Optical properties of anatase and rutile TiO$_2$ studied by GGA $+$ $U$* 

Jinping Li(李金平)$^{1,3,4}$, Songshe Meng(孟松鹤)$^1$, Liyuan Qin(秦丽媛)$^1$, and Hantao Lu(陆汉涛)$^2$

$^1$ Center for Composite Materials and Structures, Harbin Institute of Technology, Harbin 150080, China
$^2$ Center for Interdisciplinary Studies & Key Laboratory for Magnetism and Magnetic Materials (Ministry of Education), Lanzhou University, Lanzhou 730000, China
$^3$ Yukawa Institute for Theoretical Physics, Kyoto University, Kyoto 606-8502, Japan

(Received 1 November 2016; revised manuscript received 2 May 2017; published online 20 June 2017)

The optical properties of thermally annealed TiO$_2$ samples depend on their preparation process, and the TiO$_2$ thin films usually exist in the form of anatase or rutile or a mixture of the two phases. The electronic structures and optical properties of anatase and rutile TiO$_2$ are calculated by means of a first-principles generalized gradient approximation (GGA) $+$ $U$ approach. By introducing the Coulomb interactions on 3d orbitals of Ti atom ($U^3$) and 2p orbitals of O atom ($U^p$), we can reproduce the experimental values of the band gap. The optical properties of anatase and rutile TiO$_2$ are obtained by means of the GGA $+$ $U$ method, and the results are in good agreement with experiments and other theoretical data. Further, we present the comparison of the electronic structure, birefringence, and anisotropy between the two phases of TiO$_2$. Finally, the adaptability of the GGA $+$ $U$ approach has been discussed.

Keywords: TiO$_2$, first-principles, GGA $+$ $U$, electronic structure, optical properties

PACS: 71.15.–m, 71.15.Mb, 78.20.Ci, 78.20.Fm

DOI: 10.1088/1674-1056/26/8/087101

1. Introduction

TiO$_2$, as one of the wide band-gap semiconductors, with stable, nontoxic, and efficient photocatalytic activity, has been widely used in photocatalytic, solar battery, sensor, self-cleaning materials, and so on.$^{[1–4]}$ TiO$_2$ thin films usually exist in two polymorphs after high-temperature annealing, i.e., the anatase and the rutile, shorted as a-TiO$_2$ and r-TiO$_2$, respectively.$^{[5–9]}$

In experiments, optical properties of thermally annealed TiO$_2$ have shown intrinsic birefringence and anisotropy in some samples.$^{[10]}$ For example, the fundamental optical properties of optically anisotropic materials such as r-TiO$_2$ have been measured at room temperature with linearly polarized light of wavelength longer than 110 nm.$^{[7]}$ Polarized reflection spectra of single-crystal a-TiO$_2$ have been obtained in a photon energy range from 2 eV to 25 eV by using synchrotron orbital radiations, and the optical properties show anisotropy.$^{[8]}$ Spectroscopic ellipsometry measurements were made on thin-film and single-crystal a-TiO$_2$ using a two-modulator generalized ellipsometer. The results show that the complex refractive indices and dielectric function in a- and r-TiO$_2$ are quite different. Below the band edge, compared with a-TiO$_2$, r-TiO$_2$ has a higher refractive index, as well as greater value of birefringence.$^{[9]}$

Theoretically, the crystal structure, the band structure, and the density of states of a-TiO$_2$ have been analyzed by using a first-principles local density approximation (LDA) approach.$^{[11]}$ The resulting band-gap value is 2.25 eV. Near the absorption edge, it shows a significant optical anisotropy between the components with directions parallel and perpendicular to the $c$ axis.

In the case of r-TiO$_2$, the structure and electronic properties have been calculated by using “soft-core” $ab$-initio pseudopotentials constructed within the local density approximation (LDA), and the resulting band-gap value is 2.0 eV. The obtained dielectric function and reflectivity of r-TiO$_2$ for polarization vector also display difference between the directions parallel and perpendicular to the $c$ axis.$^{[12]}$

The self-consistent orthogonalized linear-combination-of-atomic-orbitals method in LDA has been used to study the electronic structure and optical properties of the three phases of TiO$_2$.$^{[13]}$ The obtained band-gap values of a-TiO$_2$ and r-TiO$_2$ are 2.04 eV and 1.78 eV, smaller than the experimental data, 3.2 eV and 3.0 eV, respectively. The theoretical calculations show a little difference in the optical properties of the three phases in TiO$_2$.

