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Ab initio study of the electronic states induced by oxygen vacancies in rutile and anatase TiO_2

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There is an impressive interest in titanium dioxide for its several technological applications which include, e.g., photocatalysis and realization of solar cells. Many of such applications utilize the anatase phase rather than the rutile one, as this appears to be more catalytically active and exhibits a higher electron mobility. In the present study, we address the origin of such differences between the anatase and rutile properties and show that they can be related to a remarkable difference in *nature* between the electronic levels induced by bulk oxygen vacancies (V_{Ox}) in the two TiO_2 polymorphs. These levels have indeed different locations in the energy gap and give rise to different localizations of the electronic charge in real space, thus indicating the V_{Ox}'s as important candidates to elucidate the different properties of the two TiO_2 phases. Present results, achieved by applying a U correction to local spin-density (LSD)–generalized gradient approximation (GGA) methods, stress also the importance of beyond-LSD methods when investigating metal oxides. They show indeed that only such methods permit to reveal the different nature of the V_{Ox} electronic states in the two TiO_2 phases.

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Titanium dioxide in its two phases, rutile and anatase, is one of the most investigated and most widely used metal oxides for several technological applications which include, e.g., photocatalysis, production of hydrogen and electric energy in solar cells, and realization of materials for spintronic devices.[1–4] Oxygen vacancies (V_{Ox}) are native defects that easily form during the preparation of this material.[1–3] Different studies have addressed the role of V_{Ox} in bulk TiO_2,[5–11] justified by the potential heavy effects that these defects may have on the material properties.[1–3] For instance, semiconductor photocatalysis starts by creating an electron (e) in the conduction band and a hole (h) in the valence band by optical excitation. These excited carriers diffuse to the surface to initiate chemical reactions with adsorbed molecules, while e-h recombination represents a competing process which tends to prevent the carriers for reaching the surface. Thus, the efficiency of a photocatalytic process depends mainly on three factors: (i) the region of absorption of electromagnetic radiation, possibly extended from UV (the region of undoped stoichiometric TiO_2) to IR and visible regions, (ii) the absorption rate of the semiconductor, which influences the initial number of photoexcited carriers, and (iii) the time required for the carriers to move to the surface to initiate reactions, as compared to their recombination lifetime. Clearly, defect states in the TiO_2 energy gap can influence all of these factors. In this regard, experiments in rutile suggest that V_{Ox}'s induce electronic levels in the energy gap at around 1 eV from the conduction-band minimum (CBM),[7,8] which are occupied by the two electrons left back by the removed O atom. On a different side, it has been suggested that electronic levels induced by V_{Ox}'s can play a significant role in the ferromagnetic behavior of TiO_2-based dilute magnetic semiconductors for spintronic devices.[9,12]

Many of the technological applications of TiO_2 utilize the anatase phase rather than the rutile one, as this appears to be more catalytically active and exhibits a higher electron mobility.[2] Notwithstanding, the origin of such differences between the properties of these TiO_2 polymorphs has not been clarified yet. In the present study, we show that these differences can be related to the different properties of V_{Ox}'s in anatase and rutile. More specifically, they can originate from a remarkable difference in nature of the electronic levels induced by these defects in the two materials. These levels present indeed different locations in the energy gap and give rise to different localizations of the electronic charge in real space. Present results also show that the different nature of the V_{Ox} electronic levels can be explained in terms of a different topology of the defect site in the two materials. Thus, V_{Ox}'s can significantly contribute (possibly with other defects, such as Ti interstitials[13]) to clarify the different properties of anatase and rutile. Finally, our results confirm the importance of beyond–density-functional theory–local-density approximation (DFT-LDA) methods and stress the need of large supercells when dealing with defects in transition-metal oxides. In fact, it has to be noted that (i) the present study has been performed by applying the U correction to the local spin-density–generalized gradient approximation (LSD-GGA) methods and (ii) the achieved results show that only such a correction combined with the use of large supercells permits to disclose the different nature of the V_{Ox} states in the two TiO_2 polymorphs. LSD-GGA calculations do not distinguish, instead, between the two defects, which are both described as shallow donors inducing electronic states close to the CBM.[5,6]

