

# BORON-DOPED ANATASE: ELECTRONIC BAND STRUCTURE, BORON ATOM LOCATIONS AND MAGNETIC STATE

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The first-principle spin-resolved GGA and GGA+U calculations for the electronic band structure of the boron-doped  $TiO_2$  with anatase structure have been performed. The locations of boron atoms in the interstitial and oxygen position have been studied. We have found two interstitial positions: a stable one with three neighboring oxygen atoms, and a metastable one in the center of the flattened tetrahedron of oxygen atoms. The boron location in interstitial position is energetically more favorable than the location inside the oxygen position. In accordance with experiments, the GGA+U approach produces spin-polarized solutions for interstitial boron positions, whereas the GGA approach fails to produce a spin-polarized solution.

**Keywords:** anatase, boron doping, photocatalyses, optical absorption, band structure, first-principle calculations.

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## 1. Introduction

The subject of this work was initialized in course of discussions on the physicochemical properties of photocatalytic compounds where the contribution of Prof. A.L. Ivanovskii was invaluable.

The most promising compound for photocatalytic applications is probably anatase-structured titanium dioxide, a good reagent for the removal of pathogenic bacteria or chemical contaminants from the environment. This compound also has potential for employment in new photoelectric cells and hydrogen producing cells by means of water photolysis. Pure  $TiO_2$  possesses a high photocatalytic activity (PCA) in the UV part of the electromagnetic spectrum, so in many works attempts have been carried out to extend its activity to the visible part of the solar spectrum, see [1]. The main aim of such studies was to obtain the  $TiO_2$ -based compounds that effectively absorb visible sunlight. Here, one of the most promising techniques is the doping of anatase with simple or transition elements, in particular, with boron, carbon or nitrogen [2, 3].

However, such researches encounter a number of problems. Probably the most serious is that the obtained photocatalysts usually have a complex phase composition that is often difficult to elucidate. There are, for example, arguments in favor of the opinion that microscopic aggregates or fine-grained phases can be constituent parts of the obtained specimens. So, the data on the properties of the photocatalysts, in particular on the optical absorption, are often very contradictory and are associated with differences in the structure.

Consequently, the microscopic structure of the defects in the  $TiO_2$ -based photocatalysts and the effect of doping on the optical properties and PCA are difficult to understand. This is especially valid for the boron-doped anatase, which demonstrates high activity in many photoreactions [4–9]. It has been shown in previous studies [4–6] that the B-doping helps to shift the absorption threshold into the visible range compatibly with its high PCA. However, the authors of the papers [7, 8] observed shifts of the absorption threshold into the UV range, which contradicts the visible range PCA. Also, the data on the locations of the boron atoms inside the anatase structure are contradictory. Some of the data obtained, mainly by means of the X-ray emission spectroscopy, confirm the replacement of oxygen atoms with the boron atoms [5]; hereafter we mark this kind of defects as  $B_O$ . But there are also data in favor of the boron atoms located in interstitial positions [6, 10], we name this a  $B_I$ -defect, or these both kinds of defects can emerge [11].

A better understanding of the optical properties and photocatalytic activity can be achieved based on the first-principle calculations of the electronic band structure. In prior works [7, 8, 12, 13], such calculations have been done for the cases of boron atoms inserted into the oxygen, interstitial and titanium atom positions. Besides, in [7, 12], the calculations of the boron insertion energy have been performed. The authors of the work [12] affirmed that the energy of boron insertion into interstitial position is almost equal to that of insertion into oxygen position, so both kinds of defects can exist. On the other hand, they affirmed that the energy of titanium with boron atoms replacement is higher by about 5 eV, hence such kind of insertion is practically impossible. These calculations [7, 8, 12, 13] have demonstrated that the boron insertion into oxygen positions induces the emergence of boron impurity states above the band gap that correlates with the shift of the light absorption threshold into the visible range [4–6]. Conversely, the insertion into interstitial positions induces the boron impurity states inside the band gap, which correlates with the data of the work [7, 8].

