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First-principles study of the electronic structure and the associated magnetism of carbon-doped TiO_2

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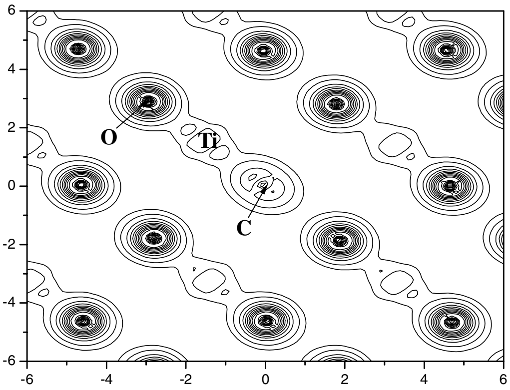
Based on first-principles calculations, the electronic structure and the associated magnetism of carbon-doped rutile TiO_2 have been investigated in the frame of the generalized gradient approximation (GGA). We find that the carbon substitutional oxygen ions can induce a magnetic moment of about $2.0\mu_B$/C, but the carbon substitutional titanium cannot provide any magnetism. Graphics of the spin density show that the magnetism is from the structure distortion around the carbon substitutional oxygen ions in the (110) plane of primitive TiO_2.

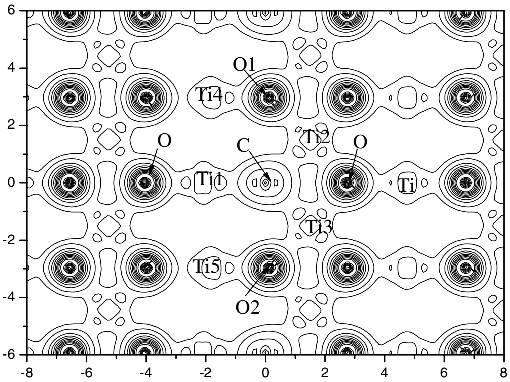
Diluted magnetic semiconductors (DMS) of impurity doped TiO_2 have been recently investigated effectually because of their potential application for spintronics [1–3]. The room temperature magnetism in anatase TiO_2 films is now under intense discussion [3–5]. In 2001, Matsumoto et al. discovered that Co-doped anatase TiO_2 films grown by the pulsed-laser deposition method can keep magnetism at temperatures up to 400 K [3]. Following this work, Shinde et al. reported that laser-deposited anatase $Ti_{1-x}Co_xO_{2-\delta}$ films can keep a magnetic moment of $1.4\mu_B$/Co when temperature is up to 700 K [4]. In 2006, Yoon et al. found that intrinsic defects can induce magnetism in anatase $TiO_{2-\delta}$ films at 800 K [5].

Recently, magnetism has been found in rutile TiO_2 films at room temperature in some works. For example, Park et al. measured the magnetic moment $0.94\mu_B$/Co in Co-doped rutile films if temperature is below 400 K [6]. Experimentally, many works have confirmed that magnetism can exist in rutile films doped with Co or other transition metal ions [7, 8]. Theoretically, Chen et al. considered that magnetism coupling exists between two Fe atoms [1]. For rutile TiO_2 films, the magnetism coupling is enhanced when oxygen vacancies are close to Fe dopants. Using the first-principles full potential linearized augmented planewave method (FP-LAPW), Gao et al. indicated that V-doped rutile TiO_2 has a stable ferromagnetic ground state for the vanadium concentration at 25% [9]. They also investigated half-metallic ferromagnetism of Cr-doped rutile TiO_2 by using first-principles calculation (FPC) [10]. Errico et al. calculated the magnetic properties of $Mn_xTi_{1-x}O_2$, $Fe_xTi_{1-x}O_2$, and $Co_xTi_{1-x}O_2$ [11, 12] using the FP-LAPW method. These investigations indicate that impurity doped TiO_2 is a kind of significant material for DMS. Up to now, the effect of magnetism being induced by doping impurities in the TiO_2 system at room temperature has been investigated only for transition metals. There are no works investigating other elements leading to the magnetic system.