V_{Ox}'s in bulk anatase and rutile have been investigated by using DFT methods as developed in the QUANTUM-ESPRESSO package.[14] Total energy calculations have been performed inside a (beyond-LDA) LSD-GGA+U approach.[15–17] In detail, total energies have been calculated by using a $2\times2\times2$ Monkhorst-Pack **k**-point mesh in a supercell approach, ultrasoft pseudopotentials,[18] and the Perdew-Burke-Ernzerhof gradient corrected exchange-correlation functional.[19] Satisfactorily converged results have been achieved by expanding Kohn-Sham orbitals in plane waves up to energy cutoffs of 25 and 150 Ry for the wave functions and the charge density, respectively. A self-consistent Hubbard U correction of 3.4 eV (3.3 eV) for the d electrons of rutile (anatase) Ti atoms has been calculated by using the

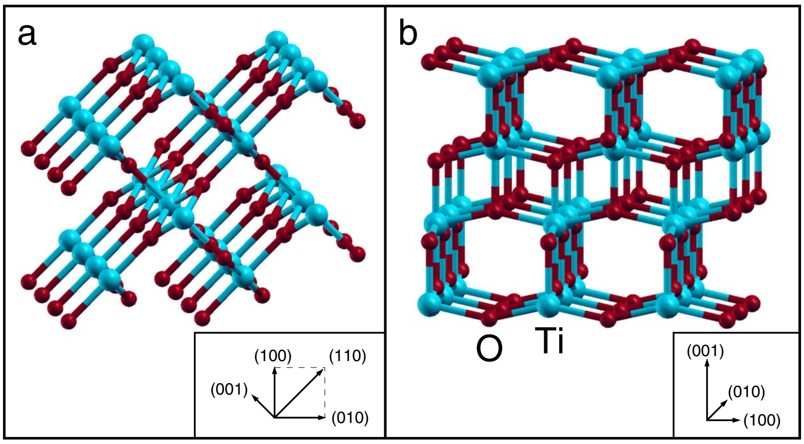

FIG. 1. (Color online) Structure of the supercells used to investigate the properties of oxygen vacancies in bulk TiO_2: (a) rutile and (b) anatase.

linear-response approach described in Refs. 16 and 17. A 96-atom supercell made up by $2 \times 2 \times 4$ unit cells has been used to simulate a rutile stoichiometric bulk crystal [Fig. 1(a)], as well as the properties of a V_{Ox}. Similarly, a $3 \times 3 \times 1$ 108-atom supercell has been used in the case of anatase [Fig. 1(b)]. Geometry optimization procedures have been performed by minimizing the atomic forces of all of the atoms in the supercell. LSD-GGA calculations have also been performed by using the same setup. The U correction has been applied to circumvent the too poor LSD-GGA electron correlation description,[11,10] which can affect the character (shallow or deep) of defect states as well as the degree of localization of the corresponding electronic charge. We have carefully checked the reliability of such a correction in the case of defects in TiO_2. As a matter of fact, the results of present LSD-GGA+U calculations as well as of similar calculations (not reported here) closely agree with those achieved by using hybrid functionals in the cases of bulk V_{Ox} in rutile[10] and surface defects in anatase (i.e., bridge OH species and vacancies),[11] respectively. More specifically, while in these cases LSD-GGA results indicate that the defect electrons are accommodated in shallow electronic states approaching the bottom of the conduction band,[5,6] both hybrid functionals and our LSD-GGA+U results indicate that the same defects induce deep levels in the energy gap.