However, the performed calculations are far from perfect. It is well known that the boron atoms inside anatase have a magnetic configuration, so the boron-doped samples demonstrate ESR spectra [11], but the calculations performed were spin-restricted. Additionally, the calculated band gap was much lower than its experimental value, 3.2 eV. Therefore the conclusions of the authors on the energy of the boron atoms states with respect to band gap are doubtful, which also makes their conclusions on the optical absorption of boron-doped anatase doubtful. The performed calculations do not help to recognize the location of boron atoms inside the anatase structure.

Therefore, we have performed new first-principle calculations for the electronic structure of the boron-doped anatase. Our calculations are free from the above mentioned drawbacks, which helps to obtain more reliable conclusions on the effect of the boron doping on the optical and photocatalytic properties of the doped anatase. Besides, we have performed first-principle calculations for the energy of the boron insertion into anatase. Comparing our data with experimental results, we draw conclusions about the most probable positions of the dopant boron atoms.

## 2. Method of research

Typically, high-activity photocatalysts have the forms of nano-structured aggregates because the nano-structurization brings about an increase in the surface area. The evaluated optimal size of the anatase nano-particles for photocatalytic applications is 5–6 nm [14, 15]. In principle, the optical absorption of the nano-particles and the locations of the doping atoms are influenced by quantum-size effects that become essential when the size of the

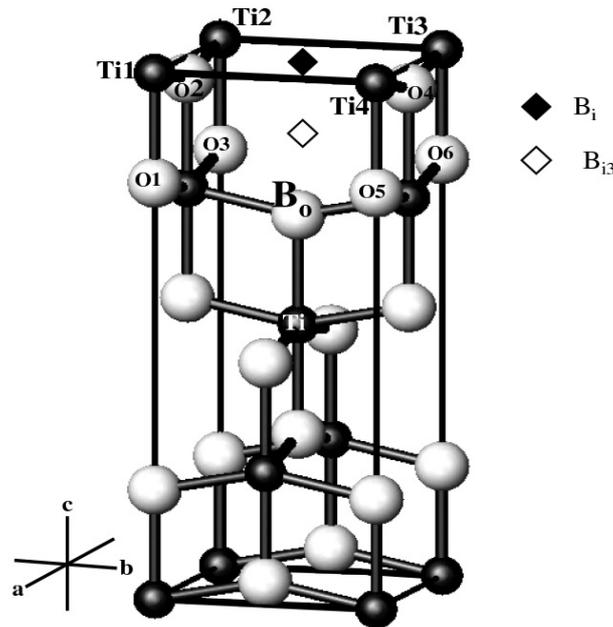


FIG. 1. The conventional unit cell of anatase. The presumed positions of boron atoms are shown. Here  $B_i$  and  $B_{i3}$  are the initial interstitial positions,  $B_o$  is the initial oxygen replacement position - see text.

nano-particles is less than or equal to the de Broglie's wavelength. Evaluations of this wavelength leads to  $\sim 0.7$  nm for anatase and  $\sim 0.2$  nm for rutile [16]. Since these are much smaller than the optimal nano-particle size, we can neglect the quantum-size effects and employ the first-principle calculation methods utilized for the bulk crystals.

Our approach is based on considering the cell of anatase that is obtained by duplicating the primitive unit cell  $Ti_2O_4$  along all the three crystallographic axes. By doing so, we arrive at the 48-atomic unit cell. Replacing one of the oxygen atom by the boron atom we can then model the electronic structure of the  $TiO_{1.9375}B_{0.0625}$  compound; inserting one boron atom we study the  $TiO_2B_{0.0625}$  compound. The positions of the boron atoms are easier to discuss considering the conventional unit cell of bulk anatase shown in Fig. 1.

The location of the boron atom that replaces the oxygen atom ( $B_o$  defects) is quite evident; it is inside the triangle of Ti atoms. However, the interstitial positions of the boron atoms are not so easy to define. We start with two assumptions. The first one is that due to the repulsion of the atomic cores, the interstitial position should probably be the most distant from all neighboring atoms. This is the center of the prism that consists of the  $O1, O2, O3 - O4, O5, O6$  atoms (position  $B_{i3}$  in the figure). Our second supposition is that if the boron atom can form chemical bonds with oxygen atoms, it can be located in the center of the  $Ti1 - Ti2 - Ti3 - Ti4$  square. This position ( $B_i$  in the figure) is also the center of the  $O_4$  tetrahedron essentially flattened along the c-axis. The actual interstitial positions we find by relaxing the crystal structure and looking for the minima of the total energy employing electronic band structure calculations.

