



Exchange mechanism of half-metallic ferromagnetism of TiO₂ doped with double impurities: A first-principles ASW study

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ARTICLE INFO

Article history:

Received 1 September 2008

Received in revised form

14 September 2009

Available online 7 October 2009

Keywords:

Impurity-doped TiO₂ (rutile)

Ab-initio calculation

ASW method

Band structure model

DMS

Magnetic property

Carrier-mediated ferromagnetism

ABSTRACT

The electronic structure and ferromagnetic properties of rutile TiO₂ doped with double-impurities Ti_{1-2x}Cr_xMn_xO₂ has been investigated using first-principles calculations within the density-functional theory (DFT) and the local density approximation (LDA), functional for treating the effects of exchange and correlation. They were performed using the scalar-relativistic implementation of the augmented spherical wave (ASW). The advantages of doping TiO₂ with double impurities instead of single impurities are the increase of the total moment of the system and the exhibition of the half-metallic ferromagnetic nature in Cr- and Mn-doped TiO₂ rutile. These behaviors are due to the hybridization of Cr 3d states and nearest-neighboring O 2p states. The spin–spin interaction between magnetic impurities examined by the total energy between parallel and antiparallel aligned states indicated that the Cr and Mn impurities are energetically favorable to be parallel coupled, which mean that the ferromagnetic state is more stable than the ferrimagnetic one. We proposed a bond magnetic polarons (BMP) model, based on localized carriers, to explain the mechanism of ferromagnetism in these systems.

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1. Introduction

Titanium dioxide has a variety of interesting physical and chemical properties. It can be found in many products, ranging from paint to food to cosmetics, and has therefore been extensively studied experimentally and using a range of theoretical approaches [1–12]. Recently, it has been observed that when doping TiO₂ with transition-metal (TM) impurities at low-concentration Ti_{1-x}TM_xO₂, with x from 0.01 up to 0.14, titanium dioxide exhibits room-temperature (RT) ferromagnetism [3,4]. In addition, for iron $x \sim 0.07$ [11,13] and cobalt $x \leq 0.12$ [1–3] doping of thin films, the material remains transparent. The doped material has potential for use in spintronics and optoelectronics if the ferromagnetism can be understood and controlled [14].

The origin of the RT ferromagnetism has been studied using a number of experimental techniques but there is still no clear consensus about the resultant lattice structure, the sites adopted by TM ions, the distribution of the ions in the lattice, their oxidation state or the magnetic moment per ion. Transmission

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electron microscopy (TEM) [1,2,4,5,9,10], scanning electron microscopy (SEM) [2,6,7] and atomic force microscopy (AFM) [2] have been used to demonstrate the solubility of TM atoms in various forms of TiO₂ at a variety of concentrations, for which no sign of segregation of an impurity phase is evident. This conclusion has been corroborated by X-ray diffraction (XRD) data, which are consistent with the incorporation of TM ions into both anatase and rutile lattices [1–3,4,5,8–10,12].

Great interest has been focused on half-metallic ferromagnetism (HMF) because of their promising application to spintronics. In HMF one of the two-spin channels is metallic, whereas the other has an energy gap around the Fermi level.

First half-metallic ferromagnet has been predicted in Heusler compound NiMnSb in 1983, by Groot et al. [15]. After that, some half-metallic ferromagnets have been predicted theoretically or conformed experimentally in ferromagnetic metallic oxides such as CrO₂ [16] and Fe₃O₄ [17], in binary transition-metal (TM) pnictides or chalcogenides with zincblende structure such as CrSb [18], MnBi [19], CrS [20], CrSe, CrTe and VTe [21].

