ISSN 1063-7834, Physics of the Solid State, 2009, Vol. 51, No. 3, pp. 507–513. © Pleiades Publishing, Ltd., 2009.
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DEFECTS AND IMPURITY CENTERS, DISLOCATIONS, AND PHYSICS OF STRENGTH

Influence of Impurities on the Stability and Electronic States of Titanium Dioxide in the Form of Anatase

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Received July 16, 2008

Abstract—The behavior of impurities (Si, Zr, Mg, Zn) in the titanium dioxide with an anatase structure is investigated using the electron-density functional method (with due regard for the spin polarization). The influence of these impurities on the formation of oxygen vacancies and the specific features of the electronic structure is studied. It is demonstrated that the impurities can both improve and deteriorate the optical characteristics of the titanium dioxide.

PACS numbers: 71.15.Mb, 71.20.-b

DOI: 10.1134/S1063783409030123

1. INTRODUCTION

Among three crystalline forms of the titanium dioxide (rutile, anatase, brookite), the anatase has attracted considerable attention of researchers owing to the extensive applications as a catalyst, a component of solar cells, and a coloring pigment. The TiO_2 dioxide possessing a large reflection coefficient has been widely used for protecting space vehicles against solar radiation. However, in this case, the important factor is the resistance of the coating with respect to the formation of color centers, which in the titanium dioxide are predominantly represented by oxygen vacancies. In recent years, investigations have been aimed at developing technologies that make it possible to increase the radiation resistance of coatings based on the TiO_2 anatase. For this purpose, the introduction of metal impurities into the titanium dioxide is one of the promising directions. In particular, Mikhaĭlov et al. [1] showed that the introduction of silicon at small doses increases the reflection coefficient, the addition of magnesium decreases the reflection coefficient, and the simultaneous doping with magnesium and zinc increases the radiation resistance. It should be noted that an increase in the concentration of all these elements (from 0.5 to 1.0%) leads to a decrease in the reflection coefficient and a deterioration of the radiation resistance. The mechanism of the influence of these impurities on the properties of the titanium dioxide remains unclear and requires detailed investigations, including with the use of theoretical approaches. The present study was devoted to the solution of this problem.

2. CALCULATION METHOD

The introduction of impurities and the formation of vacancies in the TiO_2 dioxide are frequently accompanied by the spin polarization. Therefore, the total energy and the electronic structure were calculated with the FH196spin program package, which is a modification of the FH196md program package [2] previously used with advantage for many systems, including transition metal oxides [3–5]. This program package is based on the spin-unrestricted version of the electron-density functional theory, the pseudopotential method, and the use of a plane-wave basis set. In this work, we used the pseudopotentials of titanium and oxygen that were constructed with the FHI98PP program package [6]. The pseudopotentials were checked for the absence of the so-called ghost states and used for determining the equilibrium lattice parameters and the bulk elastic modulus of the anatase. These pseudopotentials are separable, transferable, and norm-conserving pseudopotentials [6]. The calculated values of the lattice parameters and the elastic modulus differed from the experimental values by no more than 2 and 10%, respectively. A similar procedure was used for choosing the pseudopotentials of impurity atoms. In all cases (except for titanium), the pseudopotentials were calculated using the Troullier–Martins scheme [7]. For titanium, the *s* and *p* components were determined according to the Hamann technique [8] and the *d* component was calculated within the Troullier–Martins scheme. The parameters of the pseudopotentials used are listed in Table 1.

Table 1. Critical radii of the *s*, *p*, and *d* components (r_s, r_p, r_d), radii of the core correction (r_{cor}), and types of local parts (l_{loc}) of pseudopotentials

Element	r_s, Å	r_p, Å	r_d, Å	r_{cor}, Å	l_{loc}, Å
Ti	0.91	0.91	1.41	–	*s*
O	0.72	0.92	0.72	0.74	*d*
Si	0.90	0.99	1.07	–	*d*
Zr	1.36	1.62	1.24	–	*p*
Mg	1.05	1.05	1.32	–	*d*
Zn	1.06	1.20	–	–	*s*

In all cases, we used the generalized gradient correction approximation and performed the optimization of the atomic geometry (the relaxation of the lattice around impurity atoms and vacancies was taken into account). Since the flexible spin polarization (the energetically induced transition of electrons from one spin subsystem to another spin subsystem) was included in our method, the calculations did not require the specification of state multiplicity. This multiplicity was automatically obtained in a self-consistent manner.

