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Properties of hydrogen and hydrogen–vacancy complexes in the rutile phase of titanium dioxide

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The interaction of atomic H with host atoms and oxygen vacancies (V_O) in the rutile phase of the TiO_2 metal oxide has been investigated by using density-functional theory-local spin density (DFT-LSD) and DFT-LSD $+U$ theoretical methods. The achieved results show that H in rutile presents quite different and peculiar properties with respect to other semiconductors and metal oxides. It behaves indeed neither as an amphoteric impurity, as it does in Si and GaAs, nor as a shallow donor, as it has been proposed in ZnO. Moreover, H in rutile represents a failure of a theoretical model proposing a universal alignment of the H-induced electronic level in the energy gaps of semiconductors, which predicts a shallow donor behavior of H in ZnO and TiO_2. Present results show indeed that H behaves as a deep donor in rutile and always forms an OH^+ complex, independent of the position of the Fermi energy. This very unusual behavior of H can be accounted for by a peculiar property of TiO_2 regarding its capability of localizing extra electrons at Ti^{+3} sites. The electron lost by H can be accommodated indeed by a Ti^{+4} atom which evolves in a Ti^{+3} defect. This accounts for the deep behavior of H and implies that the electronic level it induces in the TiO_2 energy gap has, actually, a Ti^{+3} character quite similar to that characterizing an O vacancy (V_O), thus distinguishing H in rutile from H in other semiconductors. Finally, H can form stable $H-V_O$ complexes where it takes the place of the missing O atom by forming a bond with a prevailing ionic character, at variance with a multicenter bond model proposed for the same complexes in ZnO.

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I. INTRODUCTION

The properties of atomic hydrogen in semiconductors have been widely investigated for the unique and many different effects this impurity has on the properties of the host material.[1,2] Due to its small size and high reactivity, atomic H diffuses in the semiconductor lattice and strongly interacts with host atoms, impurities, and defects. In crystalline IV and III-V semiconductors, showing a prevailing covalent character, H generally behaves as an amphoteric, interstitial impurity.[1,3] These semiconductors present indeed a regular framework of regions of high electron density along the covalent bonds which surround low-density regions. In high electron-density regions, H tends to loose its electron by behaving as a donor and forming H^+ ions. In regions of low density, instead, H can gain one electron by assuming the stable configuration of helium and forming H^- ions, thus behaving as an acceptor. Then, in these semiconductors, H can compensate both shallow donors and acceptors. Moreover, the H^+ and H^- ions can diffuse and bind to ionized impurities forming complexes which can lead to a full passivation of the dopant by wiping the corresponding electronic levels off the semiconductor energy gap.[1,2] Similarly, H can neutralize the effects of native defects of the semiconductors such as, e.g., vacancies, by saturating the corresponding dangling bonds.[1,4,5] In several semiconductors, H behaves also as a negative-U impurity by giving rise to a H^+ and H^- pair more stable than $2H^0$. The H properties can change significantly in semiconductors showing a marked ionic character, such as metal oxides (e.g., ZnO, CdO, or SnO_2) where, as indicated by previous theoretical studies,[6–8] H is expected to behave as a shallow donor dopant which can induce an electron level close to or resonant with the semiconductor conduction band (CB). More specifically, for metal oxides, a theoretical study has proposed the existence of a hydrogen pinning level, located at a fixed position with respect to the vacuum level, which permits to predict if an oxide can be n-type doped by a shallow donor H only by looking at the position of that level with respect to the semiconductor band edges.[6] Remarkably, such a suggestion has been subsequently generalized by a different theoretical study that proposed the existence of a universal alignment for the electronic levels induced by H in the semiconductors and insulators energy gaps.[8] A further difference between the H properties in covalent semiconductors and metal oxides regards the H interaction with vacancies. As mentioned above, H tends to saturate the dangling bonds of, say, a Si or Ga vacancy. On the other hand, in ZnO, the existence of H multicenter bonds has been theoretically predicted for a H forming a complex with an oxygen vacancy (V_O), where it takes the place of the missing O atom, H_O, and binds covalently to the surrounding Zn atoms.[9] The formation of such a H_O-V_O complex has important consequences, it changes indeed the deep donor character of the V_O to a shallow one, thus it may account for the observed unintentional n-type conductivity of ZnO.

In the present study, we focus on the properties of atomic H in the rutile phase of titanium dioxide (TiO_2) as well as on the formation and properties of H_O-V_O complexes in this metal oxide. TiO_2 is a technologically strategic material for applications in different fields which can be roughly divided into "energy" (solar cells or photochromic/electrochromic devices),[10] "environment" (TiO_2 is the most important photocatalyst for environmental applications),[11] and, in perspective, "information technology" (TiO_2 doped with magnetic impurities is a promising dilute magnetic semiconductor or DMS, for realizing spintronic devices).[12] All of these applications rely on the electronic and optical properties of TiO_2 and, therefore, on the properties of its defects and dopants.

