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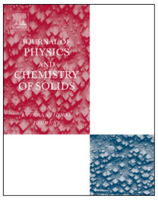

Titanium atoms dimerization phenomenon and magnetic properties of titanium-antisite (Ti_O) and chromium doped rutile TiO_2, ab-initio calculation

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ABSTRACT

The ab-initio calculations based on the Korringa Kohn Rostoker approximation approach combined with coherent potential approximation (KKR-CPA), were used to study the magnetic properties of the titanium anti-site (Ti_O) and chromium (Cr) doped TiO_2. In the considered systems, we used different concentrations for Ti_O defect and Cr doping. In $TiO_{2(0.98)}(Ti_O)_{0.02}$, the obtained results indicate that Ti_O is a donor having half-metal behavior. Ti_O[3d] band is located at the Fermi level, although isn't 100% polarized, the ferromagnetic (FM) state is verified as being more stable than disordered local moment (DLM) state. For $Ti_{0.98}Cr_{0.02}O_2$ the Cr doping introduced new states which give the material half-metallic feature. The majority spin of Cr impurities are located at the Fermi level and the conduction electrons around the Fermi level are 100% spin polarized. This indicates the stability of (FM) state. Moreover, in $Ti_{0.98}Cr_{0.02}O_{2(0.98)}(Ti_O)_{0.02}$, the top of the valence band is shifted to lower energy compared to pure TiO_2, and the n-type of TiO_2 is verified. The majority spin of Cr[3d] are located at 0.025 Ry close to the Fermi level. The predicted Curie temperatures (Tc) were calculated using the mean field approximation (MFA) and we predicted that Ti_O defect in Cr doped TiO_2 makes Tc higher. This kind of defect makes the material useful for spinotronics's applications and devices.

1. Introduction

Diluted magnetic semiconductors (DMS) are semiconductors doped by elements like transition metals or rare earths which give them magnetic features. Those materials are known by their room temperature ferromagnetism (RTFM). The main feature of DMS is that they involve the spin of electrons in electronic and optical applications. This type of materials has known a growing interest from researchers for its important properties in spintronics.

DMSs based semiconductor oxides or diluted magnetic oxides DMO form an important class of suitable materials to be used in spintronics. It was shown that the oxygen promotes the ferromagnetic coupling in Mg doped SnO_2 due to the p–p interaction between Mg and neighboring oxygen [1]. Diluted magnetic oxides have also many characteristics: their Curie temperatures which are higher than room temperature, their large band gap and their ability to be easily doped with n-type dopants [2]. As example, magnetism in pure HfO_2 films [3], and room temperature ferromagnetism in pure TiO_2 films [4,5] were both studied. These two were a new platform for a phenomenon known as d° magnetism [6]. This phenomenon is also known as intrinsic ferromagnetism as it was mentioned in [7], they investigated the ferromagnetism dependence on the number of holes substituted for Sn sites in SnO_2 host.

Oxygen vacancies act in such systems as electron Donors [8], and in Co doped SnO_2 [9], it makes the Co 3d-t_{2g} minority-spin state broadened, and therefore a t_{2g}-V_O hybrid level near the conduction band minimum forms, which results in a strong carrier-mediated ferromagnetic interaction.

DMO materials play an important role in the characterization of physical and chemical properties of transition metal oxides [10]. This was proved by Abdul et al. [2] who predicted that existing vacancies might be the reason of magnetic order. Other group reported that increment of oxygen vacancies associated with post annealing conditions in samples enhances the ferromagnetism in Vanadium doped TiO_2 [11].

Titanium dioxide TiO_2 was the subject of several studies due to its importance in spintronics devices [12,13], sensors, solar cells, and photo-catalysts [14,15].

Many experimental studies had as a goal to study the origin of magnetism in TM doped TiO_2. Groups of researchers found

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ferromagnetism above room temperature in Co doped TiO_2 Thin Film [16,17]. The intrinsic origin of ferromagnetism [18,19] and the detection of a paramagnetic or an antiferromagnetic behavior [20,21] were debated and asserted for this material. Other researchers predicted that ferromagnetism comes from precipitation of magnetic clusters [17]. The logical conclusion we can draw from these results is that magnetism is closely dependent on manufacturing methods and processing conditions of samples, as it was reported by Tian et al. [11].

Rutile Titanium dioxide is commonly known to be a strongly n-type semiconductor [22]. This property was the reason behind our interest in this stable phase of this material. In a first study we unveiled the effect of doping and double doping TiO_2 on its magnetic, structural and electronic properties [23].

The idea of discovering how all properties may change by combining the two conditions, i.e. the point defects and doping, put us on the path of the present work.

2. Crystal structure and calculation method

Before starting the study on TiO_2 material, it is necessary to have an overview of the main characteristics of the bulk material. Therefore, its crystal structures and main thermodynamic equilibrium physicochemical properties will be taken from the literature.

It is important to note that its characteristics change in a consistent manner when the material is in thin layers with a certain surface morphology.

In nature, the titanium dioxide crystallizes in several polymorphic structures. Many of them occur only in very specific conditions, particularly in the field of very high pressures. That is why only three of these phases (rutile, anatse and broukite) are more known and more important.