In this work, we investigate the magnetism of carbon-doped TiO_2 (C–TiO_2) rutile by using FPC. Because its behavior may be similar to the interesting subject of unexpected magnetism in undoped TiO_2 [13, 14], HfO_2 [15], Cu-doped TiO_2 [16], and Mg-doped AlN [17] films, we focus our study on whether magnetism can appear in the nonmagnetic and nonmetal impurity C-doped TiO_2 rutile. Our investigation is significant for the application of DMS materials, and will accelerate the studies on the nature of special magnetism.



(a) (001) plane



(b) (110) plane

Figure 1 Charge density graphics of C_O.

In our calculations, we use the Vienna ab initio Simulation Package (VASP) [18]. The potential energy functions have been described using the Vanderbilt ultrasoft pseudopotentials [19]. We described the exchange correlation interactions using the generalized gradient approximation (GGA) method. For the Ti, O and C elements, the Ti $4s^1 4d^3$, O $2s^2 2p^6$, and C $2s^2 2p^4$ states were included as valence states. The crystal structures are relaxed until the free energies on them are less than 10^{-5} eV. In the structure relaxation process, the $4 \times 4 \times 3$ mesh *k*-points of the Monkhost–Pack scheme were adopted. In the calculations of magnetic properties and electronic structure, the $6 \times 6 \times 6$ mesh *k*-points of the Monkhost–Pack scheme were adopted.

Pure rutile TiO_2 belongs to the P42/mnm space group, and the primitive cell includes two formula units. In our calculations, the lattice constants of the pure rutile TiO_2 in a tetragonal cell are a = 4.6123 Å and c = 2.9503 Å. For analyzing the effect of doping ions on the electronic structure and the magnetism, a supercell containing $3 \times 2 \times 2$ primitive unit cells has been adopted.

The effect of doping C ions on the lattice distortion is shown in Fig. 1. We find that the charge densities congregate on the oxygen ions, but the titanium ions only have lower charge densities. At the same time, we find that the charge density along O–Ti–O in the (001) plane of the TiO_2 matrix (Fig. 1a) overlaps between the Ti and O ions. This result suggests that strong bonds between the Ti and O ions are present in TiO_2 rutile.

When the carbon ions substitute the oxygen ions, the charges redistribute along the O–Ti–C direction in the (001) plane (Fig. 1a). The charge density of doping C ions is lower than the charge density of O ions in the original lattice, which induces the charges of Ti ions which are nearest-neighbors to C ions to strengthen the O–Ti–O structure in the TiO_2 matrix. As a result, the O–Ti–C structure is formed in the (001) plane (Fig. 1a). In the (110) plane of the primitive lattice (Fig. 1b), the carbon substitutional oxygen (C_O) ions repulse neighboring Ti and O ions, which causes that the distance C–Ti1 is increased from 1.98 Å (distance in perfect TiO_2) to 2.11 Å, and the distances C–Ti2 or C–Ti3 from 1.95 Å to 2.09 Å, respectively. The structural distortions were caused by the reason of the radius of C ion being larger than that of primitive O ion. Furthermore, while the O–Ti1–C structure was formed, the C_O ion also hybridized with the neighboring Ti2 and Ti3 ions. In addition, the C_O ion also induced the charge redistribution of other Ti and O ions neighboring the C ions. In the (110) plane (Fig. 1b), the O1, O2 and Ti4, Ti5 ions are close to the C ions, and the charge density between O1–Ti4 or O2–Ti5 ions has been strengthened.

For analyzing the magnetism in C-doped TiO_2 rutile, the total density of states (TDOS) of perfect TiO_2 for the primitive unit cell and the partial density of states (PDOS) of C_{Ti} and C_O for the 72-atom supercells have been considered as shown in Fig. 2. From the figure, the TDOS of perfect TiO_2 shows that the band gap of pure TiO_2 is 1.8 eV, which is close to the theoretical calculation of 1.8 eV by Eunae et al. [20]. Because the DFT method underestimates the band gap values, this result is lower than the experimental value of 3.0 eV [20]. Figure 2 shows that the doping C_{Ti} and C_O have changed the band gap structure. The impurity