For instance, a fundamental step in the photocatalytic processes is the photogeneration of an electron-hole pair by adsorption of light. The rutile energy gap (3.0 eV) requires UV radiation for such a photogeneration process whereas adsorption of visible light would be highly desirable in order to fully exploit the spectrum of solar radiation.[10,11] In principle, this condition could be favored by intrinsic defects of rutile. Electronic levels at about 1 eV below the conduction band have been observed in rutile and related to the presence of oxygen vacancies,[13] while changes of color and conductivity have been observed in reduced materials.[14] The introduction of *deep* electronic levels could affect therefore the rutile photocatalytic activity. An important role of oxygen vacancies has been also suggested in the magnetic behavior of a TiO_2-based DMS.[15] On the other hand, *shallow donor* impurities could increase the TiO_2 conductivity, which is important for solar cells or spintronics devices. In this regard, it has to be noted that the above mentioned study proposing a hydrogen pinning level in metal oxides predicts a H shallow donor behavior in TiO_2.[6] The same suggestion seems given by the study proposing a universal alignment of the H levels. Such an alignment would imply indeed a H shallow donor level in ZnO whose level band edges have locations with respect to the vacuum level almost identical to those of TiO_2.[8,16] All of the above considerations justify the present theoretical investigation of the properties of H in rutile TiO_2 devoted to give answers to the following questions: (i) how does H bind in the host rutile? Where? How stable is the bond? (ii) Does H behave as a shallow or as a deep donor in rutile? And, as a related question: does H in rutile represent a success or a failure of the universal alignment model? (iii) Is H an amphoteric, negative-U impurity in rutile? (iv) Does H form multicenter bonds in H_O-V_O complexes? (v) Can the formation of H_O-V_O complexes change a rutile V_O from a deep to a shallow donor character, as it occurs in ZnO?

Present results have been achieved by performing density-functional theory (DFT) LSD-GGA+U (local spin density-generalized gradient approximation+Hubbard U correction) calculations. The Hubbard U correction has been applied to overcome the DFT self-interaction error, which can induce an electron over-delocalization. Standard LSD-GGA calculations have been performed as well for reference. In order to avoid a parametric use of the U correction (recently criticized by Pacchioni *et al.*[17]), we have corrected for the d electrons of rutile Ti atoms applying a Hubbard U correction calculated self-consistently by means of the linear-response approach described in Refs. 18 and 19. As a good practice, especially true for corrections applied to overcome some model difficulties, the present LSD+U approach has been carefully checked by comparing its results with available experimental and theoretical findings. We performed such a comparison in two previous studies[20,21] in the cases of rutile defects such as surface V_O's and bridge hydroxyl (OHb) groups and bulk V_O's. The main results obtained there will be briefly reported here, together with those from recent studies, for the following reasons: (i) the properties of the above defects are closely related to the properties of interstitial H and H_O-V_O complexes investigated in the present study, (ii) they permit to illustrate some significant differences between the results given by LSD+U and (widely used) LSD methods, and (iii) they show that our approach provides a qualitatively correct picture of the properties of the above defects, thus making us confident on the results achieved here for H and its complexes.

Preliminarily, it should be recalled that TiO_2 has a prevailing ionic character and therefore can be formally considered made of Ti^{+4} and O^{-2} ions. Within this picture, in the following we focus on a common feature of the above-mentioned rutile defects, that is, the formation of Ti^{+3} species, as well as on the different pictures given by LSD and LSD-corrected methods. Considering V_O's and OHb's at a rutile surface, a defect level at about 0.8 eV below the CB has been experimentally observed and related to electrons localized at Ti sites which change their state from Ti^{+4} to Ti^{+3}.[22–24] A recent resonant photoelectron diffraction (RPD) study has confirmed the localization of electrons induced by surface V_O's, by specifying that the defect charge sits mainly on a subsurface Ti neighboring the vacancy.[25] A subsequent scanning tunneling microscopy investigation has suggested instead a delocalization of the V_O electrons on several surface Ti neighbors of the vacancy.[26] However, in this study, the interpretation of the results thoroughly disregards any electron localization at subsurface sites, thus making questionable the final conclusions. Then, the available experimental findings support a spatial localization of the V_O electrons as well as a deep location of the corresponding levels in the rutile energy gap. Results from LSD simulations on these defects disagree with such features by showing the appearance of defect electronic levels resonant with the CB and fully delocalized.[20,21,27] On the contrary, and in agreement with the experimental figures just summarized, hybrid functionals[27] and LSD+U results[20,21,28–30] localize the defect electrons on Ti neighboring the defect and indicate a deep character of the defect itself. In detail, for a surface V_O, recent LSD+U results localize the defect electrons at subsurface sites in a close agreement with the RPD results.[31,32] For an OHb pair, hybrid functionals give two electronic levels at 1.2 and 1.6 eV below the CB, with a band gap estimated 3.4 eV against an experimental value of 3.0 eV.[14] Our LSD+U results[20,21] show the appearance of a deep defect level at about 1.8 eV from the top of the valence band (VB), that is, 1.2 eV from the experimental CB and 0.63 eV from the CB calculated for the (110) rutile surface (2.43 eV).

In the case of bulk rutile, defect levels are observed at 0.75 and 1.18 eV below the CB and related to V_O's.[13] These levels are expected to be localized at Ti^{+3} sites, since in reduced samples, where V_O's are created in the bulk of the material, the electron-paramagnetic-resonance signal is identical to that of photogenerated electrons created in the presence of UV irradiation and trapped at Ti^{+3} sites.[11] Our LSD+U results indicate that V_O's in bulk rutile induce two electronic levels at 0.85 and 1.05 eV below a calculated CB of 2.05 eV, which are localized on two Ti^{+3} atoms neighboring the vacancy. These results closely resemble those of an hybrid functional DFT study, which localizes the vacancy electrons mainly on two Ti neighbors and locates a defect level at about 1 eV below the CB,[33] while they disagree with DFT-LSD findings indicating a delocalization of the V_O electrons and defect levels located close to the CB.[32,34]

In summary, the above experimental findings give clear evidence of both deep character and spatial localization of the V_O- and OHb-induced electronic levels in rutile. The LSD delocalization of the charge induced by the above defect states seems to be a self-interaction effect rather than a physical property of the defect itself. The presence of empty Ti 3*d* states can induce indeed the defect charge to localize, and only a good treatment of exchange and correlation terms for spatially concentrated atomic orbitals is capable to overcome the self-interaction error and its erroneous picture of a defect state delocalized and resonant with the bottom of the CB. Actually, hybrid functionals and LSD+U approaches seem to fulfill the available experimental indications.

