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METALS

Short-Range Order and Nonstoichiometry in Titanium Monoxide TiO_y from DFT Calculations

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Abstract—Structural models of short-range order in the arrangement of structural vacancies have been proposed for stoichiometric and nonstoichiometric compositions of titanium monoxide TiO_y. A combined effect of the short-range order and nonstoichiometry on the ground-state energy and the electronic structure of the compound has been investigated using the first-principles methods. The energetically favorable models of short-range order reproduce the local distribution of atoms and vacancies, which is characteristic of the $Ti_5O_{5(mon)}$ and $Ti_5O_{5(cub)}$ superstructures. In these models, the correlations between the vacancies of the metal sublattice and the vacancies of the nonmetal sublattice make a more significant contribution to the decrease in the energy of the compound as compared with the correlations between the vacancies in only one of the sublattices.

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1. INTRODUCTION

In the crystal structure of many transition-metal compounds, there are structural vacancies. Such a structural defect is a site of the crystal lattice, which is not occupied by an atom. In contrast to thermal vacancies, the concentration of structural vacancies is almost independent of temperature. Structural vacancies are associated with different effects of nonstoichiometry, short-range order, and long-range order [1–3]. These effects make it possible to synthesize a wide variety of phases and modifications with different properties by changing the number of vacancies in the sublattices, as well as the pattern of their arrangement in the structure of the compound.

In this sense, the most remarkable compound is a nonstoichiometric titanium monoxide TiO_y. The titanium monoxide has a basic crystal structure of the *B*1 type and, in contrast to the majority of other representatives of the class of strongly nonstoichiometric compounds [1–3], contains vacancies in both the metal and nonmetallic sublattices. In the titanium monoxide of nonstoichiometric composition, the unoccupied sites amount to approximately 15% of the total number of sites in the metal and nonmetal sublattices [4–7]. The nonstoichiometry is realized due to the decrease in the concentration of vacancies in one of the sublattices and due to the increase in their concentration in the other sublattice. The homogeneity region of the compound depends on the temperature. The lower and upper boundaries of the homogeneity region of the TiO_y oxide lie below the concentration $y = 0.80$ and above $y = 1.25$, respectively. Moreover, the concentration of vacancies at the boundaries of the homogeneity region reaches 25% in one of the sublattices and tends to zero in the other sublattice [8].

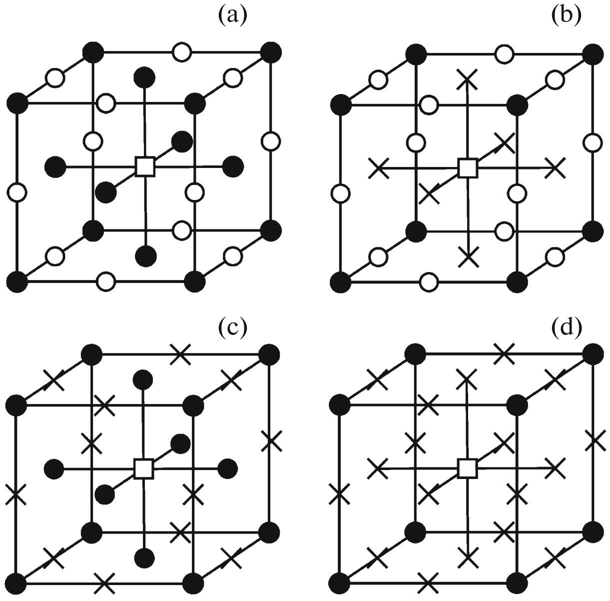
In the titanium monoxide, a disordered phase or ordered phases with the superstructures $Ti_5O_{5(mon)}$ (space group $C2/m$ ($A2/m$)) [4–7] and $Ti_5O_{5(cub)}$ (space group $Pm\overline{3}m$) can be formed depending on the pattern of the arrangement of structural vacancies in the sites of the basic crystal structure [9–11]. In the disordered phase, vacancies are arranged in the sites of the sublattices without a long-range order and do not lead to the breaking of the symmetry of the basic crystal structure. Upon the ordering, vacancies are redistributed over the sites of the sublattices, the long-range order is formed in the structure, and the symmetry of the structure is reduced [4–11].