The anatase structure is well known (see, for example, [9]). The unit cell of this compound contains four titanium atoms and eight oxygen atoms. The symmetry corresponds to space group $I4_1/amd$ (Pearson symbol *tI*12). The atomic arrangement in the unit cell is depicted in Fig. 1. The experimental unit cell parameters are as follows: a = 3.784 Å and c = 9.515 Å [10]. Our calculated equilibrium unit cell parameters are somewhat larger: a = 3.842 Å and c = 9.657 Å.

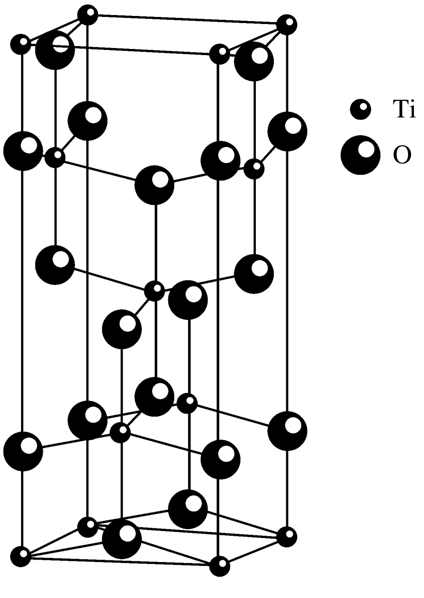

Fig. 1. Schematic atomic arrangement of the TiO_2 dioxide with an anatase structure.

In this study, we used a 2 × 2 × 1 supercell containing 16 titanium atoms and 32 oxygen atoms. For comparison, some calculations were carried out with a 2 × 2 × 2 doubled cell. As a rule, cells and clusters with this size have been used for investigating impurities and defects in the titanium dioxide (for example, Stashans et al. [11] studied the behavior of oxygen vacancies and fluorine and chlorine atoms in the rutile and the anatase with the use of $Ti_{16}O_{32}$ and $T_{32}O_{64}$ clusters). In the majority of cases (if this is not specially noted in the text), we used one point in the Brillouin zone, namely, the Γ point (0, 0, 0). However, in order to verify the reliability of the results, some calculations were tested with the use of five or eight points. In all cases, the cutoff energy of the plane-wave basis set was equal to 44 Ry. The self-consistent convergence was provided by stabilizing the total energy with an accuracy of 0.003 eV.

The charged states were examined using the technique (included in the FHI96spin program package) that made it possible to increase (or decrease) the number of active electrons in the cell. In this case, the inactive part of the charge density was uniformly distributed over the entire cell, thus ensuring the total electroneutrality.

3. RESULTS OF CALCULATIONS AND DISCUSSION

First and foremost, we calculated the electronic structure of the pure titanium dioxide. The densities of states simulated by broadening each energy level by a Gaussian curve with a half-width of 0.2 eV are shown in Fig. 2 in comparison with the results obtained in [12] with the use of full-electron calculations (Fig. 3).

It can be seen from Fig. 2a that, even in the case of one *k* point, the $Ti_{16}O_{32}$ supercell appears to be quite suitable for describing the main features of the density of states of the TiO_2 dioxide with an anatase structure. Primarily, this holds true for the band gap E_g. According to our calculations, the band gap at the Γ point is equal to 2.31 eV, which is in good agreement with values of 2.32 [12], 2.0 [13], and 2.3 eV [14]. The experimental band gap amounts to 3.2 eV [15]. It is known that the correct band gap can be theoretically obtained only with the use of the methods accounting for collective effects [16], for example, with the GW approach using Green's functions.