II. METHODS

The properties of H, V_O's, and H_O-V_O complexes in bulk rutile have been investigated by using DFT methods inside a (beyond LDA) LSD-GGA+U approach[18,19,35] as developed in the QUANTUM-ESPRESSO package.[36] Calculations have been performed in a supercell approach, with ultrasoft pseudopotentials,[37] and the Perdew-Burke-Ernzerhof gradient-corrected exchange-correlation functional.[38] A 96-atom supercell made up by $2\times2\times4$ unit cells has been used to simulate a rutile stoichiometric bulk crystal as well as the properties of H and defects. Total energies have been calculated by using a $1\times1\times1$ Monkhorst-Pack **k**-point mesh by expanding Kohn-Sham orbitals in-plane waves up to energy cutoffs of 30 and 180 Ry for the wave functions and the charge density, respectively. Careful convergence checks have been performed by passing from 96-atoms to 120-atoms ($2\times2\times5$ unit cells) supercells, from $1\times1\times1$ to $2\times2\times2$ Monkhorst-Pack **k**-point mesh, or from 30/180 to 35/210 Ry cutoffs. All give negligible differences. Convergence has been also achieved with respect to the interaction of a defect with its own replicas (the dispersion of a defect level being below 0.2 eV). LSD-GGA calculations have been performed by using the same setup. The Hubbard U correction for the d electrons of Ti atoms has a value of 3.37 eV, calculated by using the self-consistent linear-response approach described in Refs. 18 and 19. The lattice parameters have been optimized according with the computational setup, i.e., energy cutoff and Hubbard U values ($a=b=4.670$ Å, $c=2.976$ Å for LSD, $a=b=4.659$ Å, $c=3.018$ Å for LSD+U, $a=b=4.584$ Å, $c=2.953$ Å for experiment, see Ref. 14). The equilibrium geometries of interstitial H and vacancies have been optimized by minimizing the atomic forces of all of the atoms in the supercell. In the case of charged supercells, the presence of a compensating uniform background jellium has been assumed.[39]

The energetics and the electronic properties of H and its complexes have been investigated by estimating formation energies and transition energy levels. As an example, the formation energy of a complex formed by an interstitial H with a q charge is

$$\Omega_f[\mathrm{H}]^q = E[\mathrm{H}]^q - E[\mathrm{TiO_2}] - \mu_{\mathrm{H}} + q(E_F + E_{\mathrm{VB}}),$$

where $E[\mathrm{H}]^q$ is the total energy of a TiO_2 supercell containing one H atom, μ_H is the H chemical potential, assumed here equal to half the energy of a H_2 molecule or, alternatively, to the energy of a H atom in the vacuum, E_F is the Fermi energy, and E_{VB} is the top of the VB.[40,41] E_{VB} is taken at the Γ point, whose inclusion in the **k**-point mesh has negligible effects on the formation energy values. Any Makov-Payne-type correction is negligible as well, given the high dielectric constant in TiO_2 rutile.[14] The Fermi energy E_F, referenced to the top of the VB, represents the chemical potential of the electrons, assumed in a reservoir in contact with the system, and available in order to change the charge state of the defects. Analogously, μ_H is the energy of the reservoir with which H atoms are exchanged. Analogous considerations are valid for the formation energy of an oxygen vacancy, where μ_O is assumed equal to half the energy of a O_2 molecule.

At equilibrium conditions, the formation energy determines the concentration c of the impurity in the semiconductor, through the expression

$$c = N_{\mathrm{sites}} \exp(-\Omega_f/kT),$$

where N_{sites} is the number of available sites for the defect in the supercell.

Transition energy levels $\epsilon^{n/n+1}$ are estimated by the E_F position where the formation energies of the n and $n+1$ charge states of a defect are equal.[40,41] These quantities permit to estimate the charge state of the defect for a given E_F as well as the position of the electronic level induced in the TiO_2 energy gap, as could be observed by experimental techniques including relaxation effects. Energy levels of the bulk and defective charged systems are aligned through an electrostatic potential alignment.[39]

Electronic properties have been investigated by considering transition levels, Kohn-Sham electronic eigenvalues and charge-density maps. Features of the H chemical bonding have been analyzed also by calculating difference electron-density (ρ_{diff}) maps. For example, in the H_O-V_O complex (formed by a V_O with a H atom inside), $\rho_{\mathrm{diff}}[H_O-V_O]$ is given by $\rho[H_O-V_O]-(\rho[V_O]+\rho[H_O])$, where $\rho[H_O-V_O]$ is the electron density of a supercell containing the complex, $\rho[V_O]$ is the electron density of the same supercell with the empty vacancy, while $\rho[H_O]$ is the density of the single H atom positioned in an otherwise empty supercell. Thus, a $\rho_{\mathrm{diff}}[H_O-V_O]$ map indicates the charge displacements induced by the interaction between the H atom and the atoms surrounding the oxygen vacancy.

