Effect of non-magnetic impurities on the magnetic states of anatase TiO$_2$

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Abstract

The electronic and magnetic properties of TiO$_2$, TiO$_{1.75}$, TiO$_{1.75}$N$_{0.25}$, and TiO$_{1.75}$F$_{0.25}$ compounds have been studied by using ab initio electronic structure calculations. TiO$_2$ is found to evolve from a wide-band-gap semiconductor to a narrow-band-gap semiconductor to a half-metallic state and finally to a metallic state with oxygen vacancy, N-doping and F-doping, respectively. The present work clearly shows the robust magnetic ground state for N- and F-doped TiO$_2$. The N-doping gives rise to a magnetic moment of $\sim 0.4$ $\mu_B$ at the N site and $\sim 0.1$ $\mu_B$ each at two neighboring O sites, whereas F-doping creates a magnetic moment of $\sim 0.3$ $\mu_B$ at the nearest Ti atom. Here we also discuss the possible cause of the observed magnetic states in terms of the spatial electronic charge distribution of Ti, N, and F atoms responsible for bond formation.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent years the scientific world has been fascinated by the occurrence of magnetism in non-magnetic (NM) materials where unpaired d and/or f electrons are absent. For example, materials like Si [1], pyrolytic graphite [2], fullerene [3], CaO [4, 5], CaBr$_6$ [6–8], SiC [9], etc contain only s and p electrons and are reported to exhibit magnetism. In the case of Si, magnetism is shown to arise from surfaces [1] whereas the observed room temperature ferromagnetism in the pyrolytic graphite is attributed to the two-dimensional networks of point defects [2]. The origin of ferromagnetism observed in CaBr$_6$ has been a matter of controversy and two schools of thought exist. One believes that it arises from magnetic impurities, whereas the other has the opinion that defects are responsible for the ferromagnetism [8]. Similarly, defects are also found to be responsible for the creation of magnetic moments in CaO and SiC compounds [5, 10]. Thus the creation of finite magnetic moments in these systems is attributed to uncompensated spins due to the surface effect, defects, and even to magnetic impurities. In spite of these ambiguities, the phenomenon has not only provided a new dimension to spintronic based materials but also challenges us to appreciate such an occurrence from a fundamental physics point of view, since knowing the exact cause for the creation of net magnetic moments and the nature of interaction among them are non-trivial.

In this work we have attempted to explore the presence of magnetism in the well studied NM semiconducting oxide TiO$_2$ by creating oxygen vacancies and doping NM elements at oxygen sites. In order to appreciate such an attempt, it is important to note that getting the ferromagnetic (FM) state in a NM semiconductor by means of doping with magnetic impurities has attracted a great deal of attention in recent years, and has emerged as one of the important branches in condensed matter physics and materials science [11–16]. However, the origin of ferromagnetism in such diluted magnetic oxide semiconductors (DMOS) has been controversial, where the possibility of the formation of secondary phase or clusters of magnetic impurities cannot be ruled out. Recently a few reports have appeared which emphasize induction of a FM state in NM semiconducting oxides by means of doping NM elements, creating defects or changing oxygen stoichiometry [17–22]. Such DMOS will indeed be quite advantageous, since then one does not need to bother about issues related to the incorporation of magnetic impurities in the host matrix or its interaction with the carriers. Study of these doped and undoped oxide semiconductors raises the hope of manipulating the optoelectronic devices by controlling their magnetic properties. Thus our present attempt is expected to
provide some understanding of the origin of magnetic moment in an otherwise NM system and its possible applications in spintronics.

TiO$_2$ was chosen for the study due to its well documented wide range of optical, electrical, and catalytic applications. TiO$_2$ based systems also possess good optical transmission in the visible and near infrared regions, making it a suitable candidate for magneto-optic devices as well. For the present study we consider three cases: (i) create oxygen vacancies (TiO$_{1.75}$), (ii) dope nitrogen (TiO$_{1.75}$N$_{0.25}$), and (iii) dope fluorine (TiO$_{1.75}$F$_{0.25}$) and examine their magnetic states. We take these cases to compare the effect of NM anion doping of F and N atoms with the aim of evaluating the influence of electron or hole doping on the electronic and magnetic properties of the system. Our results show that oxygen vacancies do not induce any appreciable magnetization in TiO$_2$. However, doping of N and F atoms induces a magnetic ground state, with magnetic moments appearing prominently at N and Ti sites, respectively.