The influence of structural vacancies and their ordering on the electronic structure and stability of the titanium monoxide has become the subject of many theoretical studies [12–28]. The most reliable data have been obtained both for a phase without structural vacancies and for phases with perfectly ordered superstructures. Randomly arranged vacancies have been investigated using less accurate methods, which did not provide a correct comparison of the energy and specific features of the electronic structure in the disordered and ordered states. The use of high-performance calculations and the supercell method [29] in subsequent studies [30–37] made it possible to analyze the effects of long-range order and nonstoichiometry in the framework of the most accurate and unified approaches [38–41]. In particular, it was shown that the ordering of structural vacancies according to the type of the monoclinic superstructure $Ti_5O_{5(mon)}$ leads to the maximum decrease in the energy of the defect structure. The ordering of structural vacancies according to the type of the cubic superstructure $Ti_5O_{5(cub)}$ is energetically less favorable. The investigations of the short-range order in a disordered phase of the stoichiometric composition $TiO_{1.0}$ [36, 42–44] demonstrated that the influence of short-range order is comparable to the influence of long-range order and should not be ignored. At the same time, the investigations of the electronic structure of the compounds with nonstoichiometric compositions [25, 30] were carried out without taking into account the short-range order, which makes these studies not quite correct. Investigation of the combined effect of nonstoichiometry and short-range order is of interest in view of the possible metal–semiconductor transition and other effects associated with the change in the composition and the degree of order in the structure of the titanium monoxide [45, 46].

In connection with the necessity to take into account the short-range order in the quantum-chemical and thermodynamic calculations, in this paper we have proposed the simplest structural models of short-range order for nonstoichiometric compositions and investigated the combined effect of short-range order and nonstoichiometry on the electronic structure and energy characteristics of the titanium monoxide TiO_y in the composition region $0.75 \leq y \leq 1.33$.

2. STRUCTURAL MODELS OF SHORT-RANGE ORDER

In our previous studies [36, 42, 43], the short-range order in the arrangement of vacancies in the *B*1 structure was simulated by dividing the structure into cubic elementary clusters containing energetically favorable groups of vacancies. This approach is quite convenient and makes it possible to graphically depict specific features of the structure of disordered phases with a short-range order, as well as to take into account the near atomic–vacancy ordering in the calculations of the diffraction spectra and the electronic structure. However, the fact that the elementary clusters are arranged in an ordered manner cannot lead to the complete elimination of the long-range order. Let us consider more realistic models that take into account the energetically favorable correlations, but do not suggest the hidden long-range order in the arrangement of atomic–vacancy groups.



□ Vacancy of nonmetal sublattice
× Prohibited site for vacancy
● Possible vacancy of metal sublattice
○ Possible vacancy of nonmetal sublattice

Fig. 1. Rules for the arrangement of vacancies in the structural models of the disordered phase of titanium monoxide: (a) the statistical distribution of vacancies, at which the short-range order is absent; (b) the prohibition of the first coordination sphere; (c) the prohibition of the second coordination sphere; and (d) the prohibition of the first and second coordination spheres. The variants, in which the central vacancy is a vacancy of the metal sublattice, are similar to each other and can be obtained though the replacement of the metal sublattice by the nonmetal sublattice and the nonmetal sublattice by the metal sublattice.

In the energetically favorable superstructures, which correspond to the stoichiometric composition, the minimum distance between the vacancies of one sublattice is equal to the radius of the fourth coordination sphere, whereas the minimum distance between the vacancies belonging to different sublattices is equal to the radius of the third coordination sphere [4–7, 9–11]. The violation of this condition occurs only with a decrease in the degree of long-range order in structural models that do not take into account the local correlations [47–49]. Therefore, in the simplest approximation, the short-range order can be simulated by means of the prohibition imposed on the arrangement of structural vacancies spaced apart at a distance of less than the radius of the first or second coordination sphere. Such an arrangement of the vacancies is graphically depicted in Fig. 1. The combination of prohibitions within the first two coordination spheres of the *B*1 structure makes it possible to generate a wide variety of structural models for stoichiometric and nonstoichiometric compositions. The description of all the models considered in this study is given in Table 1. Model nos. 1–5 correspond to the stoichiometric composition in the case where the