Vibrational frequencies of stretching H local modes have been calculated by fitting energy vs displacement curves with fourth-degree polynomials. Harmonic frequencies as well as anharmonic corrections have been estimated according to Ref. 42. Finally, energy barriers for dissociation of H_2 molecule as well as of chemical bonds formed by interstitial H with host atoms have been estimated by using the nudged elastic band (NEB) method (see, e.g., Ref. 43).

III. RESULTS AND DISCUSSION

Generally, the results reported in this section have been achieved by using the LSD+U approach. In some cases, explicitly specified, LSD calculations have been also performed for a comparison.

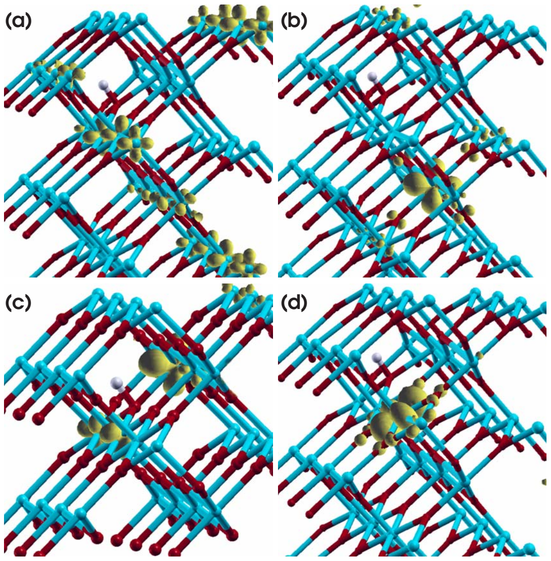

FIG. 1. (Color online) Geometries of interstitial H in rutile and isosurfaces of the charge densities (ψ^2) relative to the H-induced electronic states. (a) Equilibrium LSD results for neutral H. (b) Equilibrium LSD+U results for neutral H. (c) LSD+U results for neutral H in the unrelaxed lattice. (d) Equilibrium LSD+U results for the second electronic state induced by H^-. Electronic densities are sampled at 5×10^{-3} e/(a.u.)^3. Ti, O, and H atoms are represented in light blue, red, and light gray, respectively (medium gray, black and light gray, respectively, in printed version).

A. Structural and electronic properties of interstitial H

First, we have investigated the interstitial sites of neutral H in bulk rutile. Different sites have been sampled in the geometry optimization calculations. Both the LSD and LSD+U find the same stable configuration, shown in Figs. 1(a) and 1(b), where H forms a H-O bond having a length of 1.01 Å and perpendicular to the plane of the Ti atoms neighboring the O atom. A previous LSD study of rutile gave a quite similar result.[44] Present LSD results indicate also a H electronic level close to the calculated CB and quite delocalized, as shown by the map of the corresponding electron density (ψ^2) in Fig. 1(a). LSD+U results give instead a level located at 1.0 eV below the calculated CB (2.05 eV) and localized on a Ti atom neighboring the OH group, see Fig. 1(b), which turns from Ti^{+4} to Ti^{+3}. From the electronic map in the figure, it may be noted how the shape of the state closely resembles that of an atomic *d* orbital. The electron localization affects the local geometry of the Ti^{+3} which has Ti-O bonds ≈6% longer than a Ti^{+4}. This same feature is shown by Ti^{+3} sites originating from the above mentioned surface and bulk defects, as reported in Refs. 20, 21, and 27. The dispersion curves of the H levels induced in the band gap, shown in Fig. 2, clearly indicate a quite different description of the defect given by either LSD or LSD+U approaches. LSD sees a shallow electronic level in resonance with the bottom of the CB, while LSD+U sees a deep level, with little or no dispersion, and far away from the band edges. Not surprising, after the different space localization of the charge densities already shown in Figs. 1(a) and 1(b).

All in all, LSD+U results indicate that a neutral H binds to an O atom as a H^+ ion, gives its electron to a neighboring Ti^{+3} by forming an OH^+-Ti^{+3} pair, and induces a deep level in the rutile energy gap. Moreover, a "polaronlike" distortion, that is, an appreciable local structural rearrangement, accompanies the charge localization at the Ti^{+3} site. In order to investigate the effects of such a distortion on the H-induced level, the electronic properties of a neutral H have been also investigated in a "polaron-free" configuration obtained by hindering the structural rearrangements of the Ti and O atoms in the simulation supercell. Then, the H atom has been placed in a bulk supercell at the optimized distance of the neutral O-H pair, and it has been the only atom allowed to relax. In the resulting geometry, the O-H bond has a length of 1.03 Å, almost identical to that estimated for the OH^+-Ti^{+3} complex. Moreover, the electron lost by the H atom is localized on its nearest neighboring Ti atoms (one Ti neighbor carrying a predominant fraction of electronic charge) as shown in Fig. 1(c), which reports the electron-density map of the H-induced electronic level. Such a picture is confirmed by the analysis of the projection of the electronic state on Ti atomic orbitals (not reported here). Accordingly, the Kohn-Sham H electronic level is located appreciably below (0.3 eV) the bottom of the conduction band. These results indicate that H looses its electron to bind to an O atom, but, even in absence of a structural distortion, it does not induce an electron level close to the conduction band or having a conduction-band character (i.e., showing a delocalization on several Ti atoms). This result is closely related to