2. Computational details

The spin-unpolarized, i.e. NM, and spin-polarized (SP) electronic structure calculations of TiO$_2$, TiO$_{1.75}$, TiO$_{1.75}$N$_{0.25}$ and TiO$_{1.75}$F$_{0.25}$ compounds have been carried out by using a state-of-the-art full-potential linearized augmented plane wave (FP-LAPW) method [23]. The lattice parameters used in the calculations are $\alpha = 3.785$ Å and $\epsilon = 9.514$ Å, and the atomic position taken for the oxygen atom is $z = 0.2066$. The muffin-tin sphere radii are chosen to be 2, 1.6, 1.5, and 1.45 au for Ti, O, F, and N atoms, respectively. For the exchange correlation functional, we have adopted the recently developed generalized gradient approximation (GGA) form of Perdew et al [24]. The self-consistency was achieved by demanding the convergence of the total energy to be smaller than 10$^{-6}$ hartree/cell. The total magnitude of the force per unit cell comes out to be less than 0.003 hartree/bohr.

3. Results and discussions

The anatase TiO$_2$ crystallizes in the body center tetragonal structure (space group $I\bar{4}1/amd$) where Ti and O occupy 4a (0, 0, 0) and 8e (0, 0, z) Wyckoff positions, respectively. Therefore, the conventional unit cell contains four Ti and eight O atoms. The atomic arrangement in the unit cell is shown in figure 1. Each Ti atom is surrounded by six O atoms. Out of six Ti–O bonds, four bonds are of equal length (1.937 Å) and the other two have a bond length of 1.965 Å. In order to see the effect of non-magnetic electron and hole doping on the electronic and magnetic properties of the compound we have replaced O$_2$ by fluorine and nitrogen atoms, respectively. Similarly, the effect of oxygen vacancy is also studied by removing the O$_2$ atom.

The total density of states (TDOS) per formula unit (f.u.) of TiO$_2$, TiO$_{1.75}$, TiO$_{1.75}$N$_{0.25}$, and TiO$_{1.75}$F$_{0.25}$ compounds are shown in figure 2. The TDOS of TiO$_2$ in both the spin channels is perfectly symmetric, which is in accordance with the NM ground state of the compound. The band gap of TiO$_2$ is found to be $\sim$2.1 eV, which is about 1 eV lower than the experimentally observed value [11]. The discrepancy between the calculated and experimental results is not surprising as GGA calculations are often found to underestimate the band gap of semiconductors and insulators. The creation of an oxygen vacancy does not have much influence on the magnetic state of the system since the TDOS of TiO$_{1.75}$ in both the spin channels also looks symmetric, as evident from figure 2(b). This observation is in contrast to the previous pseudo-potential based calculations showing a magnetic ground state driven by oxygen vacancies [20]. The GGA + $U$ results of Yang et al show the formation of a magnetic moment of 1 $\mu_B$ at each of two neighboring Ti sites [20]. In order to look into the possibility that on-site Coulomb interaction ($U$) among Ti 3d electrons might be responsible for the creation of magnetic moments in the work of Yang et al, we also carried out a GGA + $U$ calculation and could not find any magnetic moment at the Ti sites even for $U = 4$ eV, which is a reasonable value of $U$ for the 3d electrons [25–27]. At this juncture, it is important to note that full-potential calculations are often found to provide more accurate results in comparison to pseudo-potential ones. Our calculations give a negligibly small magnetic moment at Ti sites, which is consistent with earlier full-potential based result [19]. Interestingly, the oxygen vacancy creates an electron-like band just below the bottom of the conduction band (CB). The band gap between top of the valence band (VB) and the bottom of the impurity band is found to be $\sim$1.1 eV and that between the top of the impurity band and the bottom of the conduction band is $\sim$0.1 eV. This result suggests that the oxygen vacancy gives rise to a significantly large increment in the number of charge carriers at room temperature, which is consistent with the available experimental data [11].

