Defect-induced ferromagnetism in rutile TiO_2: A first-principles study*

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Based on first-principles calculations, the electronic and magnetic properties of undoped and Li-doped rutile TiO_2 have been studied. The results demonstrate that a cation vacancy can arouse ferromagnetism in TiO_2 and the magnetic moment mainly comes from p orbitals of O atoms around the Ti vacancy. However, the Ti vacancy under normal conditions is very difficult to form due to its high formation energy. Our calculations indicate that Li-doped TiO_2 can reduce the formation energy while keeping the magnetism. The large magnetization energy indicates that Li-doped TiO_2 is a promising room-temperature diluted magnetic semiconductor.

Keywords: rutile TiO_2, diluted magnetic semiconductors, first-principles calculation, electronic structure

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1. Introduction

Diluted magnetic semiconductors (DMSs) have attracted more and more attention in the last two decades due to their potential applications in spintronics devices, which utilize both the charge and the spin degree of freedom of carriers to create new functionalities beyond conventional semiconductors. The original idea of DMSs was to dope magnetic transition metals (TMs), such as Fe, Cr, Mn, and Co, into a semiconductor host to make it magnetic.[1–3]

For practical applications, the DMSs should exhibit ferromagnetism with a high Curie temperature (T_C) and a homogeneous distribution of the magnetic dopants. In the last decade, 3d TM-doped TiO_2 has been paid more and more attention since Matsumoto *et al.* found its room-temperature ferromagnetism.[4] It has been reported that V-, Co- and Fe-doped TiO_2 are ferromagnetic above 300 K.[5] However, the origin of ferromagnetism in TM-doped semiconductors is still under debate. Moreover, magnetic element doping suffers from the problems of cluster, precipitates or secondary phase formation. Fabricating new DMSs free of magnetic TMs can avoid these problems. There are two approaches to achieve new classes of DMSs that are free of magnetic precipitates. The first is to make semiconductors ferromagnetic by creating native defects in host materials. For example, based on *ab initio* calculations, Elfimov *et al.* reported that Ca vacancies in CaO can produce local magnetic moments and transform the nonmagnetic CaO into a half-metallic ferromagnet.[6] A similar ferromagnetism was also predicted for the Ga vacancy in GaN.[7] Another possible solution is to dope semiconductors with non-magnetic elements other than magnetic TMs. It has been reported that non-magnetic Cu-doped ZnO favors a ferromagnetic ground state with T_C well above room temperature both theoretically and experimentally.[8,9] The above two approaches can be named defect-induced intrinsic magnetism.

In this work, using first-principles calculations, we study the ferromagnetism in rutile TiO_2. The paper is organized as follows. In Section 2, the computational methods are introduced. In Section 3, we give our discussion and results. Section 4 summarizes the paper.

2. Computational details

The calculations are performed using the full-potential linear augmented plane-wave (FP-LAPW) method implanted in the WIEN2k package.[10] The FP-LAPW method, which is among the most accurate methods for performing electronic structure calculations for crystals, divide the unit cell into (i) non-overlapping atomic spheres and (ii) an interstitial region. In the two types of regions, different basis sets are used. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) 96 is employed for the exchange–correlation potential. The GGA of PBE can be defined as $E_{xc}^{GGA}[n\uparrow, n\downarrow] = \int d^3 r n \varepsilon_x^{unif}(n) F_{xc}(r_s, \zeta, s)$. A detailed description of the GGA of PBE can be found in Ref. [11]. The radius of the muffin-tin sphere R_{MT} is chosen to be 1.55, 1.75, and 1.75 a.u. for O, Ti, and Li atoms, respectively. The convergence parameter $R_{MT}K_{max}$ is set to be 7.5, where K_{max} is the maximum modulus for the reciprocal lattice vector. This parameter has been proved to yield good convergence. Brillouin zone integrations are performed by summating over a $4 \times 4 \times 3$ Monkhorst–Pack special k-point mesh. The atomic