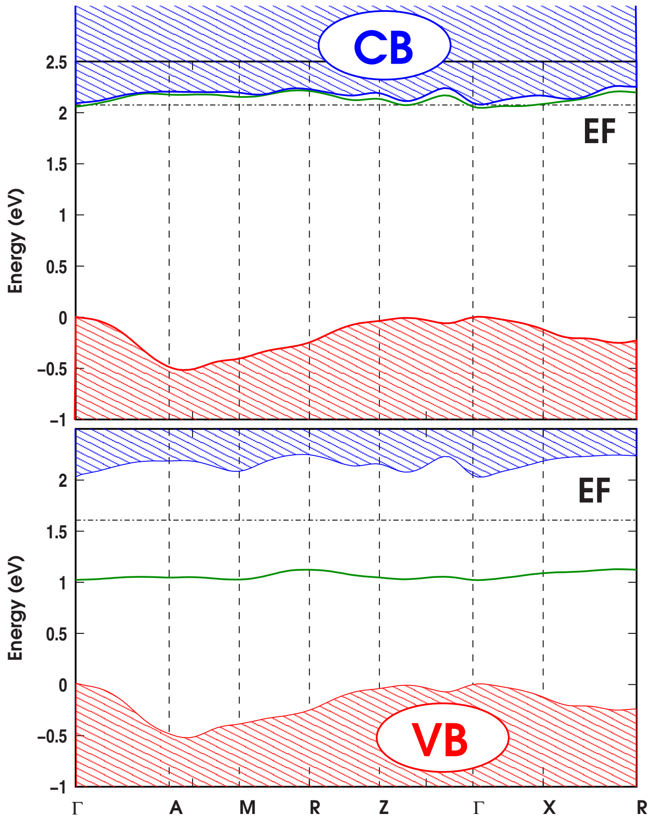

FIG. 2. (Color online) Dispersion curves in the Brillouin zone for electronic states in neutral hydrogenated rutile supercells. Upper panel, LSD results, lower panel, LSD+U results. Reference is taken on top of the valence band.

the presence of basically empty Ti 3*d* states which permit the exceeding charge to remain confined in the neighborhood of the positive charge of the proton. Such a behavior is typical of deep donor impurities, which localize the exceeding electronic charge close to their location. Our results indicate therefore that H in rutile is a deep donor at variance with the shallow character predicted by the universal alignment model. They also suggest that similar exceptions to the predictions of that model could be found in the case of metal oxides formed by transition metals having empty (e.g., Hf) or scarcely filled *d* shells.

The −1 and +1 charged states of H have been also investigated by adding and subtracting one electron to the simulation supercell, respectively. The achieved LSD+*U* results show that the neutral and charged −1 and +1 states of H give rise to the same configuration already shown in Fig. 1, the H-O bond having the same length of 1.01 Å. More specifically, they show that a H^- ion does not exist in rutile. In fact, different sites have been sampled in a negatively charged supercell but none of them reaches any stable or metastable configuration for H. In other words, there are no sites in pristine rutile where H can carry a charge of −1 by assuming the electronic configuration of the He atom, as it has been found in the case of other semiconductors such as, e.g., Si.[1] On the contrary, the electron added to the supercell to simulate the charge of −1 is localized on a further Ti atom neighboring the OH^+ complex, see Fig. 1(d). A H^+ ion does not induce levels in the energy gap, while the formal H^- species induces two levels, related to the electrons localized at the two Ti^{+3} atoms shown in Fig. 1(d), which are located at 1.04 and 0.67 eV below the calculated CB.

Formation energies of H in the above charge states have been also calculated together with the corresponding $\epsilon^{+1/0}[\mathrm{H}]$ and $\epsilon^{0/-1}[\mathrm{H}]$ transition states, which are equal to 1.74 and 1.88 eV, respectively, see Fig. 3. Transition states, calculated by using *total-energy* values of the ground state of the variously charged systems, are not directly comparable with an energy gap estimated by the Kohn-Sham *eigenvalues* (2.05 eV), which are also affected by the well-known errors of the local-density approximation in describing empty states. Although even the transition states may be partially affected by the same drawback, we assume that they can give a reasonable estimate of the location of a defect state with respect to the top of the VB (actually an occupied state) and compare such a location with the experimental energy gap of 3.0 eV.[45] In this regard, the value estimated for the $\epsilon^{+1/0}[\mathrm{H}]$ transition state would indicate that H behaves as a deep donor having a neutral charge state in intrinsic rutile and a positive one in a hypothetical *p*-type material.

All together, the above results give a coherent picture of the properties of H in rutile: (i) interstitial H ever binds to an O atom as a H^+ ion independent of the Fermi energy position, that is, even in the cases in which, formally, it has a neutral or a negative charge state. Actually, H may give rise to an OH^+ complex, when its electron compensates an acceptor, or it can form an OH^+-Ti^{+3} pair in intrinsic rutile which can be possibly accompanied by the formation of a further Ti^{+3} defect in *n*-type rutile. (ii) H can behave as a deep donor but not as an acceptor. Then, it is neither an amphoteric nor a negative-*U* impurity. (iii) The H behavior is closely related to the capability of a Ti^{+4} species to host an electron in its unoccupied *d* shell to form a Ti^{+3} species. This capability favors indeed a donor behavior of H and makes such a behavior quite similar to that of the above-mentioned defects. Noteworthy, the localization of the electron lost by H on a Ti atom implies that the $\epsilon^{+1/0}[\mathrm{H}]$ transition state represents, actually, the $\epsilon^{+4/+3}$ transition state for the Ti atom of the OH^+-Ti^{+4} pair. This also accounts for the close values of the above $\epsilon^{+1/0}[\mathrm{H}]$ and $\epsilon^{0/-1}[\mathrm{H}]$ states, both related to $\epsilon^{+4/+3}$ transition states for two neighbor Ti atoms.