The doping of NM impurities at the O$_2$ site provides a highly asymmetric energy distribution of the states closer to the Fermi level ($\epsilon_F$) in both the spin channels, as is evident
Figure 2. Total density of states (TDOS) per formula unit of (a) TiO$_2$, (b) TiO$_{1.75}$, (c) TiO$_{1.75}$N$_{0.25}$, and (d) TiO$_{1.75}$F$_{0.25}$ compounds.

from figures 2(c) and (d). This suggests the creation of net magnetic moments in the compounds. The ground state of N-doped TiO$_2$ is found to be magnetic as the energy of the SP solution is $\sim 102$ meV/f.u. less than that of the NM solution. The N-doping shifts the edge of the VB toward $\epsilon_F$ by $\sim 0.5$ eV. Moreover, it gives rise to extended VB states. As expected, N-doping provides a hole-like impurity band. Interestingly, the ground state of N-doped TiO$_2$ is found to be half-metallic as there is no density of states (DOS) at the $\epsilon_F$ in the up-spin channel and the band gap in this channel is found to be $\sim 2$ eV. The F-doping also gives rise to a magnetic ground state as the energy of the SP solution is $\sim 71$ meV/f.u. less than that of the NM solution. The VB of F-doped TiO$_2$ is extended over a wide energy range with the appearance of new states between $-10.9$ and $-8.8$ eV which were absent in earlier cases. These states are expected to arise from the fluorine atoms, which becomes clear later in this paper. As opposed to the case of an oxygen vacancy, the electron-like impurity band of F-doped TiO$_2$ is found to overlap with the CB minimum resulting in a metallic ground state as is evident from figure 2(d). Thus our results provide a simple but elegant way of controlling the electronic transport of TiO$_2$ as it evolves from a wide-bandgap semiconductor to a narrow-band-gap semiconductor to a half-metallic state and finally to a metallic state with oxygen vacancies, N-doping, and F-doping, respectively.

In order to know the energy distribution of the different states we have plotted the Ti 3d and O 2p partial density of states (PDOS) of TiO$_2$ and TiO$_{1.75}$ in figure 3. It is evident from figure 3(a) that the states closer to the top of the VB have a dominant contribution from O 2p orbitals, whereas states in the vicinity of the bottom of the VB have a mixed Ti 3d and O 2p character. Moreover, one can see the finite O 2p PDOS in the CB region above 2 eV. The finite contribution of Ti 3d and O 2p orbitals suggests the breakdown of the pure ionic model for Ti–O bonds and can be considered as a signature of strong hybridization between Ti 3d and O 2p states.
which shift $\sim -0.12$ eV deeper in comparison to Ti1 3d states and (ii) the contribution of Ti2 3d states to the impurity band is about 75%. The first feature may be attributed to the more hybridization of Ti2 3d and O2 2p orbitals in comparison to Ti1 3d and O2 2p orbitals, as the bond length of Ti2–O2 is $\sim 0.03$ Å less than that of Ti1–O2, resulting in increased separation between bonding and antibonding molecular orbitals. The second feature can be attributed to the orbital polarization. In octahedral symmetry two d electrons of the elemental Ti are expected to occupy $t_{2g}$ orbitals. In the anatase structure shown in figure 1, only the $d_{xy}$ orbital is expected to show significant overlap with the O2 2p orbital, resulting in the transfer of an electron to O2, making it negatively charged. In the case of a vacancy at the O2 site, this transferred electron would be taken back by Ti2 and would mainly contribute to the impurity band as seen from the calculation.

The N-doping at the O2 site does not have any influence on the magnetic state of the Ti atoms. The 2p PDOS of N, O1, and O3 are shown in figure 4(a) as these states are found to be most influenced by the doping. The distribution of these states is highly asymmetric in both the spin channels, suggestive of net magnetic moments at N, O1, and O3 atoms. The magnetic moment at the N site is found to be $\sim 0.4$ $\mu_B$ and those at O1 and O3 sites are $\sim 0.1$ $\mu_B$ each. The contribution of magnetic moments from the rest of the sites is negligibly small. The total magnetic moment per f.u. comes out to be $\sim 0.25$ $\mu_B$. The distribution of impurity PDOS around $\epsilon_F$ provides valuable information about the nature of magnetic interaction among the magnetic moments of the impurity atoms [28]. In the up-spin channel one can see the absence of states closer to $\epsilon_F$. However, in the down-spin channel there are finite states in the vicinity of $\epsilon_F$. These states are of highly mixed N 2p and O 2p character. One can also see the appearance of a sharp peak just above $\epsilon_F$ which has a dominant contribution from N 2p orbitals.