Table 1. Parameters of structural models for different compositions of titanium monoxide

No.	Composition	The number of vacancies of the oxygen sublattice within the radius of the first coordination sphere from the vacancy of the titanium sublattice	The number of vacancies of the titanium sublattice within the radius of the first coordination sphere from the vacancy of the oxygen sublattice	The number of vacancies of the titanium sublattice within the radius of the second coordination sphere from the vacancy of the titanium sublattice	The number of vacancies of the oxygen sublattice within the radius of the second coordination sphere from the vacancy of the titanium sublattice
1	$Ti_{0.83}O_{0.83}$	Not regulated	Not regulated	Not regulated	Not regulated
2		0	0	Not regulated	Not regulated
3		Not regulated	Not regulated	0	0
4		0	0	The minimum possible number	The minimum possible number
5	$Ti_{0.92}O_{0.86}$	Not regulated	Not regulated	Not regulated	Not regulated
6		0	0	Not regulated	Not regulated
7		Not regulated	Not regulated	0	0
8		0	0	The minimum possible number	The minimum possible number
9	$Ti_{0.86}O_{0.92}$	Not regulated	Not regulated	Not regulated	Not regulated
10		0	0	Not regulated	Not regulated
11		Not regulated	Not regulated	0	0
12		0	0	The minimum possible number	The minimum possible number
13	$Ti_{0.92}O_{1.00}$	0, because there are no vacancies in the oxygen sublattice	0, because there are no vacancies in the oxygen sublattice	Not regulated	0, because there are no vacancies in the oxygen sublattice
14		The same	The same	0	The same
15	$Ti_{1.00}O_{0.92}$	0, because there are no vacancies in the oxygen sublattice	0, because there are no vacancies in the titanium sublattice	0, because there are no vacancies in the titanium sublattice	Not regulated
16		The same	The same	The same	0
17	$Ti_{0.75}O_{1.00}$	0, because there are no vacancies in the oxygen sublattice	0, because there are no vacancies in the oxygen sublattice	Not regulated	0, because there are no vacancies in the oxygen sublattice
18		The same	The same	The minimum possible number	The same
19	$Ti_{1.00}O_{0.75}$	0, because there are no vacancies in the oxygen sublattice	0, because there are no vacancies in the titanium sublattice	0, because there are no vacancies in the titanium sublattice	Not regulated
20		The same	The same	The same	The minimum possible number

numbers of vacancies in the metal sublattice and in the nonmetal sublattice are identical and equal to 1/6. Model nos. 6–13 describe the short-range order in titanium monoxide of nonstoichiometric compositions in the case where the numbers of vacancies in the titanium sublattice and in the oxygen sublattice are close to those observed in the experiments [45]. Model nos. 14–17 also correspond to nonstoichiometric compositions, but the nonstoichiometry of the compound in these models is realized by means of the complete removal of vacancies from one of the sublattices. This situation is hypothetical and, possibly, is observed in the high-pressure disordered phase [35]. Model nos. 18–21 describe the structures at the boundaries of the homogeneity region. In this case, the concentration of vacancies in one of the sublattices is assumed to be equal to zero.

In model nos. 1, 6, 10, 14, 16, 18, and 20, there are no any restrictions that would lead to a short-range order in the arrangement of structural vacancies; i.e., the vacancies are statistically distributed (Fig. 1a), and the structure is described by the mean-field approximation [50]. In other cases, the short-range order in the arrangement of structural vacancies is described by

Table 2. Enthalpy of formation of titanium monoxide according to the calculations for different structural models (the standard deviations $\pm\sigma$ characterizing the spread in the values of the energy for ten supercells of each structural model are also presented)