Regardless of the above computational efforts, the physical mechanism for the intrinsic birefringence and anisotropy of the optical properties of TiO$_2$ found in some samples remains to be understood. Note that the band gaps obtained by the previous methods are significantly lower than the experimental values. So, it is important to investigate the electronic structures of a-TiO$_2$/r-TiO$_2$ and clarify the difference of optical properties based on the first-principles band structure calculations with electronic correlations to be taken into account.
The LDA+U method has been employed to investigate the properties of r-TiO$_2$. The results are dramatically improved when additional correlation corrections are introduced on the O 2p orbitals in the LDA+U$^d$ + U$^p$ approach. The experimental band-gap value (3.20 eV) can be reproduced when U$^d$ = 8.0 eV and U$^p$ = 7.0 eV. In a similar approach, the influence of oxygen defects upon the electronic properties of Nb-doped TiO$_2$ was studied, and the effective U parameter $U_{\text{eff}}$ = 7.2 eV has been used to correct the strong Coulomb interaction between 3d electrons localized on Ti in anatase models. The calculated results show that the anatase NbTiO$_2$ cells are degenerated semiconductors with a typical n-type degenerated characteristic in their electronic structure, which is in good agreement with the experimental evidence that anatase Nb:TiO$_2$ film is an intrinsic transparent metal. Other researchers set up a model for Zn$_1$-→Ag$_x$O (x = 0, 0.0278, 0.0417) to calculate the geometric structure and energy via the method of generalized gradient approximation (GGA+U), showing that the absorption spectrum in these systems all coincide with experimental data.

In this paper, we use the GGA+U scheme formulated by Loschen et al., to calculate the electric structures and optical properties of r-TiO$_2$ and a-TiO$_2$. The on-site Coulomb interactions of 3d orbitals on Ti atom (U$^d$) and of 2p orbitals on O atom (U$^p$) are determined so as to reproduce the experimental value of the band gap for the two phases of TiO$_2$. The comparison of the electronic structure, birefringence and anisotropy between the two phases of TiO$_2$ is also presented. Finally, the adaptability of the GGA+U approach has been discussed.

2. Computational methodology

Density functional theory (DFT) calculations are performed with plane-wave ultrasoft pseudopotential, by using the GGA with the Perdew–Burke–Ernzerhof (PBE) functional and the GGA+U approach as implemented in the CASTEP code (Cambridge Sequential Total Energy Package). The ionic cores are represented by ultrasoft pseudopotentials for Ti and O atoms. For the Ti atom, the configuration is [Ar] 3d$^2$4s$^2$, where the 3s$^2$, 3p$^6$, 3d$^2$, and 4s$^2$ electrons are explicitly treated as valence electrons. For the O atom, the configuration is [He] 2s$^2$2p$^4$, where 2s$^2$ and 2p$^4$ electrons are explicitly treated as valence electrons. The plane-wave cut off energy is 380 eV and the Brillouin-zone integration is performed over the $24 \times 24 \times 24$ grid sizes using the Monkhorst–Pack method for geometry structure optimization. This set of parameters assures the total energy convergence of 5.0 × 10$^{-6}$ eV/atom, the maximum force of 0.01 eV/Å, the maximum stress of 0.02 GPa and the maximum displacement of 5.0×10$^{-4}$ Å. We calculated the electronic structures and the optical properties of a-TiO$_2$ and r-TiO$_2$ by means of the GGA method without U and GGA+U$^d$ + U$^p$ after having optimized the geometry structure. The details of the calculation have been shown elsewhere.

3. Results and discussion

The space group of a-TiO$_2$ is I4$_1$/amd and the local symmetry is C4h-19, and r-TiO$_2$ is P4$_2$/mmm and D4h-14. The lattice constants $a$ and $c$ are experimentally determined to be $a$ = 0.3785 nm and $c$ = 0.9515 nm, $a$ = 0.4593 nm and $c$ = 0.2959 nm, respectively. The GGA calculation of the perfect bulk a-TiO$_2$ and r-TiO$_2$ is performed to determine the optimized parameters in order to check the applicability and accuracy of the ultrasoft pseudopotential. The optimized parameters are $a$ = 0.3795 nm and $c$ = 0.9837 nm, and $a$ = 0.4645 nm, and $c$ = 0.2968 nm for a-TiO$_2$ and r-TiO$_2$, respectively, in good agreement with experimental and other theoretical values. However, the value of the band gap $E_g$ in a-TiO$_2$ and r-TiO$_2$ is around 2.16 eV and 1.85 eV, respectively, smaller than the experimental value of 3.23 eV and 3.0 eV. This is due to the fact that the DFT results often underestimate the energy of 3d orbitals of the Ti atom, lowering the bottom level of conduction bands. As a result, $E_g$ of TiO$_2$ obtained by GGA is lower than the experimental one.