Contrary to the N-doping, F-doping at the O2 site gives rise to a net magnetic moment of $\sim 0.3$ $\mu_B$ for the Ti2 atom, keeping magnetic moments of the rest of the atoms negligibly small. The total magnetic moment per f.u. comes out to be $\sim 0.11$ $\mu_B$ f.u.$^{-1}$. In figure 4(b) we have shown the Ti2 3d, O1 2p, and F 2p PDOS as these states are found to be most influenced by the F-doping. Interestingly, the electron type impurity band has mainly Ti2 3d character. The energy distribution of this band in both the spin channels is highly asymmetric and responsible for the creation of a magnetic moment at the Ti2 site. The states found below $-8.8$ eV mainly arise from F 2p orbitals and O1 2p orbitals are mainly contributing between $-7.8$ and $-2.9$ eV.

The above results clearly establish the magnetic ground state on doping non-magnetic impurities at the O sites. However, N-doping creates magnetic moments at the N site whereas F-doping gives rise to a magnetic moment at the Ti2 site. An entirely different effect of N- and F-doping at the magnetic moments is unusual, and appears to be related to the spatial electronic charge distribution of Ti2, N, and F atoms responsible for bond formation. Pure TiO2 is NM as the valence electrons are equally populated in both the spin channels. The F 2p orbitals are highly localized as is evident
from figure 4(b). Such localization of p orbitals prohibits sharing of electrons from the neighboring Ti2 3d electrons and makes transfer of 3d electrons to the F site energetically more favorable. The F 2p orbitals are more than half-filled and hence only down-spin electrons are allowed to be transferred, resulting in net spin polarization of Ti2 3d electrons. Contrary to the F 2p orbitals, N 2p orbitals are extended and can easily share their electrons with neighboring Ti2 3d orbitals, making Ti2–N bonds more coherent in nature. In covalent bonds there is an equal probability of sharing the up- and down-spin electrons. Moreover, N 2p orbitals contain one more electron in comparison to Ti2 3d electrons. Thus the sharing of Ti2 3d and N 2p electrons is expected to provide net spin polarization at the N site due to inert O 2p electrons.

Finally, we explore the possibility of using the above results in real systems. The first difficulty appears to be the synthesis of such compounds as the dopant percentage (either N or F) studied here is quite high if we compare with the results of ZnO [5]. However, Chen et al have reported the synthesis of compounds with dopant percentage as high as 15% N-doped TiO2 [29]. Since the difference between the ionic radius of O and N ions is almost the same as that between O and F ions, F-doped compounds are therefore also expected to be synthesized easily. Moreover, we performed calculations on 6.125% N- and F-doped TiO2 and found similar results as far as formation of magnetic moments is concerned. Thus it appears that the synthesis of compounds, which show finite magnetic moments, is not a problem. However, the mere formation of finite magnetic moments at different sites does not guarantee the collective magnetism which is essential for any practical application. To ascertain this one needs to estimate the optimal concentration of dopant required for percolation of the magnetic interaction. Any such attempt with fair accuracy is very time consuming under the FP-LAPW method and beyond the scope of the present work. However, we feel that the dopant percentage studied here is high enough to induce collective magnetism and should motivate other workers to look into this aspect.

4. Conclusions

In conclusion, we have examined the effect of oxygen vacancies and doping of non-magnetic anions in TiO2 on its magnetic properties. It turns out that an oxygen vacancy leads to electron doping in the system but does not induce appreciable magnetic moment in the system. Interestingly, N doping gives rise to a robust FM half-metallic ground state for TiO1.75N0.25 with the appearance of magnetic moment at N and two neighboring O sites, and hence is expected to provide an innovative prospect for a novel class of DMOS materials with anion doping. On the other hand the ground state of the F-doped sample is found to be metallic with the induction of magnetic moment at the Ti site nearest to the F atom. Since we observe that the electronic state of TiO2 can be controlled from wide-band-gap semiconductor to narrow-band-gap semiconductor to half-metallic to metallic states by selectively managing the anion site, it gives us hope of being able to tune the band gap of TiO2 to further extend its application domain in photo-catalytic and magneto-optic devices. This would also provide us with an understanding of the origin of magnetism in a semiconducting oxide systems by non-magnetic anion doping.

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