Let us consider now the local structure of V_{Ox} in rutile. The positions of Ti and O atoms located on a (110) plane of the bulk material are shown in Fig. 2(a). The relaxed positions of the same atoms after removal of an O atom are shown in Fig. 2(b). The Ti atoms nearest neighboring (NN) the vacancy displace within the (110) plane by moving away from the vacancy site. Thus, rutile reacts with a sort of breathing relaxation to the vacancy formation. In fact, the above displacements produce changes in the Ti-O bond lengths which, however, do not alter the shape of the local geometry around the site of the removed O atom. The V_{Ox} formation energy, 4.4 eV, agrees with previous analogous estimates.[20] The electronic structure of this defect is characterized by two spin-parallel electronic levels located at 1.0 and 1.2 eV from the valence-band maximum (VBM), as shown by the spin density of states (spin-DOS) in Fig. 3(a). Although in the same figure the estimated CBM is at 2.0 eV from VBM against an experimental energy gap of 3.0 eV,[1] the location of the two V_{Ox} levels suggests a deep donor behavior of the defect, confirmed by the spin-density plots of Figs. 4(a) and 4(b). These plots clearly indicate indeed a high localization of the two V_{Ox} electronic levels on d orbitals of two Ti NN the vacancy. Moreover, such a localization in the real space is accompanied by a flatness of the defect levels in the Brillouin zone (BZ) [Fig. 5(a)], both features being typical of deep levels.

The above results locate the electronic levels of a V_{Ox} in rutile at about 1 eV below the CBM, in agreement with the experiment[7,8] and theoretical results based on hybrid

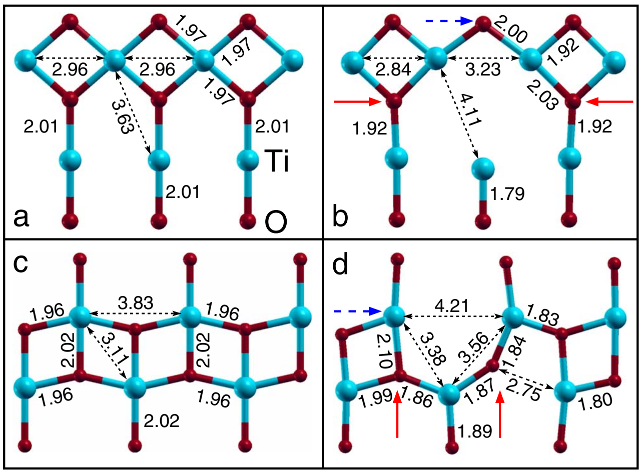

FIG. 2. (Color online) Optimized geometries of bulk rutile and of an oxygen vacancy in a (110) plane are given in (a) and (b), respectively. The analog for a (100) plane of anatase is shown in (c) and (d), respectively. The arrows indicate O atoms neighboring the vacancy site (see the text). Atomic distances are given in angstroms.

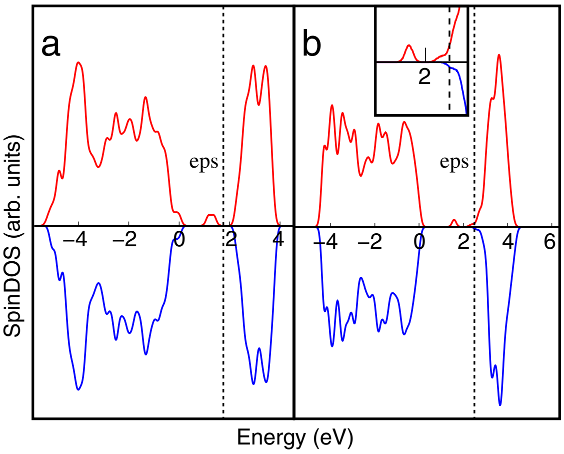

FIG. 3. (Color online) Spin-DOS evaluated for an oxygen vacancy in bulk (a) rutile and (b) anatase. ε_F is the Fermi energy. The zero of energy is at the top of the valence band.