We use in the calculation the pseudo-potential plane wave approach realized in the Quantum Espresso (QE) computer code based on the the density functional theory (DFT) [17, 18]. The ultra-soft pseudopotentials with gradient-corrected exchange-correlation (GGA) potential of Perdew, Burke and Ernzerhof [19] provided by the authors

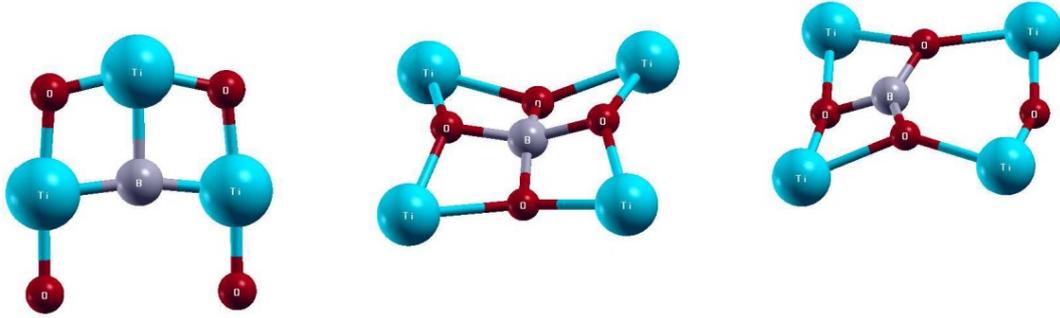


FIG. 2. The nearest vicinity of the boron atoms inserted into the anatase structure. Left image: boron atom in the relaxed  $B_O$  position; middle image: boron atom in the relaxed  $B_i$  position; right image: boron atom in the  $B_{i2}$  position.

of the QE code, was employed. Spin polarization for the energy band structure was allowed. A plane-wave basis set with an energy cutoff of 50 Ry was employed for the wave function and of 300 Ry for the electron density expansion. A grid of 72 wave-vectors per irreducible wedge of the Brillouine zone was used for the electron density calculations. The underestimation of the energy gap between the valence 2pO-like band and 3dTi-like conduction band, typical for the methods based on the DFT theory, has been eliminated by employing the single-site hubbard-like corrections to the exchange-correlation potential within the so-called GGA+U approach described in [20]. The only parameter of this approach is the  $U - J$  value where  $U$  and  $J$  are the correction parameters for the Coulomb and exchange interactions, respectively. We apply these corrections to the Ti 3d states with  $U - J = 6.5$  eV that provides the calculated band gap value equal to the experimental data, 3.2 eV.

It is essential that the application of the Hubbard-like corrections within the GGA+U approach is necessary for obtaining spin-polarized solutions: we will later show that the GGA approach leads only to spin-restricted solutions for the interstitial boron positions .

The DFT GGA approach possesses a high precision, sufficient for evaluating crystal lattice distortions near the B, C or N atoms inserted into the oxide semiconductors [21]. This evaluation is done by looking for the minima of the total energy of the unit cell. The shifts of the atoms are evaluated in correspondence to the calculated forces that act on the atoms. An iterative process of atomic shifting is realized until the forces become negligible. The results obtained by this approach, closest in vicinity to the boron atoms, is inserted into anatase as is shown in Fig. 2.

In the case of the  $B_O$  defect, the most interesting feature of the local crystal structure is the high value of the  $Ti - B - Ti$  angle,  $168^\circ$ , which reflects the trend of the boron atoms to form linear bonds with neighboring titanium atoms [21]. Very interesting are the results of the crystal structure optimization for the  $B_i$  and  $B_{i3}$  cases. The  $B_{i3}$  position appears to be unstable. Boron atoms set initially in this position shift upwards and finally form three short boron-oxygen bonds, with one B - O length equal to 1.40 and two bonds equal to 1.38 Å. The total energy calculation (Table 1) demonstrates that this new position, which we denote  $B_{i2}$ , is stable. The relaxation of the structure with the boron atom set into the  $B_i$  position leads to the shift of the nearest oxygen atoms towards the boron atom. Owing to this shift, four short boron-oxygen bonds occur whose lengths, 1.44 Å, are much less than the  $Ti - O$  bond length, 2.06 Å. This position is metastable, however. This means