Several works were devoted to investigate the origin of the half-metallic ferromagnetism and to study its implication in various physical properties. However, new half-metallic ferromagnets are looked for, which are more promising in basic properties and for applications. Actually, some half-metallic ferromagnets have also been found in diluted magnetic semiconductors (DMS) such as

Mn-doped GaAs [22], V- and Cr-doped CdTe [23]. The discovery of room-temperature ferromagnetism in Co-doped anatase TiO₂ by Matsumoto et al. [1], using a combinatorial molecular beam epitaxy (MBE) technique, has motivated intensive studies on the structural and physical properties of this material [24]. Studies on anatase TiO₂-doped by other TM such as Mn, Fe and Ni [25] have also been made. It is well known that TiO₂ has three commonly encountered polymorphs in nature: anatase, rutile and brookite. Many investigations were devoted to TM-doped rutile TiO₂. Geng and Kim [26] found that Co-doped rutile TiO₂ is a ferromagnetic semiconductor by means of the first-principles ultrasoft pseudopotential calculations with generalized gradient approximation (GGA). Other TM doping has been performed: Cr-doped rutile [27], Mn-, Fe-, Ni- and Cu-doped rutile [28], V-doped rutile [29], Fe-doped rutile [30] and crystallographically oriented Fe nanocrystals formed in Fe-implanted TiO₂ [31].

To our knowledge, there are no theoretical studies on doped rutile TiO₂ with double impurities of transition-metal Cr and Mn till now. In this paper, we investigate the electronic structure and the ferromagnetism of Cr, Mn-codoped rutile TiO₂ by spin-polarized calculations with the first-principles augmented spherical wave (ASW) method, and predict that Cr, Mn-codoped rutile TiO₂ is half-metallic. The ferromagnetic stabilization and mechanism are discussed. It may be useful in semiconductor spintronics and other applications.

2. Method and computational details

2.1. First-principles calculations

The calculations of the present study are performed in the framework of the density-functional theory using the local density approximation (LDA), exchange-correlation functional parametrized by Vosko et al. [32]. The scalar-relativistic augmented spherical wave method [33,34,35] based on the atomic sphere approximation (ASA) is mainly used. In this method, the wave function is expanded in atom-centred augmented spherical waves, which are Hankel functions and numerical solutions of Schrodinger's equation, respectively, outside and inside the so-called augmentation spheres. In order to optimize the basis set, additional augmented spherical waves were placed at carefully selected interstitial sites, the choice of these sites as well as the augmentation radii were automatically determined using the sphere-geometry optimization SGO algorithm [36]. Self-consistency was achieved by a highly efficient algorithm for convergence acceleration [37]. The Brillouin zone (BZ) integrations were performed, within the irreducible wedge of the Brillouin zone [35,38], with an increasing number of *k*-points (4 × 3 × 6) in order to ensure convergence of the results with respect to the space grid. The geometry was fully relaxed using Hellman–Feynman force and total energy. The convergence criterion is fixed to 10⁻⁸ Ry in the self-consistent procedure and charge difference ΔQ = 10⁻⁸ between two successive iterations.

2.2. Computational details

The rutile structure of TiO₂ is based on a simple tetragonal lattice with space group P4₂/mnm and lattice constants *a* = 4.4219 Å, *c* = 2.9166 Å [39]. The metal atoms are located at the Wyckoff positions (2a): (0;0;0), (½;½;½) and the oxygen atoms occupy the positions (4f): ±(*u*; *u*; 0); ±(½ + *u*, ½ - *u*, ½) with *u* = 0.3024. For doped TiO₂ with double impurities Cr and Mn, we mainly take account of the co-doping of 8.34%. The room-temperature ferromagnetic ordering of Co-doped rutile TiO₂ has

been observed for Co concentration up to 12%. The doping *x* = 4.167% of Cr and Mn (Ti_{1-2*x*}Cr_{*x*}Mn_{*x*}O₂) is based on the 2 × 3 × 2 supercell containing 12 primitive unit cells of rutile, where two Ti atoms are replaced by Cr and Mn atoms.