Our ab-initio calculations are based on the density functional theory DFT and the Korringa–Kohn–Rostoker approach which is the standard approach to theoretically study disordered and periodic systems [24,25]. We used the AKAI-KKR (MACHIKANEYAMA 2002V09) electronic structure calculations' code developed by H. Akai [26] which uses the DFT combined with coherent potential approximation CPA and the local density approximation LDA [27] based on the parameterization given by Moruzzi, Janak and Williams (MJW). That enables us to take into consideration in our calculation the randomness doping of the impurity elements. KKR-CPA method is widely used to study magnetism in different alloys [28–30].

The crystalline structure of rutile TiO_2 is widely considered to be a strongly n-type semiconductor [22] for its tendency for oxygen deficiency. Its tetragonal unit cell shown in Fig. 1 has as lattice parameters of $a=b=4.584$ Å and $c=2.953$ Å [31]. The system integrate also the primarily empty-spheres ($Z=0$) as an inter-sites, then, 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 rutile TiO_2 belongs to the space group P42/mnm with six atoms, two titanium atoms occupying the 2a Wyckoff positions (0,0,0), (½, ½,½) and four oxygen ones occupying the 4f Wyckoff positions: (u,u,0), (−u,−u,0), (½+u,½−u,½), (½−u,½+u,½) when $u=0.305$ Å is the internal parameter. The eight empty-spheres sites are localized at the following positions (½,0,−0.1610), (0,½,−0.1610), (0,½,0.1610), (½,0,0.1610), (−0.1875,−0.1875,0.3220), (−0.3125,0.3125,0), (0.3125,−0.3125,0), (0.1875,0.1875,0.3220). The considered valence states are Ti([Ar]$3d^2$ $4s^2$) and O($1s^2 2s^2 2p^4$).

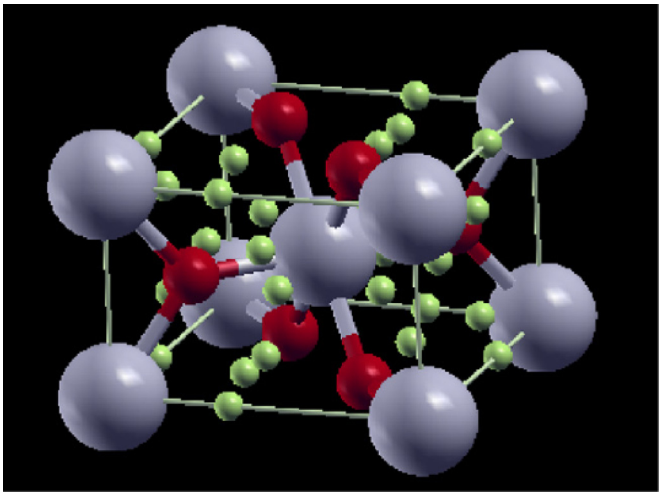

Fig. 1. The unit cell of rutile TiO_2 (the big gray balls correspond to titanium atoms, the small red balls to the oxygen atoms and the green balls to empty spheres).

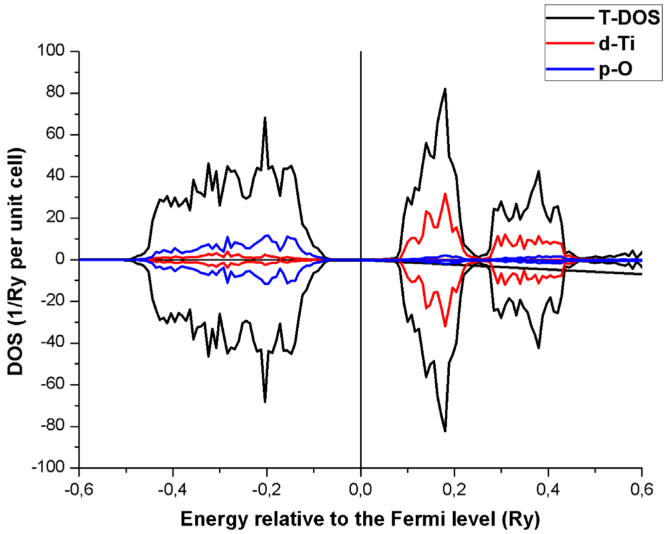

Fig. 2. Total and partial densities of states of pure rutile TiO_2. The black, Red and blue lines, respectively corresponds to the TDOS, Ti[d] and O[p] shells.

3. Results and discussion

3.1. A. Pure rutile TiO_2

Total (T-DOS) and partial (P-DOS) densities of states related to Ti[3d] and O[2p] of rutile TiO_2 are presented in Fig. 2. In the left of this figure we have the valence band which represents the occupied states. And in the right we have the conduction band relative to the empty states.

The zero total magnetic moment found and the symmetry between up and down spins in both conduction and valence bands allow us to say that TiO_2 semiconductor have no magnetic properties. These results are in agreement with previous researches [23,32].

The LDA calculations underestimate the electron correlation effects, and the band-gap energy of semiconductors and occupied d states are systematically predicted at too high energies. As a result, the hybridization between d states and ligand p states is generally over-estimated in the LDA [33]. This is why we have a small difference between found valence band width and gap energy using KKR MACHIKANEAMA code (respectively 5.76 eV and 2.04 eV) and experimental results (6 eV for the valence band and 3.04 eV for gape).