Model no.	Enthalpy of formation, kJ/mol	Model no.	Enthalpy of formation, kJ/mol	Model no.	Enthalpy of formation, kJ/mol
1	−521.8 ± 3.5	8	−465.3 ± 1.3	15	−470.8 ± 0.8
2	−532.3 ± 1.6	9	−599.3 ± 3.2	16	−474.3 ± 1.1
3	522.3 ± 1.8	10	−609.4 ± 0.9	17	−693.0 ± 3.2
4	−534.3 ± 2.9	11	−606.9 ± 1.2	18	−697.5 ± 3.4
5	−456.0 ± 2.3	12	−611.6 ± 2.8	19	−401.9 ± 1.0
6	−462.6 ± 1.8	13	−559.5 ± 0.7	20	−403.3 ± 0.9
7	−462.6 ± 1.8	14	−566.1 ± 2.5		

one of the rules illustrated in Figs. 1b–1d. It should be noted that the strict prohibition on the arrangement of vacancies in particular sites of the disordered structure becomes possible when the concentration of vacancies in the sublattices is less than a specific value [42]. If in the case of the stoichiometric composition $Ti_{0.83}O_{0.83}$, a certain number of vacancies can be arranged following the prohibition on the first coordination sphere, then the prohibition on the second coordination sphere will be strict only when the concentration of vacancies is decreased by approximately 2%. Therefore, in similar situations, the short-range order is taken into account by minimizing the number of vacancies in forbidden positions. The number of vacancies in the corresponding structural models presented in Table 1 is indicated as the "minimum possible" value.

3. QUANTUM-CHEMICAL CALCULATIONS OF THE GROUND-STATE ENERGY

The inclusion of the structural disorder and, especially, the short-range order in quantum-chemical calculations is complicated because of the lack of accurate and effective methods. The most reliable results can be obtained using the supercell method [29]. In the calculations of disordered states, as in the case of a perfect long-range order, the supercell method makes it possible to use the most accurate techniques and approaches based on the electron density functional theory [38, 39] and pseudopotentials. In our case, it is convenient to use a supercell obtained by twofold translations of the unit cell of the ordered monoclinic phase $Ti_5O_{5(\mathrm{mon})}$ [6, 7] along the crystallographic directions a and b. This supercell contains 96 sites of the $B1$ basic structure: 48 sites belong to the metal sublattice and the same number of sites is contained in the nonmetal sublattice. By placing different numbers of vacancies in sites of the supercell according to specific rules, it is possible to approximately reproduce specific features of the proposed structural models (Table 1).

The quantum-chemical calculations for supercells were performed in the framework of the electron density functional theory [38, 39] with the use of plane waves and pseudopotentials. For the calculations, we used the Quantum ESPRESSO code [39]. The titanium pseudopotential included the $3s3p4s3d$ states, while the oxygen pseudopotential contained the $2s2p$ states. For each structural model, we constructed ten supercells with different arrangements of vacancies. The results for ten supercells were averaged. According to the quantum-chemical calculations of the ground-state energy, the enthalpy of formation of titanium monoxide was calculated using the formula

$$\Delta H = k\left(E_{\mathrm{TiO}_y} - N_{\mathrm{Ti}}E_{\mathrm{Ti}} - \frac{1}{2}N_{\mathrm{O}}E_{\mathrm{O}_2}\right)/N_{\mathrm{TiO}_y}, \quad (1)$$

where k is the coefficient of conversion to units of kJ/mol; E_{TiO_y} is the total energy of titanium monoxide per supercell; N_{Ti} and N_{O} are the numbers of titanium and oxygen atoms in the supercell, respectively; E_{Ti} is the total energy of metallic titanium per atom; E_{O_2} is the total energy of the oxygen molecule with the inclusion of the spin-polarization effect; and N_{TiO_y} is the number of TiO_y structural units in the supercell (which corresponds to the number of atoms in the titanium sublattice).