In order to reproduce the band gap, we first introduce U$^d$ for 3d orbitals of the Ti atom. Using the experimental lattice parameters, we optimize the geometry structure and calculate the band structure and density of state (DOS) of r-TiO$_2$. The band gap $E_g$ obtained from the band structure is shown in Fig. 1(a) as a function of U$^d$. It can be seen that $E_g$ firstly increases, and then drops with increasing U$^d$, showing a maximum value (2.46 eV) at U$^d$ = 6.75 eV, where the lattice parameters of the optimized structure are $a$ = 0.4664 nm and $c$ = 0.3086 nm. The maximum value is smaller than the experimental one (3.0 eV). The saturation of $E_g$ with U$^d$ may be related to the approach of 3d states toward 4s and 3p states, though the microscopic mechanism is not yet fully understood. Next, we introduce U$^p$ for 2p orbital of O atom, while keeping U$^d$ = 6.75 eV. The results in Fig. 1(b) show that $E_g$ monotonically increases with U$^p$. When U$^d$ = 6.75 eV and U$^p$ = 3.5 eV, the calculated band gap of r-TiO$_2$ is 3.0 eV, well consistent with the experiment one, where the lattice parameters of the optimized structure are $a$ = 0.4664 nm and $c$ = 0.3082 nm. For a-TiO$_2$, when U$^d$ = 7.75 eV and U$^p$ = 1.0 eV, the calculated band gap of a-TiO$_2$ is 3.229 eV, well coinciding with the experiment one, where the lattice parameters of the optimized structure are $a$ = 0.38891 nm and $c$ = 0.9870 nm.
Fig. 1. (color online) Calculated band gap $E_g$ of r-TiO$_2$ as a function of (a) $U^d$ and (b) $U^p$.

By adopting these $U$ values: $U^d = 6.75$ eV and $U^p = 3.5$ eV, ($U^d = 7.75$ eV and $U^p = 1.0$ eV for a-TiO$_2$), we perform the GGA+$U$ calculation for r-TiO$_2$. The band dispersion is shown in Fig. 2(a). The bottom of the conduction band is located at the G/B point. Since the bottom shifts to higher energy with $U^d$ accompanied by the reconstruction of the conduction band, the separated density of states at 3.03 eV and 6.26 eV obtained by the generalized gradient approximation without $U$ (not shown here) merges to one sharp structure at 3.74 eV as shown in Fig. 2(b). The conduction band is predominantly constructed by Ti 3d states, while the valence band is by O 2p states (as shown in Fig. 2(c) and Fig. 2(d)). Therefore, the excitations across the gap are mainly from the O 2p states to the Ti 3d states.

Fig. 2. (color online) The band structure and DOS of r-TiO$_2$ obtained by GGA+$U^d$+$U^p$ ($U^d = 6.75$ eV, $U^p = 3.5$ eV). (a) Band structure. The total DOS, the partial DOSs of Ti and O atoms are shown in panels (b), (c), and (d), respectively.

Fig. 3. (color online) Total DOSs of the two phases of TiO$_2$ by GGA without $U$, and GGA+$U^d$+$U^p$ ($U^d = 6.75$ eV, $U^p = 3.5$ eV, and $U^d = 7.75$ eV and $U^p = 1.0$ eV for r-TiO$_2$ and a-TiO$_2$, respectively) in a wide region (a), and zoom of the region near Fermi surface (b).

Figure 3 shows the comparison of the total DOSs between a- and r-TiO$_2$ obtained by GGA and GGA+$U^d$+$U^p$ ($U^d = 6.75$ eV, $U^p = 3.5$ eV, and $U^d = 7.75$ eV, $U^p = 1.0$ eV for r-TiO$_2$ and a-TiO$_2$, respectively). From the wide region (shown in Fig. 3(a)), the total DOSs of r-TiO$_2$ and a-TiO$_2$ obtained by GGA and GGA+$U^d$+$U^p$ look quite similar; while zooming into the region around the Fermi surface (Fig. 3(b)), we can see that compared with the results of GGA without $U$,
a significant change after including $U$ is that the conduction bands are pushed to higher energies, which accordingly produces larger band gaps.