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coordinates are fully relaxed until the maximum force on each atom is less than 0.01 eV/Å; the self-consistency is considered to be achieved when the total energy difference between succeeding iterations is less than 10^{-5} Ry per supercell unit. The $2\times2\times2$ supercell is employed in our calculations. This corresponds to 48 atoms in a unit cell and one or two defects (titanium atoms substituted by vacancies or impurities) are presented. A larger $2\times2\times3$ supercell with 72 atoms has also been used to test the calculated results; we found that our conclusion is not affected by the supercell size. In fact, the 48-atom supercell is usually used to simulate TiO_2.[12–14] The stability of the ferromagnetism is estimated by calculating the total energy difference ΔE_M ($\Delta E_M = E_{AFM} - E_{FM}$) between the ferromagnetic state (FM) and the anti-ferromagnetic state (AFM), where E_{FM} and E_{AFM} are the total energies of the FM and AFM ordering, respectively. The positive ΔE_M means that the FM state is energetically more favorable than the AFM state. At equilibrium and in the dilute limit, the concentration of a defect in a crystal depends upon its formation energy of E_f, which can be calculated by

$$E_f = E[X] - E[TiO_2, \text{bulk}] - \sum n_i \mu_i, \quad (1)$$

where $E[X]$ is the total energy of the defect-containing TiO_2 supercell and $E[TiO_2, \text{bulk}]$ is the total energy of the equivalent supercell of TiO_2 containing no defects. Here, n_i indicates the number of atoms that have been added to ($n_i > 0$) or removed from ($n_i < 0$) the supercell; μ_i are the corresponding chemical potentials of these species.

3. Results and discussion

3.1. Cation vacancies in TiO_2

The calculated lattice constants, a and c, of the rutile TiO_2 unit cell are 4.39 Å and 2.98 Å, respectively, which are in agreement with the experimental values.[15] Based on this unit cell, a $2\times2\times2$ supercell is constructed, as shown in Fig. 1. The defect of a neutral Ti vacancy (V_{Ti}) is created by removing one Ti atom from the supercell ($Ti_{15}O_{32}$). Atomic coordinates are fully relaxed, while the lattice constants are fixed. The calculated total energy of the spin-polarized state is 300 meV lower than that of the non-spin-polarized state. A similar situation is also found in anatase TiO_2.[16] When a Ti atom is removed, the oxygen atoms surrounding the neutral Ti vacancy move outward by about 0.15 Å. This is in good agreement with the theoretical research on Ga vacancy in GaN.[17] The spin-resolved density of states (DOS) of this supercell ($Ti_{15}O_{32}$) as well as that of bulk TiO_2 ($Ti_{16}O_{32}$) are shown in Fig. 2. For bulk TiO_2 (see Fig. 2(a)), the DOS of the majority spin and minority spin are symmetric and exhibit a good semiconducting feature. The valence band states are mainly formed from O 2p orbitals hybridized with Ti 3d orbitals, while the conduction band states are mainly composed of Ti 3d states with weak hybridization with O 2p states. Due to the special ligand field, the Ti 3d orbitals are split into two sets of t_{2g} and e_g orbitals. Since there is no spin polarization, the bulk TiO_2 is non-magnetic. However, when a Ti vacancy is introduced, the DOS near the Fermi level are modified significantly. As shown in Fig. 2(b), the Fermi level traverses the minority spin channel, which means that the Ti vacancy introduces holes into O 2p states and turns TiO_2 into a p-type semiconductor. Furthermore, the vacancy leads to an asymmetric DOS. At the Fermi level, there is a peak in the minority-spin channel, while there are few states in the majority-spin channel. It is the partially occupied O 2p states induced by the Ti vacancy that lead to the asymmetric DOS, which is necessary to form a spin polarization. The strong spin polarization produces a spin magnetic moment of 2.5 μ_B per supercell. Since there is no other ferromagnetic dopant, these observations suggest that the origin of magnetism in this supercell must be due to the titanium vacancies. The projected DOS of O 2p orbitals indicates that the magnetic moments are mainly contributed by the unpaired 2p orbitals of the O atoms around the vacancy site and each O atom contributes about 0.17 μ_B. To examine this defect-induced magnetic coupling, two V_{Ti} with the largest possible separation in the $Ti_{14}O_{32}$ supercell, are considered. The calculations show that the FM state is the ground state and its energy is 283.7 meV lower than that of the AFM state. This energy difference is larger than that of Cu-doped ZnO (42 meV),[8] which is reported as a room-temperature ferromagnet, so V_{Ti} may make TiO_2 ferromagnetic with T_C above the room temperature too.