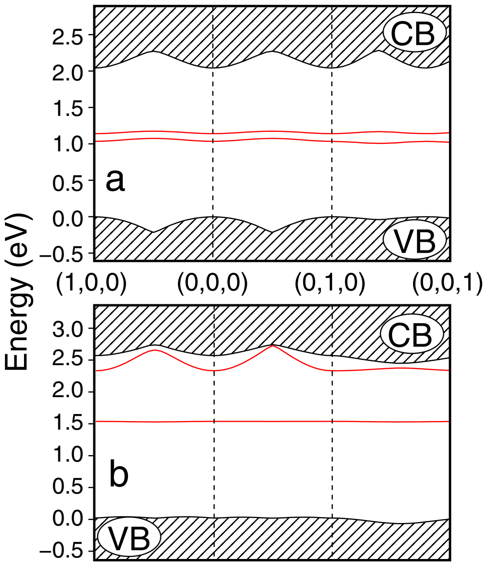

FIG. 5. (Color online) Dispersion of oxygen vacancy levels (red lines), top of the valence band and bottom of the conduction band, along three main symmetry directions in the Brillouin zones of the investigated supercells: (a) vacancy in bulk rutile and (b) vacancy in bulk anatase.

functionals.[10] Present results suffer instead for the well-known underestimate of the energy gap produced by the LSD approximation. In spite of that, our results clearly show that a thoroughly different picture emerges for a V_{Ox} in bulk anatase. Figures 2(c) and 2(d) show the geometry of Ti and O atoms located on a (100) plane of this material and their rearrangement after the vacancy formation, respectively. These figures show that, at variance with the case of rutile, the removal of an O atom induces a dramatic change in the local geometry around the vacancy site: one of the NN O atoms breaks indeed its bond with a Ti atom and approaches two NN Ti atoms by strengthening the corresponding Ti-O bonds and becoming twofold coordinated (O_{2c}). Such a remarkable structural difference between the V_{Ox} geometries in anatase and rutile induces a parallel remarkable difference in the electronic structure of the defect in the two compounds. In fact, for a V_{Ox} in anatase, two spin-parallel electronic levels are found at 1.5 and 2.3 eV from VBM, as shown by the spin-DOS reported in Fig. 3(b), where the CBM is at 2.4 eV from VBM against an experimental energy gap of 3.2 eV.[1] These results suggest a quite different character, deep and shallow, respectively, for the two electronic levels induced by a V_{Ox} in anatase. The shallow character of the level higher in energy is supported by its closeness to the estimated CBM and by its dispersion in the BZ which *parallels* that of the conduction band [Fig. 5(b)], as typically found for shallow levels. The spin-density plots corresponding to the two electronic levels (Figs. 4(c) and 4(d)) confirm their different characters. The lower level is indeed localized on the Ti neighbor less perturbed by the structural rearrangement [see the blue arrow (dashed line) in Figs. 2(d) and 4(c)], whereas the higher level is widely delocalized on Ti atoms far from the vacancy [Fig. 4(d)]. The formation energy of the V_{Ox} in anatase, 4.0 eV, agrees with previous estimates.[20]

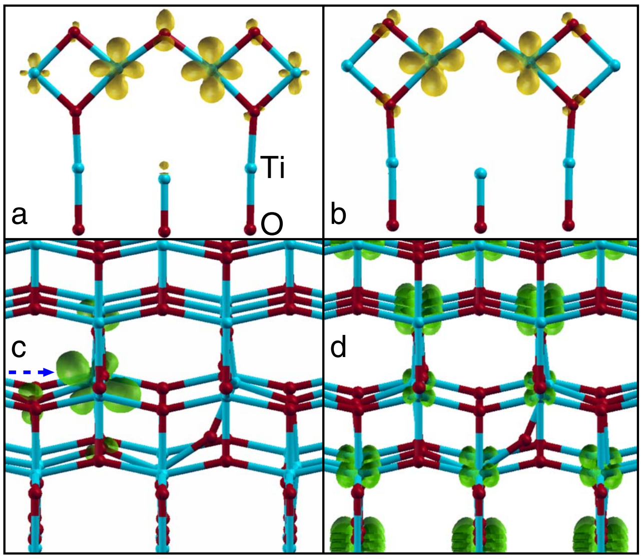

FIG. 4. (Color online) Spin density distributions corresponding to defect states induced by an oxygen vacancy (V_{Ox}): [(a) and (b)] defect states in rutile and [(c) and (d)] defect states in anatase.