Ferromagnetic stability is determined by the total energy difference (Δ*E*) of the supercell between spin antiparallel alignment (ferrimagnetic) state and spin parallel alignment (ferromagnetic) state. If Δ*E* is negative, the ferrimagnetic state is more stable; if Δ*E* is positive, the ferromagnetic state is more stable. In this way the structure of Ti₂₂CrMnO₄₈ is obtained. They were performed using the scalar-relativistic implementation of the augmented spherical wave method implemented in ASW program PACKAGE. The radii *R*_{mt} of the muffin tins are chosen to be 1.94, 1.94, 1.94 and 1.63 a.u. for Ti, Cr, Mn and O, respectively.

3. Results and discussion

We first calculated the density of states (Figs. 1 and 2) and the electronic band structure (Fig. 3) of TiO₂ without co-doping Cr and Mn atoms, with an increasing number of *k*-points (9 × 9 × 14). Fig. 3 shows that TiO₂ is a directed band gap (Γ–Γ) semiconductor. The direct gap, 2.8 eV, we obtained using the ASW method (LDA-VWN) (Fig. 1) is comparable to the experimental value 3.00 eV [40]. It is better than 1.79, 1.85 and 2 eV obtained with LDA, GGA-PBE of Cambridge serial total energy [41] and LDA of WIEN2K [27], respectively. This difference mainly arises from the exchange-correlation functional, which generally underestimates the energy gap. Fig. 2 shows that the states of O-2p and Ti-3d are mainly located at the valence band (VB) and the conduction band (CB), respectively. However, the crystal field split Ti-3d orbital into two parts, the *t*_{2g} (*d*_{*x*²-*y*²}, *d*_{*xz*}, *d*_{*yz*}) and *e*_g (*d*_{*xy*}, *d*^{3Z²-r²}) states. The CB is divided into lower and upper parts. The VB and the upper CB are composed of O-p and Ti-*e*_g states, whereas the lower CB consists of the O-p and Ti-2g states, the bottom of the lower CB consisting of the Ti-*d*_{*x*²-*y*²}, contributes to the metal–metal interaction. The total (Fig. 4) and partial (Fig. 5) densities of states (DOS) of TiO₂ doped with double-impurities Ti_{1-2*x*}Cr_{*x*}Mn_{*x*}O₂, *x* = 0.04167, are obtained using the tetrahedron method with Bloch corrections. It is clear from the partial DOS of Cr- and Mn-doped TiO₂ rutile (Fig. 5) that the valence and conduction bands are predominantly contributed of O-2p and Ti-3d, respectively, so spin polarization around the Fermi level is mainly composed by the Cr 3d (Fig. 5)

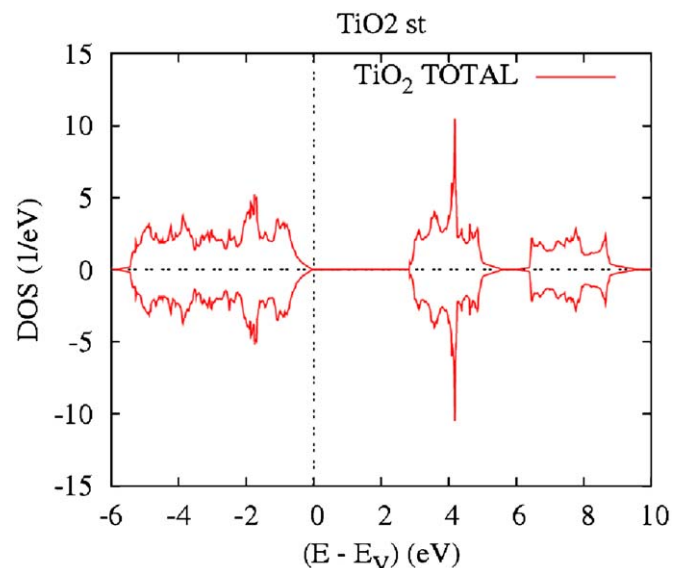


Fig. 1. Total DOS of rutile TiO₂.

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