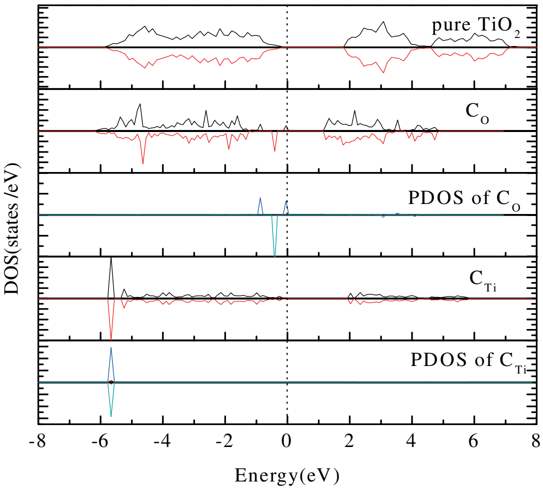
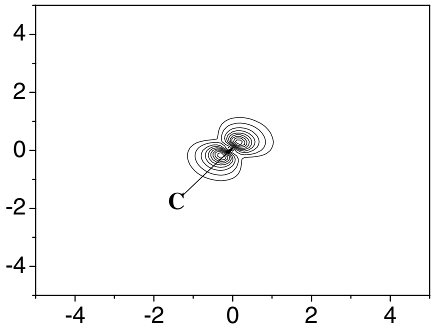
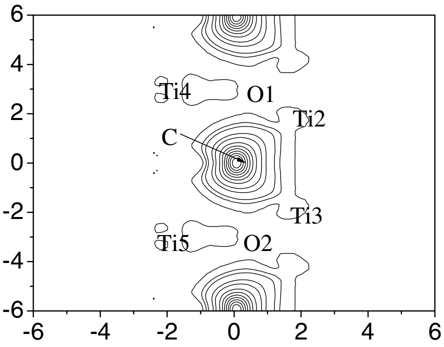


Figure 2 (online colour at: www.pss-rapid.com) TDOS and PDOS for C_O and C_{Ti} in C-doped TiO_2.



(a) (001) plane



(b) (110) plane

Figure 3 Spin charge density graphics of C_O in C-doped TiO_2.

energy level locates at –5.6 eV for C_{Ti}. In Fig. 2, C_O induces that the impurity energy level appears in the band gap near the valence-band maximum. In Fig. 2, it can be seen that the densities of states (DOS) of majority and minority spin have a symmetrical structure for C_{Ti}, but for C_O the DOS of majority and minority spin are asymmetrical. It suggests that C_O is an important potential candidate for inducing the magnetism properties in C-doped TiO_2 rutiles. In our calculations, C_O can provide a magnetic moment of $2.0\mu_B$/C for C-doped TiO_2 rutile, which is larger than the magnetization 20 emu/cm^3 (about $1.7\mu_B$/72 atom supercell) in undoped TiO_2 [14]. The results suggest that the magnetism appears in C-doped TiO_2 due to C_O ions.

Figure 3 shows that the spin density distribution of the C_O ions is around the C ion. From Fig. 3a, the spin density is mostly located at C ions, and no other magnetic interaction appears. In the (110) plane (Fig. 3b), it is clear that the spin density is present around the doping C ion and mainly locates at the C ions. The magnetism also appears in the nearest-neighbor Ti and O ions just as O1, O2, and T2–T5 ions, but these ions cannot become the dominating magnetic provider, because they only provide a spin magnetism much lower than the magnetism of C. No magnetism appears in other O and Ti ions far away from C ions. It suggests that the magnetism induced by carbon substitutional oxygen ions mainly results from the structure distortion in the (110) plane of the primitive TiO_2 lattice, and the dominating magnetism provider is the doping C ion.

In summary, we investigated the electronic and magnetic properties of carbon-doped TiO_2 rutile using FPC. The doping positions of both carbon substitutional titanium and carbon substitutional oxygen were considered in our calcualtions. Calculations of the total density of states and partial density of states show that the carbon substitutional oxygen (C_O) can provide an impurity energy level in the band gap near the valence-band maximum which has an asymmetrical majority and minority spin DOS. The charge density graphics and spin density distribution show that the crystal structure and charge density distortion in the (110) plane of the primitive TiO_2 were induced by the C_O ions, and a magnetic moment of $2.0\mu_B$/C has been generated in the supercell. Our results show that the magnetism results from this special mechanism in the C-doped TiO_2 rutiles, and C-doped TiO_2 could be a significant candidate of DMS.

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