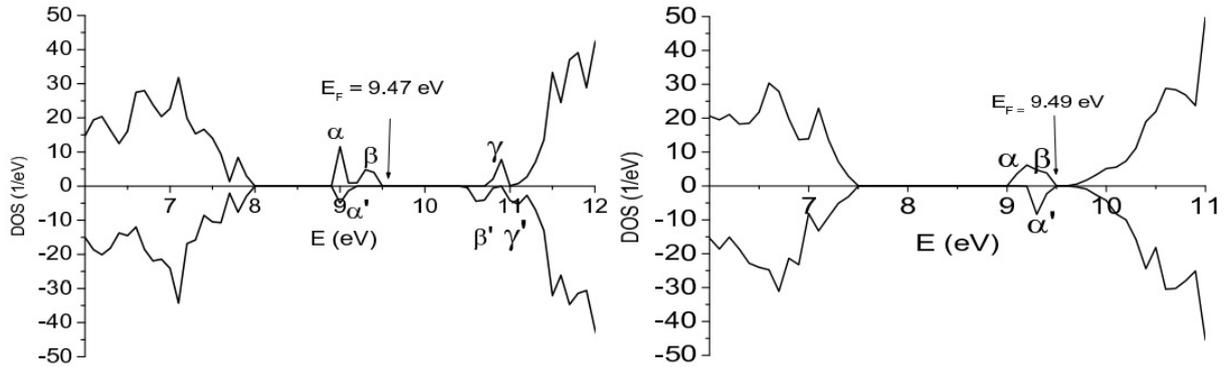


FIG. 3. The spin-resolved densities of states for anatase containing the  $B_O$  defect with the U-J exchange-correlation corrections considered (left panel) and neglected (right panel). The densities of spin-down states are shown with negative sign. The boron-like states are those marked as  $\alpha$ ,  $\beta$  and  $\gamma$  for spin-up states and  $\alpha'$  for spin-down states.

that the total energy of the structure with this kind of defect is higher than the energy of the structure with the  $B_{i2}$  defect. However, the final forces acting on the boron atom set in the relaxed  $B_i$  position are very small, less than 0.002 Ry/at.unit. Infinitely continuing the process of lattice relaxation, we do not find that the boron atom shifts from the  $B_i$  into the  $B_{i2}$  position.

The results, discussed below, for the density of states and total energy were obtained for optimized  $B_O$ ,  $B_i$  and  $B_{i2}$  structures.

### 3. Discussion of results

In Fig. 3, the spin-resolved densities of states are shown for anatase containing the  $B_O$  defect, which were calculated by means of the GGA+U and GGA approaches.

With the GGA+U approach, the states below 8 eV are 2pO valence band states, whereas the states above 11 eV are the 3dTi conduction band states. The boron-like spin-up band states  $\alpha$ ,  $\beta$ ,  $\gamma$  and spin-down states  $\alpha'$  are located inside the band gap. Since there are two spin-up and one spin-down occupied states, the boron atom has a magnetic moment of  $1 \mu_B$ . The energy gap between the Fermi level and the bottom of the conduction band is equal to 1.53 eV, so the calculations predict that anatase with such a defect should have absorption in the visible range. The calculated band structure is in principle similar to that calculated before by means of the LMTO-TB method [21], but our new boron-like bands have the energy, with respect to the bottom of the conduction band, lower by 0.8 eV. The most probable explanation for this difference is that the LMTO-TB method uses a simplified spherically-symmetric potential inside atomic spheres whereas the more exact QE method is free of this simplification. The only-GGA approach also leads to the spin-polarized solution with boron magnetic moment equal to  $1 \mu_B$ , but with the 2pO-3dTi band gap which is approximately 2.2 eV. Although the experimental data on this gap are contradictory, one can hardly expect that the doping with typically small concentration of boron atoms can markedly reduce the value of the gap. So, the results for the band gap calculated with the GGA approach band is unreliable. The densities of states for anatase with the  $B_i$  defect are shown in Fig. 4. The main features of the DOS are similar to that in Fig. 3. The GGA+U solution is also spin-polarized with a magnetic moment of  $1 \mu_B$  per boron atom, with the boron-like states having a higher energy. The essential circumstance