3.1. Formation of Vacancies in the Pure TiO_2 Dioxide

The energy of formation of an oxygen vacancy was calculated taking into account that the oxygen atoms escaped from the titanium dioxide bind into O_2 molecules. The energy E_{vac} of vacancy formation was determined from the relationship

$$E_{\mathrm{vac}} = E(\mathrm{vac}) - E(\mathrm{perf}) + \frac{1}{2}E(O_2),$$

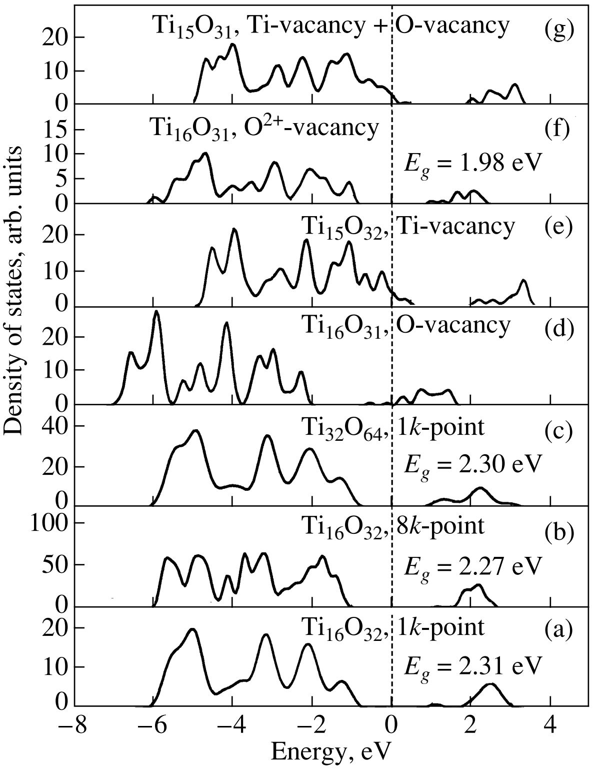

Fig. 2. Electronic structures of the pure TiO_2 dioxide with an anatase structure: (a) perfect TiO_2 ($Ti_{16}O_{32}$ supercell, one *k* point), (b) perfect TiO_2 ($Ti_{16}O_{32}$ supercell, eight *k* points), (c) perfect TiO_2 ($Ti_{32}O_{64}$ supercell, one *k* point), (d) neutral oxygen vacancy ($Ti_{16}O_{32}$ supercell, one *k* point), (e) neutral titanium vacancy ($Ti_{16}O_{32}$ supercell, one *k* point), (f) charged (+2) oxygen vacancy ($Ti_{16}O_{32}$ supercell, one *k* point), and (g) oxygen and titanium neutral vacancies ($Ti_{16}O_{32}$ supercell, one *k* point). The vertical dashed line indicates the Fermi level.

where *E*(perf) is the energy of a defect-free crystal, *E*(vac) is the energy of a crystal with an oxygen vacancy, and $E(O_2)$ is the energy of an oxygen molecule.

For the neutral vacancy, the energy of formation is equal to 4.85 eV (the corresponding energy available in the literature amounts to 4.2 eV [17]). The vacancy level lies 0.32 eV below the conduction band (Fig. 2d), which is close to the theoretical data (0.2 eV) [11] and the experimental results (0.2–0.3 eV) [18]. The calculations performed with five *k* points lead to a value of 0.30 eV.

In actual fact, the oxygen vacancy in the TiO_2 dioxide at finite temperatures attracts a positive charge of +2. Consequently, two electrons that should be bound to the absent oxygen atoms go from the vacancy region to the conduction band. In this case, the band gap slightly decreases as compared to that of the defect-free material and becomes equal to 1.98 eV (Fig. 2f). A similar effect was described by Na-Phattalung et al. [12], who noted that the presence of oxygen vacancies with due regard for the charge transfer does not lead to the appearance of states inside the band gap. Therefore, we can believe that the oxygen vacancy in the titanium dioxide is a thermal source of electrons and plays the role of a donor impurity.