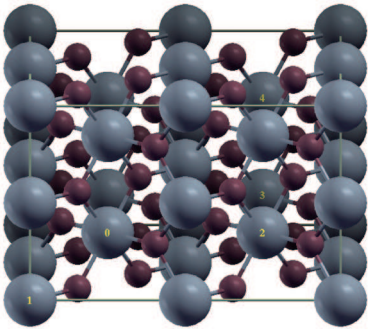


Fig. 1. (color online) The $2\times2\times2$ supercell of rutile TiO_2. Small (red) and large (gray) spheres represent the O and Ti atoms, respectively. Numbers labeled on Ti atoms are used to identify the doping configurations.

The numerical results with other different V_{Ti} concentrations show that the magnetic moment is 3.76 μ_B and 4.01 μ_B for a V_{Ti} concentration of 12.5% and 25%, respectively. These results show that the magnetic moment depends on the vacancy concentration. It is well known that the concentration of a defect depends upon its formation energy E_f.[18] Figure 3 shows the formation energy of various defects as a function of the oxygen chemical potential, which is measured relative to the energy of an oxygen atom in an oxygen molecule. As

shown in Fig. 3, the formation energy of V_{Ti} is very high ($E_f = 2.5$ eV and -0.36 eV for the Ti- and O_2-rich growth condition, respectively), which indicates that titanium vacancies are difficult to form under normal conditions. Therefore, fabricating DMSs by introducing Ti vacancies to TiO_2 is impractical. We will focus on reducing the formation energy of V_{Ti} in the following discussion.

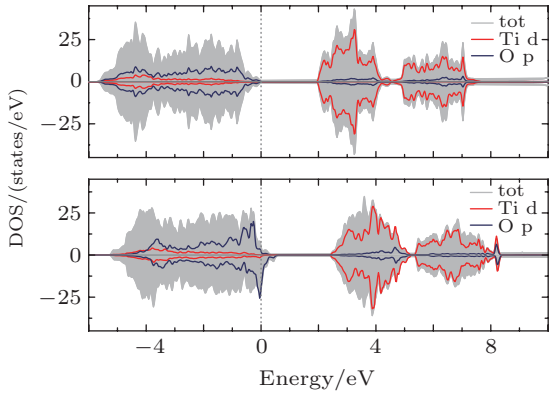


Fig. 2. (color online) Total and projected DOS of (a) undoped and (b) one Ti vacancy in a $2\times2\times2$ TiO_2 supercell. The dotted line represents the Fermi level at 0 eV. To make the impurity states more visible, the intensity of the projected DOS of O 2p and Ti d are multiplied by a factor of 16.

3.2. Li-doped TiO_2

The high formation energy of titanium vacancies in TiO_2 is mainly caused by the unpaired O 2p electrons. Thus, it can be reduced by partly saturating these unpaired electrons while keeping the magnetism. It is known that IA and IIA metal substitutional doping at the cation site can introduce holes into TiO_2 and keep O 2p orbitals partly occupied. To lower the formation energy, IA and IIA metal X (X = Li, Na, Be, Mg) atoms are placed at the cation sites in the $2\times2\times2$ supercell of TiO_2, forming X_{Ti} defects. Figure 3 shows the formation energies of the substitutional X_{Ti} defect as a function of oxygen chemical potential. As shown in Fig. 3, for all dopants (except Na), the substitutional X atom at Ti sites can significantly lower the formation energy. Among all substitutional doping, Li_{Ti} has the lowest formation energy (-8.2 eV and -6.7 eV for O-rich and O-poor circumstance, respectively) in the entire range of oxygen chemical potentials, indicating that Li_{Ti} is very easy to form under normal conditions. The lowest formation energy of Li_{Ti} can be attributed to Li^+ and Ti^{4+} having the same ion radius ($R_{Li} = R_{Ti} = 0.68$ Å).[18] The low formation energy would result in a high dopant concentration under normal conditions. Except for the Li_{Ti} defect, which will be discussed below, Li interstitials (Li_I) also have a very low formation energy (-7.5 eV). Furthermore, our calculations show that Li_I prefers non-spin polarized states. As can be seen in Fig. 3, the formation energy of Li_I is lower than that of Li_{Ti} under the O-poor growing condition, but under an O-rich condition, the formation energy of Li_{Ti} is lower than that of Li_I, which indicates that Li_{Ti} is the most stable defect type under the O-rich condition. Thus, we can restrain the concentration of Li_I by adopting an O-rich condition.