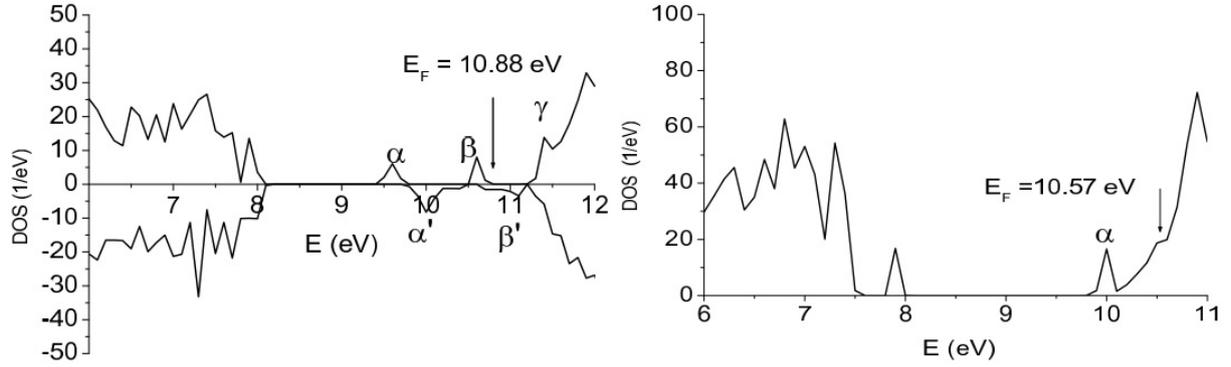


FIG. 4. The spin-resolved densities of states for anatase containing the  $B_i$  defect. The destinations of the lines and the marks are the same as in Fig. 3

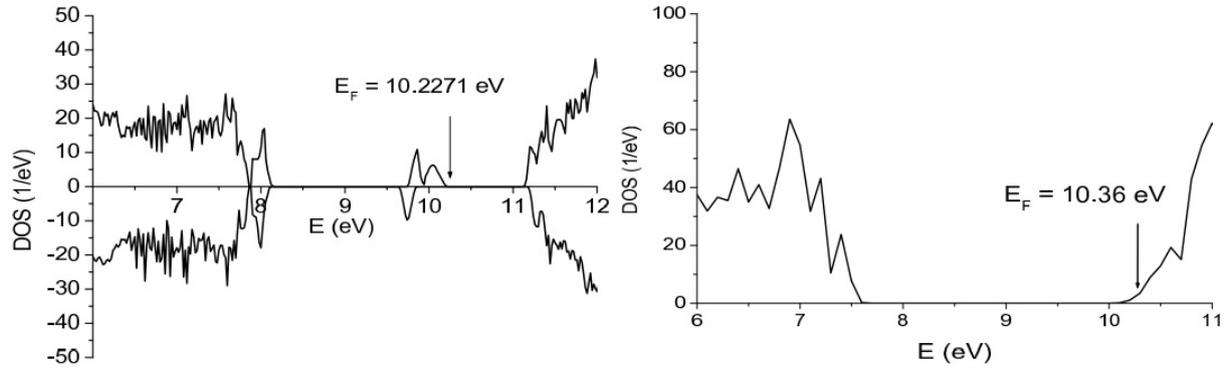


FIG. 5. The spin-resolved densities of states for anatase containing the  $B_{i2}$  defect. The destinations of the lines and the marks are the same as in Fig. 4

is that the only-GGA solution started with the trial boron magnetic moment more than  $1 \mu_B$  converges to the spin-restricted solution. The densities of states for the case of the  $B_{i2}$  defect are shown in Fig. 5. The GGA+U solution is also spin-polarized, however, the only-GGA solution is spin-restricted.

When one considers that the experimental ESR data demonstrate the presence of a magnetic moment on the boron atom, we are forced to conclude that the spin-restricted GGA-approach, is in this case inaccurate. We can come to a definite conclusion on the admissible approximation and to reveal also the preferable location of the boron atom using the first-principle calculations for the energy of defect formation.

