09 and 0.13)-doped system depending on the Cr concentration. Moreover, we estimated the Curie temperature (T_c) for the Cr-doped tin dioxide (SnO_2), and we explained the origin of magnetic behaviour through the total density of states for different doped and co-doped SnO_2 systems.

1. Introduction

Diluted magnetic semiconductors (DMS) are compounds based on the typical types of semiconductors (ZnO, TiO_2, SnO_2, etc.). Recently, tin dioxide (SnO_2) attracted much attention, and this is due to its potential application in spintronic devices [1]. In fact, SnO_2 has diverse optical and electrical properties [2]; these properties are suitable in many fields as in thin solid films and photovoltaic devices. It should be noted that SnO_2 is an *n*-type semiconductor [3], including a direct wide band gap with $E_g =$ 3.6 eV [4]. For this reason, many efforts have been devoted to study the magnetic properties of systems that are SnO_2 doped and co-doped with various transition metals (TMs) (Co, Cr, Fe, W, F, Rh, etc.), experimentally [4–7] and theoretically [8–13].

Punnoose et al. [14] show that the chemically synthesised $Sn_{1-x}Co_xO_2$ nanoscale powders with $x \leq 0.01$ are ferromagnetic at room temperature when prepared by precipitation and annealing in the narrow temperature window of 350–600 °C. Relating to thin films and Fe-doped SnO_2 films, Torres et al. [15] noticed that the transparent pure and Fe-doped SnO_2 thin films were grown by pulsed laser deposition (PLD) technique on the $LaAlO_3$ substrates; X-ray diffraction shows that the films are polycrystalline and have a rutile structure. Surprisingly, the pure film presents a magnet-like behaviour at room temperature with a saturated magnetisation of almost one-third of the doped film ($\sim$3.6 and 11.3 emu g^{-1}, respectively) and its magnetisation could not be attributed to any impurity phase. Besides this fact, Fitzgerald et al. [16] indicate that the room temperature ferromagnetism is observed in $Sn_{1-x}M_xO_2$ (M = Mn, Fe) polycrystalline samples with magnetic moments of 0.11 and 0.95 μ_B for Mn and Fe ions, respectively; Curie temperature (T_c) is 360 K for 5% Fe-doped SnO_2 sample; the ferromagnetism cannot be associated to the minor impurity phase. Hong [17] studied the TM-doped SnO_2 films and observed that magnetic moments could be very large, with the maximum saturation of 6 μ_B per impurity atom for the Cr-doped SnO_2 thin films, but this could be influenced very much by the nature of the substrate type. On the other hand, results on the TM-doped ZnO films have interestingly revealed that in these systems, the magnetism more likely resulted from defects and/or oxygen vacancies.

Concerning the numerical simulations, Bouamra et al. [10] show, using the density functional theory (DFT) within the (CRYSTAL03 code), that in the Rh-doped SnO_2(110) system, $Sn_{48-2x}Rh_{2x}O_{96}$ ($x = 2$, 3, 4 and 5) with ($4 \times 2 \times 1$) supercells, the Rh impurities substituted with Sn ions acquire magnetisation with important values of magnetic moments because the Rh[4d] states hybridised with O[2p] states in the vicinity of the Fermi level. For the Co-doped (110) SnO_2 thin film [11], the full-potential linearised augmented plane wave (FLAPW) method implemented

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[*] Corresponding author.
E-mail addresses: akenzele@yahoo.com, elkenz@fsr.ac.ma (A. El Kenz).

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in a numerical simulation code called WIEN2k indicates that a clustering of Co atoms around O takes place at higher Co concentrations, and the magnetic coupling between Co ions is FM. The strong hybridisation between Co[3d] and O[2p] is found to be responsible for the ferromagnetic (FM) coupling. In addition, different geometries with FM, antiferromagnetic and non-magnetic configurations are also found in Co-doped SnO_2 surface layers of the thin film. Also, the DFT was implemented by Wang et al. [18] to study the (V, Mn, Fe and Co)-doped SnO_2 in the well-tested Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) code; thus, they showed that ferromagnetism is obtained by doping SnO_2 with Fe and Co ions, and paramagnetism is at the ground state in the V- and Mn-doped SnO_2; oxygen vacancy has a strong influence on the magnetic properties of these TM ion-doped compounds.

In this work, we used the calculations based on the Korringa–Kohn–Rostoker (KKR) approximation method combined with coherent potential approximation (CPA) (KKR–CPA) employing the generalised gradient approximations (GGA) and local density approximation (LDA) [19] implemented in the Akai-KKR code [20] to study the effect of Mn-, Cr- and co-doped SnO_2, on the electronic and magnetic structures. First, we discuss the stability of magnetic states in the ($Sn_{1-x}TM_xO_2$; $x = 0.07$, 0.09, 0.12 and 0.15; TM = Mn or Cr)- and ($Sn_{0.98-x}Mn_{0.02}Cr_xO_2$; $x = 0.05$, 0.09 and 0.13)-doped and co-doped systems within GGA and LDA. The purpose of this work is to study the stability of ferromagnetic, ferrimagnetic or disorder local moment states, for systems that are SnO_2 doped and co-doped with two TMs, that is, chromium and manganese. The new finding is the stabilisation of the ferrimagnetic phase in the co-doped SnO_2 depending on the Cr concentration.