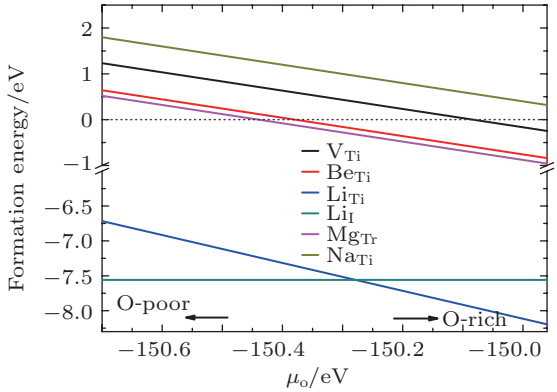


Fig. 3. (color online) The formation energy as a function of the oxygen chemical potential for various defects in TiO_2.

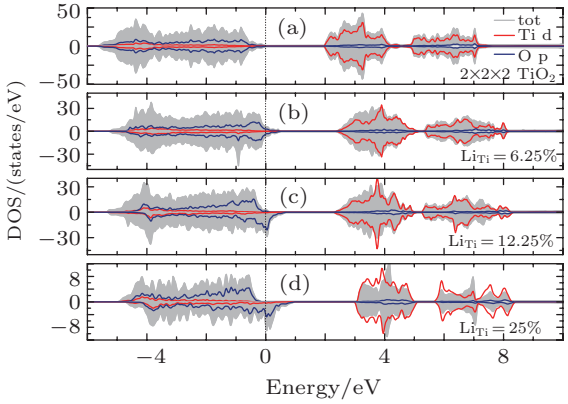


Fig. 4. (color online) Total and projected DOS of Li-doped TiO_2 is plotted for (a) 0%, (b) 6.25%, (c) 12.5%, and (d) 25% concentration of Li atoms. The dotted line represents the Fermi level at 0 eV. To make the impurity states more visible, the intensity of the projected DOS of O 2p and Ti d are multiplied by a factor of 16.

To investigate the electronic and magnetic properties of Li_{Ti} in TiO_2, the DOS of Li-doped TiO_2 are calculated and shown in Fig. 4. It is found that the replacement of Ti atoms by Li atoms introduces holes and a magnetic moment into TiO_2. It is worthwhile mentioning that the calculated spin magnetic moment is impacted by the doping concentration of Li_{Ti}. To examine the influence of the doping concentration of Li_{Ti} on the magnetic properties of TiO_2, various doping concentrations are calculated. When one Ti atom is replaced by Li in a $2\times2\times2$ TiO_2 supercell, which is equal to a doping level of about 6.25%, the calculated total magnetic moment is 0.34 μ_B. The corresponding spin-resolved DOS is shown in Fig. 4(b). It is clear that the peaks in the DOS of both the majority and minority spin lie below the Fermi level and no notable spin polarization appears in the valence band. By comparison with Fig. 2(b), there are fewer hole states in the minority spin due to the partial saturation of the unpaired O 2p orbitals. For a doping level of 12.5% (see Fig. 4(c)), however, the valence band

is notably spin-polarized, which results in a spin magnetic moment more than 2.3 μ_B per Li impurity. The numerical results show that the magnetic moment increases with the increase in the doping level. More interestingly, when the Li concentration is increased to 25% (see Fig. 4(d)), the valence band is completely spin-polarized, and the Fermi level crosses only the down-spin states, thus resulting in a half-metallic property with a magnetic moment of 3.0 μ_B per Li. This result indicates that the doped Li has an electron configuration resembling that of Li^+ ($1s^2 2s^0$) and the replacement of Li^+ by Ti^{4+} produces three unpaired O 2p electrons, thus generating an integer spin moment of 3.0 μ_B per Li impurity.