The standard definition for the energy of the  $B_O$  kind of defect formation can be written as

$$E_f(B_O) = [E_{tot}(Ti_{16}O_{31}B) + \mu(O)] - [E_{tot}(Ti_{16}O_{32}) + \mu(B)], \quad (1)$$

where  $E_{tot}(\dots)$  are the total energies of the unit cells,  $\mu(O)$  and  $\mu(B)$  are the chemical potentials of the oxygen and boron atoms inside the reaction medium. Similarly, the energy of formation for an interstitial defect  $I = i$  or  $i_2$  is written as:

$$E_f(B_I) = E_{tot}(Ti_{16}O_{32}B_I) - [E_{tot}(Ti_{16}O_{32}) + \mu(B)]. \quad (2)$$

A problem of such an approach is the evaluation of chemical potentials. Since the doping reactions are usually realized in an oxygen atmosphere, we can admit that  $\mu(O)$  is equal to one half the energy of an oxygen molecule. This value, calculated in the GGA approach with spin polarization included, and pseudo-potential identical to that in the band structure

calculation, is equal to  $-31.94$  Ry. However, the chemical potential of the boron atom is difficult to evaluate because of very complicated and rather indefinite structures of the compounds that serve as boron sources. We therefore define the value that we name the interstitial site preference energy as follows:

$$E_{pr}(B_I) = E_f(B_I) - E_f(B_O) = E_{tot}(Ti_{16}O_{32}B_I) - E_{tot}(Ti_{16}O_{31}B_O) - \mu(O). \quad (3)$$

TABLE 1. The values of unit cell total energy  $E_{tot}$  and interstitial site preference energy  $E_{pr}$  calculated with different approaches

Energy characteristics	GGA approach	GGA + sp approach	GGA+sp+U approach
$E_{tot}(i)(Ry)$	-2905.35	-2905.35	-2897.92
$E_{tot}(i2)(Ry)$	-2905.43	-2905.43	-2898.02
$E_{tot}(B_O)(Ry)$	-2872.86	-2872.87	-2865.47
$E_{pr}(i)(eV)$	-7.50	-7.37	-6.91
$E_{pr}(i2)(eV)$	-8.63	-8.50	-8.23

The boron chemical potential is absent here, so this value is easy to calculate. All the values necessary for this evaluation are given in Table 1. We see that  $E_{pr}$  has a large negative value with all the approaches used, so a robust conclusion follows that the formation of interstitial defects  $B_i$  and  $B_{i2}$  is much more favorable in comparison to the replacement defect  $B_O$ . Moreover, the absolute value of the preference energy is essentially higher for the  $B_{i2}$  defect than for  $B_i$  defect. The conclusion then follows that the  $B_{i2}$  defect, with three short boron-oxygen bonds, is the most probable kind of defect.

#### 4. Conclusion

We have performed the electronic band structure calculations for anatase with two kinds of boron atom incorporation: insertion into interstitial positions and replacement of oxygen atoms with boron atoms. The spin-polarization of the band structure was allowed; the Hubbard-like corrections for the Coulomb and exchange correlations in atoms have been included in order to cancel the under-evaluation of the band gap. The total energy of the compounds has been optimized, which helped to find three possible positions of the boron atoms, one of oxygen replacement position and two interstitials. The most stable interstitial position is that inside a trio of oxygen atoms with very short boron-oxygen bonds, whereas the second position, in the center of flattened tetrahedron of oxygen atoms, is metastable. First-principle calculations for the interstitial site preference energy have shown that the insertion of boron atoms into the interstitial positions is energetically more favorable than the replacement of an oxygen atom. The calculations predict that this kind of doping leads to absorption in the visible part of the solar spectrum, which improves its photocatalytic activity.

Our calculations help to elucidate the applicability of two approaches, GGA and GGA+U. The calculations within the both approaches, including and disregarding the spin polarization, lead to equal conclusions on the localization of boron atoms. However, the GGA+U approach that includes the Hubbard-like corrections is preferable since it produces a spin-polarized band structure, whereas the only-GGA calculations for the most stable boron position converge to non-magnetic solutions that contradicts experimental observations.

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