The results of the calculation of the enthalpy of formation of titanium monoxide are presented in Table 2. The stability of the compound increases with an increase in the oxygen concentration, which corresponds to the experimentally observed tendency [51]. The short-range order in the arrangement of structural vacancies is energetically favorable in all the cases considered above, but the value of the energy gain varies depending on the composition and the structural model. In the cases where the compound contains vacancies both in the metal sublattice and in the nonmetal sublattice, the most energetically favorable are structural models in which the prohibition is imposed on the arrangement of vacancies in the first and second coordination spheres (model nos. 4, 8, 12). It is

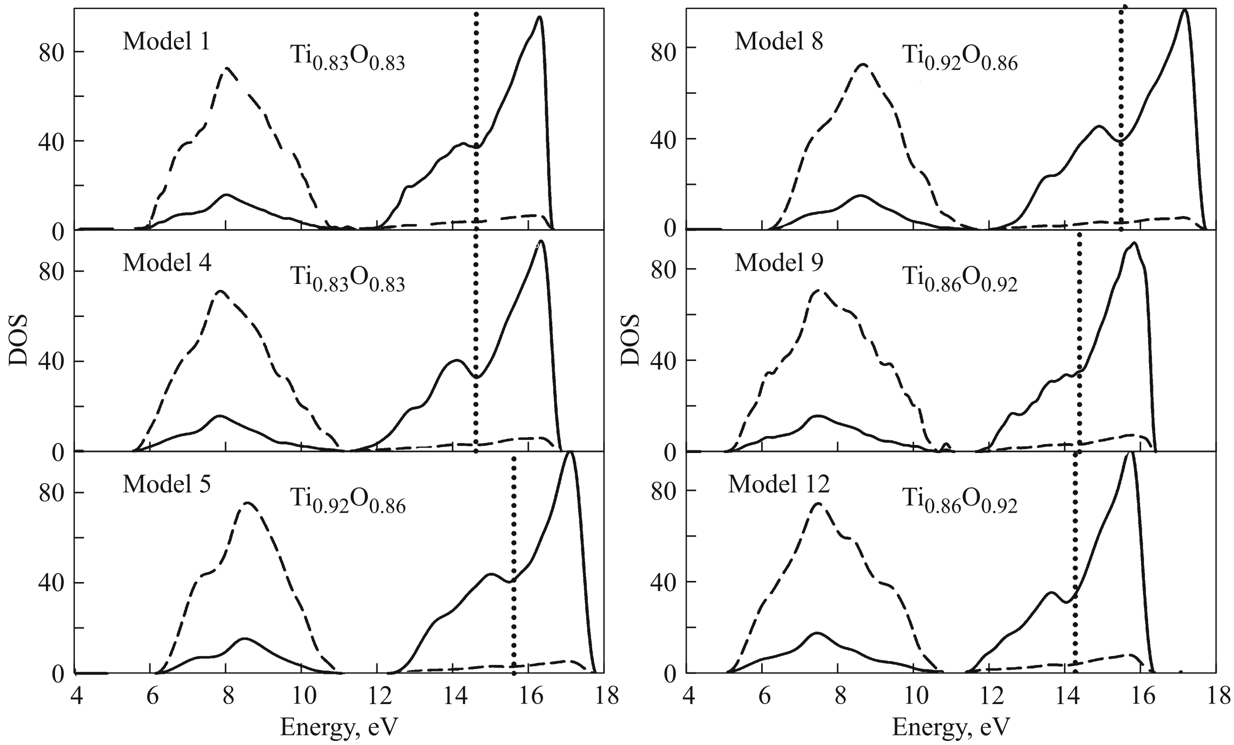


Fig. 2. Energy distributions of the density of oxygen 2*p* states (dashed line) and the density of titanium 3*d* states (solid line) calculated for the completely disordered state and the most energetically favorable models of short-range order in the case where the metal and nonmetal sublattices of the compound contain vacancies. Vertical dotted lines indicate the position of the Fermi level.