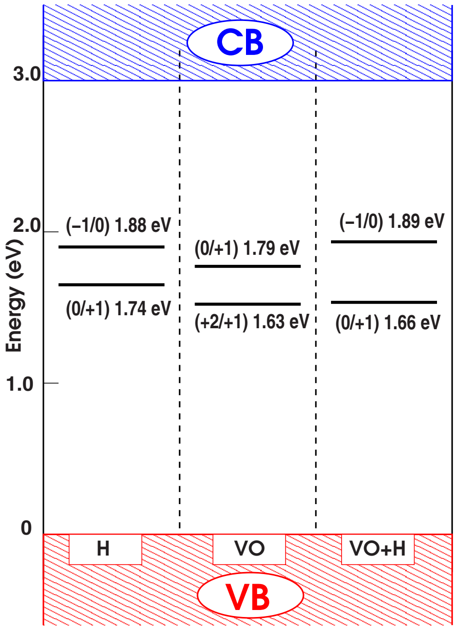

FIG. 3. (Color online) Transition energy levels for H and oxygen vacancy V_O related defects in the bulk rutile. From left to right, H bound to an O atom, O vacancy, H_O-V_O complex. Reference is the top of the valence band, the band-gap value is the *experimental* one (3.0 eV).

The above results answer some of the questions posed above. In particular, they imply that H in rutile cannot induce a shallow donor level in the energy gap of this semiconductor, at variance with the prediction made in Ref. 6 and the universal alignment model proposed in Ref. 8.

The energetics of H in rutile has been carefully investigated here by considering its neutral charge state, that is, the properties of the OH^+-Ti^{+3} pair. Generally, rutile shows indeed the features of a slightly *n*-type doped semiconductor, which should favor the formation of such a H configuration. The formation energy estimated for the OH^+-Ti^{+3} pair, referred to as $\Omega_f[\mathrm{H}]^0$, is +0.10 eV when assuming μ_H equal to half the energy of a H_2 molecule. A positive sign indicates an endothermic process, that is, H is more stable when forming a H_2 molecule in the vacuum than when bonded to an O atom in rutile. However, if μ_H is taken equal to the energy of a H atom in the vacuum, which would correspond to a hydrogenation process employing a plasma of H atoms, $\Omega_f[\mathrm{H}]^0$ results to be equal to −2.13 eV, which suggests a quite high solubility of atomic H in rutile. An estimate of the H concentration at equilibrium and at room temperature, corresponding to the two above formation energies, gives the values of 0 and 7×10^{16} cm^{-3}, respectively.

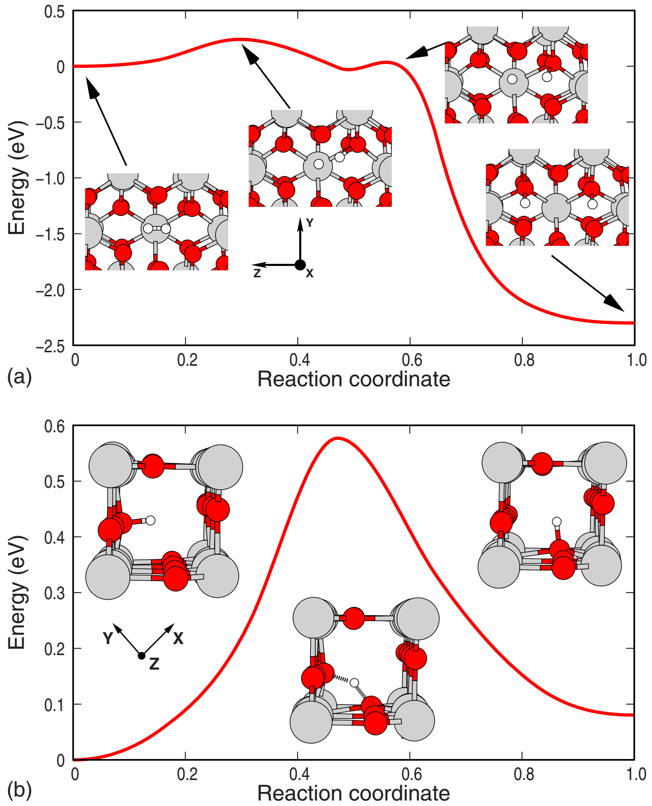

FIG. 4. (Color online) Reaction energy paths for H_2 molecule dissociation, upper panel, and H atom displacement along the [001] direction, lower panel. Insets show the geometries of the systems at the relevant points in the paths. In both panels cartesian axes (x, y, and z corresponding to the crystallographic directions [100], [010], and [001], respectively) are sketched to define the orientation of the figure. Note that in upper panel one Ti atom has been removed from the figure to allow the view of the reaction site. Ti atoms are represented by gray balls, O by red ones, and H by white ones (gray, black and white balls, respectively, in printed version).