Figure 4 shows the dielectric function of r-TiO$_2$ obtained by GGA $+U^d + U^p$ ($U^d = 6.75$ eV and $U^p = 3.5$ eV) (a) parallel and (b) perpendicular components. The parallel and perpendicular components of the real part $\varepsilon_1$ have maximums of 12.53 at 3.86 eV and 10.98 at 3.94 eV, respectively. The calculated static dielectric constants are 6.298 and 5.485 along the different directions, coinciding with the experimental value 6.33.[24] The parallel and perpendicular components of the imaginary part $\varepsilon_2$ show the maximums of 10.28 at 6.74 eV and 9.50 at 4.90 eV, respectively. Other optical properties can be computed from the complex dielectric function.[25] For example, we can obtain the refractive coefficient of r-TiO$_2$, whose parallel and perpendicular components are $n_e = 2.75$ and $n_o = 2.46$. It is obvious that the values by GGA $+U^d + U^p$ are closer to the experimental values $n_e = 2.7$ and $n_o = 2.4$,[7] or $n_e = 2.76$ and $n_o = 2.44$.[26]

![Fig. 4. (color online) Dielectric function of r-TiO$_2$ obtained by GGA $+U^d + U^p$ ($U^d = 6.75$ eV and $U^p = 3.5$ eV). (a) The parallel and (b) the perpendicular components.](image)

Figure 5 shows the dielectric function of the parallel and perpendicular component in a-TiO$_2$ obtained by GGA $+U^d + U^p$ ($U^d = 7.5$ eV and $U^p = 1.0$ eV). From Fig. 5, we can see that the maximums of the parallel and perpendicular components of the real part $\varepsilon_1$ are 11.79 at 3.75 eV and 12.56 at 3.75 eV, respectively. The static dielectric constants of the two components are 6.137 and 5.995, coinciding with the experimental value 5.62.[24] The maximums of the parallel and perpendicular components of the imaginary part $\varepsilon_2$ are 10.29 at 4.74 eV and 11.22 at 4.52 eV, respectively. Other optical properties can be computed from the complex dielectric function.[25] The parallel and perpendicular components of the refractive coefficient of r-TiO$_2$ are $n_e = 2.34$ and $n_o = 2.29$. It is obvious that the values by GGA $+U^d + U^p$ are closer to the experimental values of $n_e = 2.32$ and $n_o = 2.28$.[27]

From Fig. 4 and Fig. 5, we can notice the optical anisotropies in both a- and r-TiO$_2$ between parallel and perpendicular components. The rutile form of TiO$_2$ has comparatively high anisotropy, both above and below the band gap, which makes r-TiO$_2$ a very useful optical material.[9] Below the band gap, r-TiO$_2$ has a large birefringence (difference between refractive indices of the parallel and perpendicular components) $\Delta n = n_e - n_o = 0.29$ in our calculation, which is in good agreement with the experiment data ($\Delta n = 0.27$)[28] or 0.30[7]).

![Fig. 5. (color online) Dielectric function of a-TiO$_2$ obtained by GGA $+U^d + U^p$ ($U^d = 7.5$ eV and $U^p = 1.0$ eV). (a) The parallel and (b) the perpendicular components.](image)

To study the adaptability of the GGA $+U$ approach, we further calculate the electronic structure of a titanium-vacancy and of hafnium-substitution solid solutions in rutile TiO$_2$. For titanium-vacancy solid solutions of rutile TiO$_2$, we first set $2 \times 2 \times 2$ supercell. Namely, in one super cell, there are 16 titanium and 32 oxygen atoms. We delete only one Ti atom in the...
center of the super cell, whose vacancy rate is 6.25%, and we obtain the electronic structure of titanium-vacancy solid solutions of rutile TiO$_2$ by GGA or by GGA+U ($U^{3d} = 7.0$ eV and $U^{2p} = 3.5$ eV for Ti 3d and O 2p, respectively) after geometry optimization. The calculation results are shown in Fig. 6(a).