worth noting that, in this case, a decrease in the energy of the compound occurs primarily due to the prohibition imposed on the first coordination sphere. In the case of the stoichiometric composition (model nos. 1–4), the structural model, which takes into account the prohibition on the arrangement of vacancies in the first coordination sphere (model no. 2), gives a decrease in the energy by 2.0% as compared to the disordered state, whereas the prohibition on the arrangement of vacancies in the second coordination sphere leads to a very small decrease in the energy, or, more precisely, within 0.1%, which is significantly less than the standard deviation calculated for ten supercells of each structural model. The prohibition imposed simultaneously on the arrangement of vacancies in both the first and second coordination spheres (model no. 4) eventually leads to a decrease in the energy by 2.4%. It should be noted that the result obtained for model no. 2 is close to the data previously obtained in [36, 42, 43], where the simulation of short-range order was carried out using the same type of prohibition, but the structure was divided into cubic elementary clusters. Thus, in the calculations of the energy characteristics of disordered phases, the proper choice of atomic–vacancy correlations is of crucial importance, and the residual long-range order associated with the partition of the structure into clusters has no significant effect on the result.

In the case of nonstoichiometric compositions, the prohibition on the arrangement of structural vacancies in the second coordination sphere has a more significant effect as compared to the case of the stoichiometric composition: 0.9% for $Ti_{0.92}O_{0.86}$, 1.3% for $Ti_{0.86}O_{0.92}$, 1.2% for $Ti_{0.92}O_{1.00}$, 0.7% for $Ti_{1.00}O_{0.92}$, 0.6% for $Ti_{0.75}O_{1.00}$, and 0.3% for $Ti_{1.00}O_{0.75}$. Moreover, if the two sublattices of the nonstoichiometric compound contain vacancies, the prohibition on the first coordination sphere is still more significant. In the case where vacancies are present in only one of the sublattices, the contribution from the correlations between the vacancies in the second coordination sphere depends on the number of vacancies, which can be seen from a comparison of the compositions $Ti_{0.92}O_{1.00}$ and $Ti_{0.75}O_{1.00}$, as well as $Ti_{1.00}O_{0.92}$ and $Ti_{1.00}O_{0.75}$.

In the case of the stoichiometric composition with the most energetically favorable type of short-range order (model no. 4), the decrease in the energy of the compound amounts to 48% of the energy decrease provided by the long-range order according to the type of the monoclinic superstructure $Ti_5O_{5(mon)}$ [32]. On the other hand, the contribution from the short-range order in the arrangement of structural vacancies, when the vacancies are present in only one of the sublattices, exceeds the contribution from the long-range order according to the type of the model superstructures