The stability of the OH$^+$-Ti^{+3} pair has been also investigated by comparing its total energy with that of an interstitial H_2 molecule in rutile as well as by simulating a breaking of the O-H bond. Preliminarily, we have obtained that H as a molecule does not enter in rutile. An interstitial H_2 molecule is indeed 2.61 eV higher in energy than the molecule in the vacuum. The interstitial molecule is also 2.4 eV higher in energy than two H atoms forming two OH$^+$-Ti^{+3} pairs. Moreover, a quite small energy barrier of 0.24 eV has been estimated by performing NEB calculations for the dissociation of a H_2 molecule in rutile leading to the formation of two OH$^+$-Ti^{+3} pairs, see Fig. 4 upper panel. Thus, H in rutile tends to exist in the form of OH complexes. We have estimated also the energy barriers for the breaking of the O-H bond and the formation of a new O-H bond with an O atom nearest neighboring the OH$^+$ complex. A path for an O-H breaking where H displaces almost perpendicularly to the bond along the [001] direction (i.e., along the channel of the structure) has been considered, see Fig. 4 lower panel. The estimated energy barrier is 0.58 eV. A different path (not illustrated here) sees a H displacement along the [1–10] direction (i.e., across the channel) with an energy barrier of 0.50 eV.

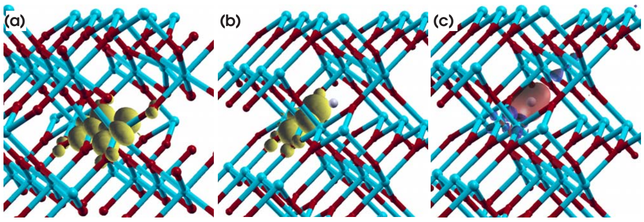

FIG. 5. (Color online) Equilibrium geometries and charge-density (ψ^2) isosurfaces of an oxygen vacancy V_O and H$-V_O$ complexes, where H takes the place of the missing O atom, H_O, from LSD+U simulations. (a) Electronic states induced by the O vacancy. (b) The unquenched state of the H_O-V_O complex (see the text). (c) Charge-density difference map for the H_O-V_O complex; in red regions of charge accumulation, in blue of charge depletion. Surfaces are sampled at 5×10^{-3} e/(a.u.)^3. Ti, O, and H atoms are represented in (light blue, red, and light gray, respectively, in printed version).

Finally, a vibrational frequency of 3261 cm^{-1}, with an anharmonic correction of 279 cm^{-1}, has been estimated for the stretching mode of H in the OH$^+$-Ti^{+3} pair, which is in a very good agreement with a vibrational line measured at 3279 cm^{-1} and related to O-H groups in rutile.[46] In annealing experiments, such a vibrational line reduces considerably only at $T>500$ K. All together, the above results indicate that H can be introduced, at room temperature, in appreciable concentrations (i.e., corresponding to a moderate doping) in rutile, where it forms quite stable O-H bonds.

B. Properties of V_O's and H_O-V_O complexes

Some structural and electronic properties of an isolated V_O in rutile have been already investigated in two previous studies by using the same LSD+U methods employed here.[20,21] The previous results will be briefly reported in this section together with the new results. When a V_O forms in rutile, its three Ti neighbors relax by moving away from the vacancy site. Prior to relaxation, the vacancy site is surrounded by two equivalent nearest-neighbor Ti$_{eq}$ atoms at a distance of 1.97 Å and by one Ti$_{ne}$ atom at a distance of 2.01 Å from the vacancy site. Ti$_{eq}$ and Ti$_{ne}$ atoms move away from the vacancy, by reaching the distances of 2.25 and 2.31 Å, respectively, in agreement with other theoretical studies.[33,34] As mentioned above, the two electrons left by the O removal occupy two spin-parallel electronic levels in the energy gap at 0.85 and 1.05 eV below the calculated CB (2.05 eV), and very similar to each other, being both localized on two equivalent Ti^{+3} atoms neighboring the vacancy, see Fig. 5(a). Assuming μ_O equal to half the energy of an O_2 molecule in the vacuum, the formation energy of a neutral oxygen vacancy, $\Omega_f[V_O]$, has been estimated to be +393 kJ/mol (+4.03 eV), close to the experimental value of +439 kJ/mol.[33] From V_O formation energies, we estimate the values of 1.63 and 1.79 eV for the $\epsilon^{+2/+1}[V_O]$ and $\epsilon^{+1/0}[V_O]$ transition levels, see also Fig. 3, which indicate a deep donor behavior of this defect. The two V_O transition states are very close in value to the $\epsilon^{+1/0}$[H]. Present results suggest therefore the existence of strong similarities between these two kinds of defects. Both defects behave indeed as deep donors and induce electronic levels, as described by both Kohn-Sham eigenvalues and transition states, located close to each other in the energy gap, see Fig. 3. As mentioned above, such defect levels are so similar because corresponding to electrons both localized on *d* orbitals of neighboring Ti atoms, actually Ti^{+3}. The close similarities between the properties of these two defects may have interesting consequences. Possible benefits produced by oxygen vacancies on the rutile optical and electronic properties or on the magnetic properties of rutile-based DMS could be indeed produced also by the introduction of atomic H under milder conditions. In this regard, an advantage of hydrogenation with respect to the introduction of vacancies could be represented by the high H solubility predicted here (even at room temperature) and by a significant reduction in the damage of the lattice structure.