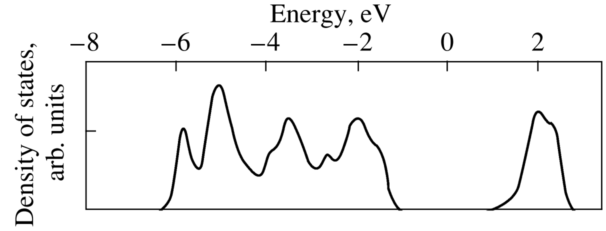

Fig. 3. Density of states for the TiO_2 dioxide with an anatase structure according to the data taken from [12].

The energy of formation of a titanium vacancy was calculated as the energy of escape of a single titanium atom from the TiO_2 dioxide without regard for subsequent condensation, because the last process is ambiguous and depends strongly on the environmental conditions. The energy thus determined is equal to 21.40 eV. In this case, the vacancy level is located 0.18 eV below the valence band (Fig. 2e). Consequently, the titanium vacancy behaves as a hole source.

The simultaneous formation of the oxygen and titanium vacancies results in the electronic structure that differs insignificantly from the structure formed in the case of the titanium vacancy (Fig. 2g).

3.2. Influence of Impurities

We investigated the simplest case, i.e., the replacement of one titanium atom in the $Ti_{16}O_{32}$ supercell. For one impurity atom, this corresponds to 6.25 at % Ti. This concentration is higher than those noted in [1]. For a reliable quantitative comparison, the number of atoms in the cell should be increased by one order of magnitude. Unfortunately, this could not be done from technical reasons due to the limited random-access memory of the computer.

3.3. Introduction of Silicon and Zirconium

Silicon as a tetravalent element replaces titanium [19, 20]. The replacement of one titanium atom by one silicon atom leads to an insignificant change in the electronic structure (Fig. 4a). The band gap slightly narrows from 2.31 to 2.10 eV. The energy of formation of the neutral oxygen vacancy increases to 5.0 eV, which is 0.15 eV larger than that for the pure TiO_2 dioxide. The vacancy level lies 0.27 eV below the conduction band. As for the pure compound, the charged vacancy (+2) provides approximately the same band gap (2.07 eV). In order to generalize the results, we carried out similar calculations for one more tetravalent element (zirco-

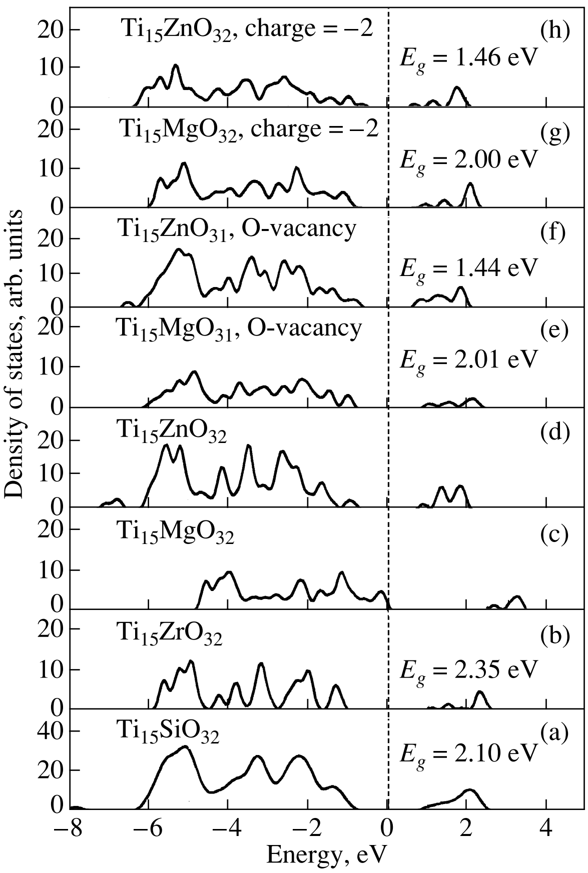

Fig. 4. Electronic structures of the TiO_2 dioxide with the anatase structure upon doping with different impurities: (a) Si atom, (b) Zr atom, (c) Mg atom, (d) Zn atom, (e) Mg atom + O vacancy, (f) Zn atom + O vacancy, (g) Mg atom (charge, –2), and (h) Zn atom (charge, –2).

nium). It was revealed that the replacement of one titanium atom by one zirconium atom leads to the same band gap (2.35 eV). The energy of formation of the neutral oxygen vacancy is equal to 6.0 eV, and the band gap with the charged vacancy turns out to be 2.12 eV. Therefore, in this case, we observe an increase in the stability of the zirconium dioxide with respect to the formation of oxygen vacancies. These results are in agreement with the experimental data obtained by Hirano et al. [21], who noted that the introduction of the zirconium impurity leads to a broadening of the band gap.