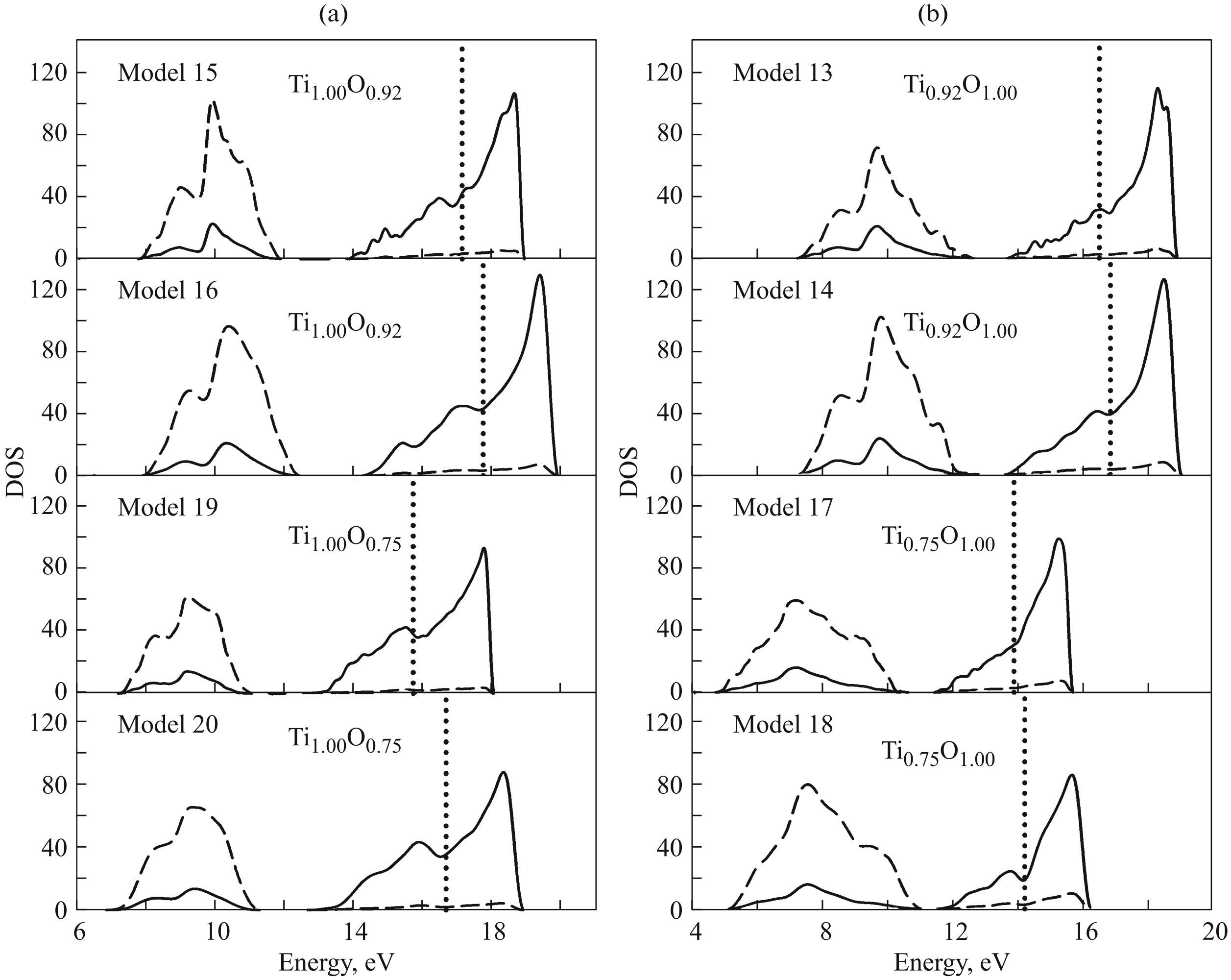


Fig. 3. Energy distributions of the density of oxygen 2*p* states (dashed line) and the density of titanium 3*d* states (solid line) calculated for the completely disordered state and the most energetically favorable models of short-range order in the case where only one of the sublattices of the *B*1 structure of the compound contains vacancies: (a) substoichiometric compositions and (b) superstoichiometric compositions. Vertical dotted lines indicate the position of the Fermi level.

$Ti_6O_{5(mon)}$ and $Ti_5O_{6(mon)}$ [35] formed by the removal of vacancies from one of the sublattices of the $Ti_5O_{5(mon)}$ superstructure despite the fact that the minimum distance between the vacancies in the $Ti_6O_{5(mon)}$ and $Ti_5O_{6(mon)}$ superstructures is also greater than the radius of the second coordination sphere. The formation of a long-range order in these cases should occur in accordance with the type of other superstructures, which, in addition to the energetically favorable near atomic–vacancy correlations, will include factors decreasing the long-range interaction energy.

4. ELECTRONIC STRUCTURE

The energy distributions of the electron density of states calculated for the completely disordered state and the most energetically favorable structural models of short-range order proposed for different compositions of the titanium monoxide are shown in Figs. 2 and 3. In all the cases under consideration, the valence band is represented predominantly by the oxygen 2*p* states, whereas the conduction band is represented primarily by the titanium 3*d* states. An increase in the oxygen concentration and, accordingly, a decrease in the titanium concentration lead to a decrease in the amount of the titanium 3*d* states in the valence band, as well as to a decrease in the density of states at the Fermi level. This is consistent with the experimentally observed decrease in the electrical conductivity of the superstoichiometric compositions of the titanium monoxide [45]. At the same time, the decrease in the electrical conductivity is not related to the hypothetical metal–semiconductor transition [45], the short-range order does not lead to the formation of an energy gap at the Fermi level, and the compound retains the metallic character.