The above discussion of the properties of an isolated V_O and of interstitial H represents a basic premise to consider the interaction between these two defects and the formation of H_O-V_O complexes. Present results indicate the existence of a stable site for a H atom located at a vacancy site in place of an O atom, see Fig. 5(b). In this configuration, H is surrounded by two equivalent nearest-neighbor Ti_{eq} atoms at a distance of 2.04 Å and by one Ti_{ne} atom at a distance of 2.15 Å, that is, the Ti neighboring the vacancy site displace towards the H_O atom, partially recovering their positions in pristine material. The H_O-V_O complex is 0.49 eV lower in energy than the two isolated defects, that is, in presence of vacancies that complex represents the stable site of H in rutile. In order to clarify the nature of the chemical bonding of H in the H_O-V_O complex, first, we have carefully analyzed the density of states projected on the atomic orbitals of the Ti atoms neighboring the H in the complex as well as on the H atomic orbital (not reported here). While in the case of the above-mentioned multicenter bond proposed for the same complex configuration in ZnO, such an analysis revealed some bonding between H and its Zn neighbors, in our H_O-V_O complex no covalent-bond interaction showed up. Then, we have considered a difference electron-density map for this complex, see Fig. 5(c), which shows the displacement of electronic charge induced by the interaction of the H atom with its Ti neighbors. With a covalent bonding between two atoms, charge difference maps are expected to show an accumulation of electronic charge in the region midway between the two atoms. On the contrary, the map in Fig. 5(c) shows a charge accumulation on the H atom and a depletion on the neighboring Ti atoms. This suggests that the H_O carries some negative charge in the complex by assuming the electronic configuration of the He atom, that is, it attempts to substitute an O atom by forming H-Ti chemical bonds with a prevailing ionic character. Such a result is very different from the multicenter bond proposed in ZnO. It is also quite different from the H interaction with vacancies in Si or GaAs where H generally saturates dangling bonds carried by the atoms neighboring the vacancy site.

The electronic structure of the H_O-V_O complex is characterized by a singly occupied electron level located in the energy gap at 1.3 eV below the CB, quite close to the levels of the isolated V_O. Such a level is localized at a Ti atom neighboring the vacancy, see Fig. 5(b), similarly to the two levels of the vacancy. The corresponding $\epsilon^{+1/0}$ transition state is equal to 1.66 eV, a value close to those of the transition states related to the isolated V_O and to the OH^+-Ti^{+3} pair, see Fig. 3. In a simplified picture, the above results indicate that one electron of the V_O and the H electron contribute to pile up electronic charge on the H_O and are accommodated therefore in electron levels deep in the valence band. The second electron of V_O occupies a level similar to those induced by the isolated V_O [i.e., the unquenched level of Fig. 5(b)]. Moreover, the H_O-V_O complex should behave as a deep donor like its two components. Even this result is therefore quite different from that found in ZnO, where H_O changes the V_O donor character from deep to a shallow. Notwithstanding, even in rutile, the formation of H_O-V_O complexes may have interesting effects. These complexes present indeed an unpaired electron, a feature which may favor the magnetic coupling in rutile derived DMS's.[15]

IV. CONCLUSIONS

In the present study, a DFT-LSD+U investigation has been performed on the properties of interstitial H, oxygen vacancies, V_O, and complexes formed by a V_O and a H taking the place of the missing O atom, H_O-V_O, in the rutile phase of TiO_2. The achieved results have been discussed having in mind the properties of H in widely used semiconductors, such as Si or GaAs, as well as in metal oxides, such as ZnO. Present results show that H behaves as a deep donor in rutile by forming a OH^+ complex in (hypothetical) *p*-type rutile and a OH^+-Ti^{+3} pair when in intrinsic or in *n*-type rutile. It never assumes the configurations of a neutral H atom or of a negative H^- ion when located in interstitial sites. Then, H in rutile presents quite different properties, in comparison with the cases of Si and GaAs, since it is neither an amphoteric nor a negative-U impurity. It shows also a different behavior with respect to H in ZnO, where H was predicted to behave as a shallow donor. Even the interaction of H with the V_O defect presents some peculiarities. H in rutile does not saturate vacancy dangling bonds as it does in Si and GaAs, rather it forms a stable complex by substituting the O atom missing in the V_O, as it does in ZnO. However, at variance with ZnO, no multicenter bonds are formed in the H_O-V_O complex. Only in such a complex, H assumes indeed the features of a negative H^- ion by forming bonds with a prevailing ionic character. Moreover, still at variance with ZnO, the formation of a H_O-V_O complex does not change the character of the oxygen vacancy, which remains a deep donor.

Present results show that interstitial H, V_O, and the H_O-V_O complex share two main features: they behave as deep donors, and their electronic levels are localized on some Ti neighbors, therefore inducing the formation of Ti^{+3} species. These results are closely related to the failure in the prediction of H behaving as a shallow donor in TiO_2 rutile, as well as of the universal alignment model, which implies the same prediction. All of these issues have indeed a common ground represented by a peculiarity of Ti atoms in rutile, i.e., a *d* shell roughly free of electrons, which can accommodate one electron by leading to the formation of Ti^{+3} species. Such a capability, strongly supported by the experiments in case of Ti^{+3} species formed in nonstoichiometric materials and connected with the breaking of the translational symmetry induced by a defect, allows the localization of the extra electrons accompanying the formation of the defect itself. This may account for the common deep donor behavior shown by the above three defects. On the contrary, in the case of ZnO, H can behave as a shallow donor because it forms an OH^+ complex and its extra electron can be accommodated only in a conduction-band derived defect state, the *d* shell of Zn being full of electrons. In other words, (partially) empty *d* levels in the metal atom are on the ground of the capability to change the oxidation states and localize the excess electrons. It is clear, therefore, how this matters in defining the deepness/shallowness of a donor defect. From present results, the model of universal alignment proposed in Ref. 8, fails for H in rutile, since it neglects the effects played by empty or scarcely occupied metal *d* states. In the presently discussed case of rutile, such effects result in a H defect level which has actually the character of a Ti induced level. This discriminates H in TiO_2 rutile from H in other semiconductors.

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