Table 1. Values of the Li_{Ti}–Li_{Ti} distance after relaxation, the relative energies (ΔE), the magnetization energy (ΔE_M), and the total magnetic moment (M_{tot}) of the Li-doped TiO_2 supercell. The relative energy is referred to as the (0, 2) configuration.

(i, j)	Li_{Ti}–Li_{Ti}/Å	ΔE/meV	ΔE_M/meV	M_{tot}/μ_B
(0, 1)	3.597	34.9	44.6	4.7
(0, 2)	4.594	0.0	61.4	4.6
(0, 3)	6.497	49.0	132.2	5.3
(0, 4)	7.14	78.4	146.9	5.5

To examine the magnetic coupling between these hole-induced spin moments, we consider four different unique arrangements of two Li atoms doping models (using a $2 \times 2 \times 2$ rutile supercell), which corresponds to a doping concentration of 12.5%. The two substitution Li atoms are placed at four possible separation distances in the supercell. The relative positions of two Li atoms are labeled as (i, j) for convenience, as seen in Fig. 1. The atomic positions in each case are fully optimized. The relative energy ΔE with respect to the energy of the (0, 2) structure ($\Delta E = E(i, j) - E(0, 2)$), magnetization energy ΔE_M, and the total magnetic moment for each Li_{Ti}–Li_{Ti} separation are listed in Table 1. It is noted that the FM state is the ground state for all configurations. The magnitude of ΔE_M as well as M_{tot} (except for the (0, 1) configuration) becomes larger when two Li_{Ti} are farther from each other, which means that the FM state becomes more stable when the Li_{Ti}–Li_{Ti} distance increases. For configurations (0, 2), (0, 3), and (0, 4), the magnitude of ΔE also becomes larger when two Li_{Ti} are farther from each other, indicating that these structures become more unstable when two Li_{Ti} are farther from each other; however, this is not true for configurations (0, 1) and (0, 2), in which the (0, 2) configuration has the lower total energy. Therefore, the doped Li atoms in the TiO_2 do not prefer to form a cluster. This makes the Li-doped TiO_2 system superior to TM-doped TiO_2,[19–21] in which dopant prefers to form a cluster. For the (0, 2) configuration, which has the lowest total energy in all configurations, the magnitude of the magnetization energy is as high as 64.4 meV. This magnetization energy is larger than that of Cu-doped ZnO (42 meV),[8,9] which is known to be a room-temperature DMS. The large magnetization energy indicates that Li-doped TiO_2 is a possible room-temperature DMS.

4. Conclusions

In conclusion, the electronic and magnetic properties of Ti vacancy and Li dopant in rutile TiO_2 are studied based on the first-principles calculations. The numerical results presented here indicate that the Ti vacancy in TiO_2 can introduce holes into the O 2p orbital and lead to a spontaneous spin polarization. However, the formation energy of the Ti vacancy in TiO_2 is too high to reach a sufficiently high concentration of V_{Ti}. It is unpaired O 2p orbitals that result in a high formation energy. In order to partly saturate these unpaired orbitals, some light metal X (X = Li, Be, Na, Mg) doped TiO_2 are studied. It is found that the formation energy of substitutional X-doped TiO_2 is much lower than that of the Ti vacancy under both O-poor and O-rich growth conditions. Li-doped TiO_2 produces the ferromagnetic ground state and has the lowest formation energy. A large magnetic energy indicates that Li-doped TiO_2 may be a possible room-temperature diluted magnetic semiconductor.

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