In addition to the decrease in the density of titanium 3*d* states, the deviation from the stoichiometry leads to a change in the shape of the oxygen $2p$ band, as well as to a change in the width of the p–d band gap. In this case, strictly speaking, the p–d band gap is observed only in defect-free titanium monoxide and also in the ordered monoclinic phase $Ti_5O_{5(mon)}$ [32]. Furthermore, in the region of the p–d band gap, the electron density of states is nonzero, but the band edges do not touch with each other, in contrast to the ordered cubic phase $Ti_5O_{5(cub)}$ [37].

The short-range order leads to an increase in the depth of the dip in the distribution of the density of titanium $3d$ states at the Fermi level. This effect is most pronounced in the case where the structure of the compound contains vacancies both in the titanium sublattice and in the oxygen sublattice, so that the vacancies in the oxygen sublattice make a more significant contribution. Therefore, with a decrease in the concentration of oxygen in substoichiometric compositions, the depth of the dip in the distribution of the density of states increases despite the fact that the density of states by itself increases due to the increase in the titanium concentration. The dip in the distribution of the density of titanium $3d$ states, as well as the pseudogap formed as a result of the increase in the depth of the dip, is associated with the energetically favorable structural models. In particular, the maximum depth of the pseudogap is characteristic of the monoclinic phase $Ti_5O_{5(mon)}$, which has the minimum ground-state energy [32]. The depth of the pseudogap of the less energetically favorable cubic superstructure $Ti_5O_{5(cub)}$ is smaller than that of the monoclinic superstructure [37]. For the structural models of short-range order [36, 42, 43] and long-range order [35], which have an increased energy as compared to the completely disordered structure, are characterized by the disappearance of the dip in the density of titanium $3d$ states at the Fermi level. In addition to the aforementioned effect, the short-range order results in a narrowing of the p–d band gap due to the broadening of the oxygen $2p$ band. In a number of cases (model nos. 4, 8, 16), there is a splitting of the titanium $3d$ band below the Fermi level, which is also controlled predominantly by the oxygen vacancies. The observed splitting in the distribution of the density of titanium $3d$ states is in agreement with the experimental data on X-ray emission spectroscopy [52], which were obtained on samples of the ordered monoclinic phase of the titanium monoxide.

5. CONCLUSIONS

In this paper, we proposed the simplest energetically favorable structural models of short-range order for stoichiometric and nonstoichiometric compositions of the disordered cubic phase of the titanium monoxide TiO_y. It was shown that these models reproduce the local atomic–vacancy groups, which are characteristic of the energetically favorable superstructures $Ti_5O_{5(mon)}$ and $Ti_5O_{5(cub)}$, and were obtained by means of the constraints imposed on the minimum permissible distances between the vacancies. We examined the correlations between the vacancies in only one of the sublattices of the $B1$ basic structure, the correlations between the vacancies in both sublattices, and also the correlations between the vacancies in one sublattice and, simultaneously, between the vacancies in different sublattices. It was found that, in the last case, there is the greatest decrease in the energy of the compound as compared to the model of the statistical distribution of vacancies.

The nonstoichiometry of the compound was simulated by two methods: (a) due to the decrease in the concentration of vacancies in one of the sublattices and the increase in their concentration in the other sublattice, which corresponded to the disordered cubic phase of the titanium monoxide TiO_y, and (b) due to the complete removal of vacancies from one of the sublattices, which corresponded to the hypothetical high-pressure phase. In the first case, the short-range order gives a more significant energy gain, because the decrease in the energy of the compound occurs primarily due to the correlations between the vacancies in different sublattices.

The short-range order in the structure of the compound leads to an increase in the dip of the distribution of titanium $3d$ states at the Fermi level, as well as to a decrease in the width of the region of the p–d band gap due to the broadening of the oxygen $2p$ band. The shape of the conduction band in the case where the short-range order exists in the structure is in better agreement with the experimental data in comparison with the model of the statistical distribution of vacancies.

The results obtained in this study can be used in the interpretation of experimental data on X-ray, neutron, and electron diffraction by samples of disordered phases with an abnormally high concentration of structural vacancies, in thermodynamic calculations of the phase equilibria taking into account the atomic–vacancy ordering, and in the search for new superstructures in strongly nonstoichiometric compounds.

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