The difference in nature of the electronic states of a V_{Ox} in rutile and anatase originates from an intrinsic property of the defect, that is, the topology of the defect site. In this regard, two O atoms surround the anatase V_{Ox} [see red arrows (full lines) in Fig. 2(d)], both bonded to two Ti neighbors. In rutile, instead, three O atoms surround the V_{Ox}, the two equivalent (by symmetry) O atoms indicated by the red arrows (full lines) in Fig. 2(b) and the O atom indicated by the blue arrow (dashed line) in the same figure. The two equivalent O atoms have a different topology with respect to the two O neighboring the anatase V_{Ox} because they are bonded to only one of NN Ti. This implies that these O atoms cannot break an O-Ti bond to produce an O_{2c} configuration and benefit from the structural relaxation of two NN Ti. The third O neighbor does not play a significant role in the structural rearrangement accompanying the V_{Ox} formation. Even more, it cannot become twofold coordinated. In fact, even if this atom is bonded to two Ti NN the vacancy like the O neighbors of the anatase V_{Ox}, its hypothetical twofold coordination would require an increase in the distance between the two involved Ti neighbors [the atoms distant 3.23 Å in Fig. 2(b)] (Ref. 21) which is hindered by the presence of the *close Ti atoms* located on the same line. On the contrary, the corresponding increase in the Ti-Ti distance in anatase [that involving the two Ti NN at 3.56 Å in Fig. 2(d)] is favored by Ti displacements pointing toward *empty spaces* in the lattice channels. Even this result is related to the different topologies of the defect sites.

The importance of topology is further elucidated by the geometry relaxation patterns. Geometry optimizations were performed starting with unrelaxed structures, without symmetry constraints and by sampling both singlet and triplet states of the V_{Ox}. The stable configurations correspond to the triplet states, which are lower in energy than the singlet states by 0.1 and 0.5 eV in the cases of rutile and anatase, respectively. In rutile, the optimized V_{Ox} configuration maintains the local symmetry of the unrelaxed one both in the singlet and triplet states. In anatase, the local symmetry of the unrelaxed configuration is maintained only in the singlet state. For the triplet state, instead, the relaxation pattern shows a breaking of the (local) symmetry equivalence between the two NN O atoms, which basically occurs in a spontaneous way by leading to the O_{2c} configuration. It should be noted that, in this configuration, the O_{2c} atom not only breaks one Ti-O bond but also induces a shortening and strengthening of several Ti-O bonds surrounding the vacancy [see Fig. 2(d)].

The different topologies of the V_{Ox} site are responsible for the different local structural rearrangements which, in turn, are intimately related to the electronic charge localization. In fact, in the unrelaxed V_{Ox} configurations, such a localization involves all of the three NN Ti as shown by spin-density distributions of the defect states (not reported here). In the relaxed configurations, instead, the formation of shorter Ti-O bonds is related to the absence of localized charge on the involved Ti atoms (compare Figs. 2 and 4). This accounts for the appearance, only in anatase, of a deep level localized on NN Ti faced to the O_{2c} and of a shallow delocalized level.

In conclusion, present results show that only in anatase a V_{Ox} can induce a shallow electronic level, high in energy and strongly delocalized, together with a deep and localized level. In rutile, instead, the same defect induces only deep localized levels. The existence of a shallow level in anatase indicates the V_{Ox}'s as native defects which can significantly contribute to clarify the main differences observed between the properties of anatase and rutile of interest for technological applications. In fact, such a level may account for, e.g., the superior electron transport in anatase.[22,23] It can also favor the activation of electrons in the conduction band, their diffusion on the surface, as well as a longer *e-h* recombination time, thus accounting for the superior photocatalytic activity of the same material.

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