The band gap of vacancy solid solutions by GGA and by GGA+U is 1.695 eV and 2.593 eV, respectively. As everyone knows, DFT (either by GGA or by LDA) usually undervalues the band gap. From Fig. 6(a), there are two clear sharps by GGA and GGA+U (in red color). If the GGA is used, the two sharps will merge together and the sharp height becomes bigger than those by GGA, much similar to our other works like cubic HfO$_2$ and monoclinic HfO$_2$. For hafnium-substitution solid solutions in rutile TiO$_2$, we first set $2 \times 2 \times 1$ super cell. Namely, in one super cell, there are 8 titanium and 16 oxygen atoms. We substitute only one Ti atom by hafnium in the center of the super cell, whose substitution rate is 12.5%, and we obtain the electronic structure of hafnium-substitution solid solutions and rutile TiO$_2$ by GGA+U ($U^{3d} = 8.0$ eV, $U^{3d} = 7.0$ eV, and $U^{2p} = 3.5$ eV for Hf 5d, Ti 3d, and O 2p, respectively) after geometry optimization. The calculation results are shown in Fig. 6(b). The band gap of the pure and Hf-doped rutile TiO$_2$ by GGA+U is 3.0 eV and 2.895 eV, respectively. From Fig. 6(b), we can see that the two lines are much similar between the pure and Hf-doped rutile TiO$_2$. Considering the similar electronic configuration of Ti and Hf in the fourth subgroup with 4 valence electrons, it is reasonable that the pure r-TiO$_2$ has a very similar DOS with the doped one by 12.5% Hf. Besides, the calculated results of Mulliken atomic population in r-TiO$_2$ and the doped r-TiO$_2$ by 12.5% Hf are much similar, and the transfer charge of the O atoms in r-TiO$_2$ and the doped one by 12.5% Hf is $-0.645$ and $-0.657$, respectively.

4. Conclusion

The electronic structures and optical properties of anatase and rutile TiO$_2$ are calculated by means of first-principles generalized gradient approximation GGA and GGA+U approaches. By GGA, the resulting band gaps $E_g$ in a-TiO$_2$ and r-TiO$_2$ are around 2.16 eV and 1.85 eV, smaller than the experimental values. Introducing the Coulomb interactions of 3d orbitals on the Ti atom ($U^{3d}$) and of 2p orbitals on the O atom ($U^{2p}$), we can reproduce the experimental values of the band gap for a- and r-TiO$_2$. The best values for $U^{3d}$ and $U^{2p}$ are $U^{3d} = 6.75$ eV and $U^{2p} = 3.5$ eV, $U^{3d} = 7.5$ eV and $U^{2p} = 1.0$ eV for r- and a-TiO$_2$, respectively. The complex dielectric functions and refractive index of r-TiO$_2$ and a-TiO$_2$ are calculated. The results show optical anisotropy in both a-TiO$_2$ and r-TiO$_2$. The r-TiO$_2$ has relatively large anisotropy with birefringence $\Delta n = 0.29$, which makes it a useful optical material. We further calculate the electronic structure of the titanium-vacancy and of hafnium-substitution solid solutions in rutile TiO$_2$, and the calculation results show that the GGA+U approach has wide adaptability.

References

[1] Woan K, Pyrgiotakis G and Sigmund W 2009 Adv. Mater. 21 2233
[2] Gumy D, Giraldo S A, Rengifo J and Pulgarin C 2008 Appl. Catal. B: Environ. 78 19
[3] Meen T H, Water W, Chen W R, Chao S M, Ji L W and Huang C J 2009 J. Phys. Chem. Solids 70 472
[4] Belcarz A, Biemas J, Surowska B and Ginalska G 2010 Thin Solid Film 519 793
[5] Triyoso D H, Hegde R I, Zollner S, Ramon M E, Kalpat S, Gregory R, Wang X D, Jiang J, Raymond M, Rai R, Werho D, Roan D, White B E Jr and Tobin P J 2005 J. Appl. Phys. 98 054104
[6] Cisneros-Morales M C and Aita C R 2008 Appl. Phys. Lett. 93 021915
[7] Manuel Cardona and Gunther Harbeke 1965 Phys. Rev. A 137 1467
[8] Noriko Hosaka, Takao Sekiya, Chikatoshi Satoko and Susumu Kurita 1997 J. Phys. Soc. Jpn. 66 877
[9] Jellison G E Jr, Boatner L A, Budai J D, Jeong B S and Norton D P 2003 J. Appl. Phys. 93 9537
[10] Chen H 2009 Chin. J. Lumin. Sci. 30 697 (in Chinese)
[11] Zhang Y W, Yin C H, Zhao Q, Li F Q, Zhu S S and Liu H S 2012 Acta Phys. Sin. 61 027801 (in Chinese)
[12] Keith M Glassford and James R Chelikowsky 1992 Phys. Rev. B 46 1284
[13] Mo S D and Ching WY 1995 Phys. Rev. B 51 13023
[14] Park S G, Blanka M K and Nishi Y 2010 Phys. Rev. B 82 115109