The statement that the introduction of silicon deteriorates the radiation resistance of the titanium dioxide [1] cannot be treated as conclusively proved, because the experimental technique used in [1] cannot reliably separate the influence of silicon from the effect of other factors (for example, the influence of fluorine atoms). Moreover, Iwamoto et al. [19] noted that silicon increases the stability of the TiO_2 dioxide with the anatase structure.

3.4. Introduction of Magnesium

When titanium atoms are replaced by divalent magnesium atoms, the titanium dioxide experiences a deficit of electrons in order to saturate the bonds of the oxygen atoms. In the neutral state, this results in the appearance of the electronic level in the vicinity of the valence band (Fig. 4c). In the charged state (–2), there arises a band gap of 2.00 eV (Fig. 4g). Approximately the same band gap (2.01 eV) appears upon formation of the oxygen vacancy in the magnesium-doped uncharged titanium dioxide (Fig. 4e). The energy of formation of this vacancy is very low and amounts to 1.10 eV. Consequently, the presence of magnesium favors the formation of neutral oxygen vacancies; however, in this case, the band gap is relatively wide and the optical properties are not deteriorated substantially. A significant change in the electronic structure (the disappearance of the band gap) is observed only after the formation of the second oxygen vacancy in the vicinity of the magnesium atom (the energy of formation is equal to 4.65 eV, which is 0.2 eV lower than that for the pure titanium dioxide). Therefore, the resistance with respect to the formation of optically active defects decreases. Ranjit and Viswanathan [22] experimentally demonstrated that an increase in the magnesium content leads to an increase in the absorption, the shift in the fundamental absorption edge toward the long-wavelength range, and, hence, a decrease in the band gap of the TiO_2 dioxide. This confirms the results obtained in our work.

3.5. Introduction of Zinc

Like magnesium, zinc is a divalent element but behaves somewhat differently in the titanium dioxide. In the neutral state, zinc even in the absence of oxygen vacancies forms the band gap, which is equal to 1.76 eV (Fig. 4d). In the charged state, the band gap narrows to 1.46 eV (Fig. 4h). The energy of formation of the neutral oxygen vacancy is equal to 3.41 eV, and the corresponding band gap amounts to 1.44 eV (Fig. 4f). The second oxygen vacancy is formed with an energy of 5.44 eV, which is almost 0.6 eV higher than the energy of formation of the oxygen vacancy in the pure titanium dioxide. Therefore, the introduction of zinc into the titanium dioxide decreases the probability of formation of oxygen vacancies and, hence, increases the radiation resistance of the material. However, the optical properties of the matrix in this case are deteriorated as a result of a considerable decrease in the band gap.

3.6. Simultaneous Doping with Magnesium and Zinc

According to Mikhaĭlov et al. [1], the introduction of both magnesium and zinc into the titanium dioxide results in an increase in the radiation resistance and an improvement of the optical properties (an increase in the reflection coefficient).

When explaining the simultaneous introduction of magnesium and zinc, it is reasonable to assume that the observed effect is associated with the formation of pairs (with the approach) of Mg and Zn atoms. However, since these atoms are divalent, their approach (“literal pairing”) can be represented so that two atoms (Mg + Zn) replace one tetravalent Ti atom. We investigated this variant, and revealed that it is energetically unfavorable. The energy loss is equal to 7.0 eV. The Mg + Mg and Zn + Zn pairs also appear to be unfavorable. The energy losses for these pairs are equal to 3.1 and 8.7 eV, respectively.