Some values of T_c are estimated from the total energy difference between the disordered local moment (DLM) and FM states according to the Heisenberg model. Second, we calculate transition temperatures of doped and co-doped SnO_2 systems.

This article is organised as follows: Crystal structure and calculation method are briefly described in Section II and the results and discussion are presented in Section III, followed by a conclusion in Section IV.

2. Crystal structure and calculation method

The present calculations are based on the DFT, using the KKR method [21,22], which enables us to take into consideration the randomness of the impurity elements during the calculation. Here, we are going to use the Akai-KKR (MACHIKANEYAMA 2002V09), Osaka, Japan developed by H. Akai [20], which uses the DFT combined with the CPA, including the KKR–CPA–GGA and KKR–CPA–LDA. On the one hand, several different parameters of the GGA have been proposed and examined on a variety of materials. The GGA significantly improves the properties of the ground state of atoms, molecules and lightweight solids and generally tends to produce larger network balance parameters regarding the LDA; the GGA we used is the Perdew–Wang functional, called GGA91 [23], which is one of the most widely used functional in calculations involving solids; important publications in DMS using the same approach are present; namely, Refs. [13 and 18] used GGA of Perdew–Burke–Ernzerhof (PBE), Ref. [26] used the LDA–Vosko–Wilk–Nusair (VWN) method and Refs. [20 and 23] used GGA which was also Perdew–Wang functional.

On the other hand, LDA is based on the parameterisation given by Moruzzi, Janak and Williams (MJW) [24]. Here, we should say that the most widely used approximation, in density functional theory, is the LDA, wherein the functional depends only on the density at the coordinate where the functional is evaluated, while GGAs are still local and also take into account the gradient of the density at the same coordinate. Very good results have been obtained for molecular geometries and ground-state energies, using the GGA. We restrict the comparison between these approximations to phase stability, in order to show the advantage of GGA with respect to LDA for doped and co-doped SnO_2.

In this work, the rutile structure of SnO_2 has been considered. This crystalline structure has a tetragonal unit cell with two lattice parameters. The first is $a = 4.7373$ Å and the second one is $c = 3.1864$ Å with $u = 0.307$ Å according to Ref. [25]. To improve the quality of our calculations, initially the empty spheres (ES) with $Z = 0$ are added as inter-sites. For each atom, the sphere radius is taken such that the volume of the unit cell is the sum of the volumes of all atomic spheres. The method used in this work is KKR–CPA; in this case a different doping concentration may be obtained within one unit cell.

Our SnO_2 system has $P4_2/mnm$ as a space group, with six atoms; two tin (Sn) atoms occupy the 2a Wyckoff positions (0,0,0); (½,½,½) and four oxygen (O) atoms occup the 4f positions (u,u,0); (−u,−u,0); (½+u,½−u,½); (½−u,½+u,½), with eight ES sites localised at the following positions: (½,0,−0.1682); (0,½,−0.1682); (0,½,0.1682); (½,0,0.1682); (−0.3125,0.3125,0); (−0.1875,−0.1875,0.3363); (0.1875,0.1875,0.3363); (0.3125,−0.3125,0) as indicated in Fig. 1. The valence states considered are Sn – $4d^{10}5s^25p^2$), O – $1s^22s^22p^4$, Mn – $3d^54s^2$ and Cr – $3d^54s^1$.

3. Results and discussion

Based on the previously indicated methods, the electron structure of rutile SnO_2 has been determined. First, the total energy obtained within GGA is lower than that within LDA, −25314.1919072 versus −25284.7996419 Ry, respectively. Second, the total density of states (DOS) and the partials O(2p) and Sn(4d), obtained within GGA and LDA, related to the pure SnO_2 as presented in Fig. 2 (a,b), reveal that the valence band (VB) included two parts – the first one is noted as high VB, which has an energy range from −0.54 to −0.17 Ry, and the second one, which is called short VB, ranges from −0.7 to −0.54 Ry.

For SnO_2 without doped elements, the DOS of minority and majority spin states are symmetrical because SnO_2 is not magnetic and the sum of moment spin is null. On the other hand, the experimental value of band gap is 3.6 eV [4], while in our calculation it is 2.0481 eV with the GGA and LDA (Fig. 2 (a,b)). The application of LDA and GGA to solids can lead, for example for semiconductors and insulators, to band gaps which is not in full agreement with the experimental results, this is due to the use of a potential which is the same for all orbitals. The band gap calculated from the eigenvalue spectrum differs from the true band gap by the derivative discontinuity of the exchange-correlation potential [27,28].

3.1. Magnetic properties in Mn- and Cr-doped SnO_2

In this section, the magnetic properties have been estimated for the doped and co-doped SnO_2 system with the transition elements (Mn and Cr) which are examined and compared for both approximations, GGA and LDA, and for different concentrations. The electronic structures, total energies and magnetic moments of various SnO_2-based DMS with or without (TM elements) are calculated.

Concerning the Mn-doped SnO_2, the stabilisation of the magnetic states is evaluated through the estimation of the total energy difference ΔE, between the DLM and ferromagnetic states: ($\Delta E = E_{DLM} - E_{ferro}$) [26], where E_{DLM} and E_{ferro} stand for the total energies of the DLM and ferromagnetic states, respectively. The DLM states are simulated by states in which half of the impurity