At the same time, the simple approach of impurity atoms singly replacing the titanium atoms turns out to be energetically favorable. The dependence of the total energy on the distance between the impurity atoms was not studied in detail. However, in the case where the impurity atoms are placed at the positions of the next-nearest neighbor titanium atoms, the energy gain is equal to 1.0 eV for the Mg + Zn pair, 1.5 eV for the Mg + Mg pair, and 3.3 eV for the Zn + Zn pair. In this case, the approach of the Mg + Mg atoms leads to the formation of a band gap of 1.7 eV (without oxygen vacancies) and the approach of the Zn + Zn pair results in band gap $E_g = 1.3$ eV, whereas the Mg + Mg pair (like the single Mg atom) does not form an insulating gap. The energies of formation of oxygen vacancies and the band gaps for all the cases under consideration are presented in Table 2.

It is evident that the approach of similar atoms is most probable at their high concentration. It can be seen from Table 2 that an increase in the magnesium concentration leads to an improvement of the optical properties and an increase in the radiation resistance. An increase in the zinc concentration deteriorates the optical properties and the resistance of the titanium dioxide to the formation of radiation-induced defects.

It can also be seen from Table 2 that, in the case of doping with magnesium, the approach of the impurity atoms almost does not change the optical properties of the titanium dioxide. In the case of zinc, which deteriorates the optical properties, the approach of the atoms results in a further narrowing of the band gap. The variant of Mg + Zn pairs seems to be most preferable. After the escape of excess oxygen from the material (the first and second oxygen vacancies), this variant ensures the optical properties almost identical to those observed for the pure titanium dioxide. As regards the radiation resistance, this characteristic increases in all cases.

Table 2. Energy characteristics (eV): bands gap E_g, energy $E_{\mathrm{vac(O)}}$ of formation of oxygen vacancies, and energy gain ΔE upon replacement of two titanium atoms in the $Ti_{16}O_{32}$ supercell by single impurity atoms as compared to the location of these atoms in different cells

Impurity	Oxygen vacancy	E_g	$E_{\mathrm{vac(O)}}$	ΔE
Mg	Absent	*	–	–
	First vacancy	2.01	1.00	–
	Second vacancy	*	4.45	–
Zn	Absent	1.76	–	–
	First vacancy	1.46	3.41	–
	Second vacancy	1.44	5.44	–
Mg + Mg	Absent	*	–	1.50
	First vacancy	2.02	0.20	–
	Second vacancy	2.03	0.30	–
	Third vacancy	*	5.45	–
Zn + Zn	Absent	1.30	–	3.30
	First vacancy	1.45	1.29	–
	Second vacancy	1.41	3.02	–
	Third vacancy	*	5.19	–
Mg + Zn	Absent	1.70	–	1.00
	First vacancy	2.30	0.80	–
	Second vacancy	2.21	2.23	–
	Third vacancy	1.00	5.31	–

* The band gap is absent.

3.7. Spin Polarization and Relaxation of the Atomic Structure

The spin polarization (in the cases where this effect occurs) and the relaxation of the atomic structure around the impurities and vacancies undeniably affect the energy characteristics and the electronic structure. We did not discuss these effects above and focused our attention on the final results, namely, the energy characteristics and the electronic structure. This approach seems to be quite justified because we do not discuss the magnetic properties of the systems under investigation and experiments on the study of a detailed atomic arrangement. However, in order to describe more completely the influence of defects on the properties of the titanium dioxide and with allowance made for possible subsequent applications of our calculations, we analyzed the values of the spin polarization and the atomic displacements in the cell (maximum displacements $\Delta_{\max}$ and minimum displacements $\Delta_{\min}$). The results obtained are summarized in Table 3. The spin polarization p is considered to mean the difference between the numbers of electrons in different spin subsystems ($p = n^{\uparrow} - n_{\downarrow}$). The maximum displacements are observed for the atoms that are the nearest neighbors (1.96 Å) and the next-nearest neighbors (3.07 Å) with respect to the defect sites in the lattice. The atoms located at the periphery of the cell are characterized by the minimum displacements. Depending on the defect type (single, composite), the corresponding distances from the defects lie in the range 3.5–5.0 Å.

Table 3. Spin polarizations *p* and atomic displacements Δ (Å) in the titanium dioxide

System	*p*	$\Delta_{max}O$	$\Delta_{min}O$	$\Delta_{max}Ti$	$\Delta_{min}Ti$
Single defects					
$Ti_{16}O_{31}$	2.0	0.05	0.01	0.10	<0.01
$Ti_{15}O_{32}$	3.8	0.11	0.02	0.07	<0.01
$Ti_{15}Si_1O_{32}$	0	<0.01	<0.01	<0.01	<0.01
$Ti_{15}Zr_1O_{32}$	0	0.21	0.02	0.11	<0.01
$Ti_{15}Mg_1O_{32}$	0	0.28	0.03	0.09	0.01
$Ti_{15}Zn_1O_{32}$	0	0.90	0.03	0.27	<0.01
Complex defects					
$Ti_{15}Mg_1O_{31}$	0	0.28	0.02	0.09	0.01
$Ti_{15}Mg_1O_{30}$	2.0	0.20	0.03	0.20	0.10
$Ti_{15}Zn_1O_{31}$	0	0.53	0.24	0.10	0.08
$Ti_{15}Zn_1O_{30}$	2.0	0.20	0.10	0.20	0.10
$Ti_{14}Mg_2O_{32}$	0	0.30	0.01	0.15	0.05
$Ti_{14}Mg_2O_{30}$	0	0.20	0.02	0.10	0.05
$Ti_{14}Mg_2O_{29}$	0	0.33	0.05	0.12	0.02
$Ti_{14}Zn_2O_{32}$	0	0.40	0.10	0.12	0.05
$Ti_{14}Zn_2O_{30}$	0	0.38	0.05	0.11	0.04
$Ti_{14}Zn_2O_{29}$	0	0.42	0.07	0.14	0.03
$Ti_{14}Mg_1Zn_1O_{32}$	0	0.39	0.06	0.10	0.04
$Ti_{14}Mg_1Zn_1O_{30}$	0	0.31	0.02	0.10	0.05
$Ti_{14}Mg_1Zn_1O_{29}$	0	0.42	0.05	0.13	0.03

It can be seen from Table 3 that the spin polarization arises only in the case of formation of single titanium and oxygen vacancies in the pure titanium dioxide (the $Ti_{16}O_{31}$ and $Ti_{15}O_{32}$ systems) and two oxygen vacancies in the titanium dioxide doped with magnesium and zinc (the $Ti_{15}Mg_1O_{30}$ and $Ti_{15}Zn_1O_{30}$ systems). The maximum atomic displacements in the vicinity of the single defects, as a rule, do not exceed 0.3 Å and decrease rapidly with an increase in the distance from the defects. The exception is provided by the system doped with zinc, in which the displacements of oxygen atoms are equal to 0.9 Å. Possibly, this is indirectly associated with the fact that, among the impurities under consideration, zinc has a minimum atomic radius. It should be noted that, as could be expected, the lattice disordering associated with the introduction of the tetravalent impurities (Si, Zr) is weaker than the disordering formed after introduction of the divalent impurities (Mg, Zn).

In the case of complex defects containing impurity atoms and oxygen vacancies, the maximum displacements increase (except for the systems involving zinc). The minimum displacements also increase but do not exceed 0.1 Å (except for the systems involving zinc with $\Delta_{min}O$ = 0.24 Å). This circumstance suggests that the lattice distortion around defects relaxes rather rapidly and that the sizes of the used supercell are sufficient for investigating the problem posed in our work (possibly, except for the systems containing zinc).

4. CONCLUSIONS

Thus, the calculations based on the electron-density functional theory demonstrated that the introduction of tetravalent impurities (Si, Zr) into the titanium dioxide with an anatase structure makes it possible to improve the optical characteristics and the radiation resistance of the compound. As regards the use of divalent metals (Mg, Zn), the separate doping with these metals deteriorates the optical characteristics of the titanium dioxide; however, their simultaneous introduction leads to an increase in the radiation resistance without loss of the optical quality.

ACKNOWLEDGMENTS

This study was supported by the Presidium of the Far East Division of the Russian Academy of Sciences.

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Translated by O. Borovik-Romanova

SPELL: 1. Relochnyi