

# CUBIC ORDERED MODIFICATION OF TITANIUM MONOXIDE WITH STRUCTURAL VACANCIES ON METAL AND NONMETAL SUBLATTICES: ELECTRONIC STRUCTURE AND STABILITY

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The electronic structure of the recently suggested cubic ordered phase  $\text{Ti}_5\text{O}_5(\text{cub.})$  of titanium monoxide has been studied by means of accurate first-principles calculations within the density functional theory with pseudo-potential approach based on the plane wave basis. It was found that  $\text{Ti}_5\text{O}_5(\text{cub.})$  is the only phase of titanium monoxide without  $p$ - $d$  gap in the occupied states region. In this sense, calculated DOS's of the cubic modification is closer to the experimental electronic spectrum of the ordered titanium monoxide than that of the well studied ordered monoclinic modification  $\text{Ti}_5\text{O}_5(\text{mon.})$ . The enthalpy of formation of  $\text{Ti}_5\text{O}_5(\text{cub.})$  is higher than the enthalpy of  $\text{Ti}_5\text{O}_5(\text{mon.})$  but is less than that of the disordered cubic phase  $\text{TiO}_{1.0}$ .

**Keywords:** vacancies, ordering, titanium monoxide, electronic structure.

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Nonstoichiometric titanium monoxide  $\text{TiO}_y$  is a unique compound owing to (a) wide homogeneity region from  $\text{TiO}_{0.7}$  to  $\text{TiO}_{1.25}$ , (b) high vacancy content both in metallic and nonmetallic sublattices and (c) formation of new phases under ordering of the vacancies [1–4]. The compound has a  $B1$  (NaCl) type of crystal structure. At stoichiometric composition  $y = 1.0$ , about 16 % of the sites are vacant in every sublattice. Another compound with similar high concentration of structural vacancies in both metallic and nonmetal sublattices is vanadium monoxide  $\text{VO}_y$ , but ordering for  $\text{VO}_{1.0}$  was not found [1]. With allowance for the vacancies in the sublattices, the chemical formula for titanium monoxide can be written as  $\text{Ti}_x\text{O}_z$  or  $\text{Ti}_x \blacksquare_{1-x} \text{O}_z \square_{1-z}$ , where  $x$  and  $z$  are the fractions of vacancies in titanium and oxygen sublattices, respectively,  $\blacksquare$ ,  $\square$  are the symbols for titanium and oxygen vacancies, respectively. The composition  $y$  in the formula  $\text{TiO}_y$  equals  $z/x$ .

Disordered cubic titanium monoxide is an equilibrium phase at the temperatures higher than 1600 K [1]. At these temperatures, the vacancies are nearly randomly distributed. Heat treatment below 1600 K leads to redistribution of the vacancies on the  $B1$  lattice sites and the ordered phases form. The type of the ordered structure depends on the composition of the titanium monoxide and treatment conditions. At present, only the structures of monoclinic  $\text{Ti}_5\text{O}_5(\text{mon.})$  ( $\text{Ti}_5 \blacksquare_1 \text{O}_5 \square_1 \equiv \text{Ti}_{10} \blacksquare_2 \text{O}_{10} \square_2$ ) and tetragonal  $\text{Ti}_4\text{O}_5$  ( $\text{Ti}_4 \blacksquare_1 \text{O}_5 \equiv \text{Ti}_8 \blacksquare_2 \text{O}_{10}$ ) phases

are described fairly [1–4]. The other  $B1$  derived ordered structures: cubic  $Ti_5O_5(cub.)$ , orthorhombic  $Ti_3O_2(orth.)$  and  $Ti_2O_3(orth.)$  are poorly studied. From the last group, the cubic  $Ti_5O_5(cub.)$  is the most interesting superstructure, as it corresponds to the equiatomic composition and is an alternative to the well-studied monoclinic  $Ti_5O_5(mon.)$ . The unit cell of  $Ti_5O_5(mon.)$  is shown in fig. 1.

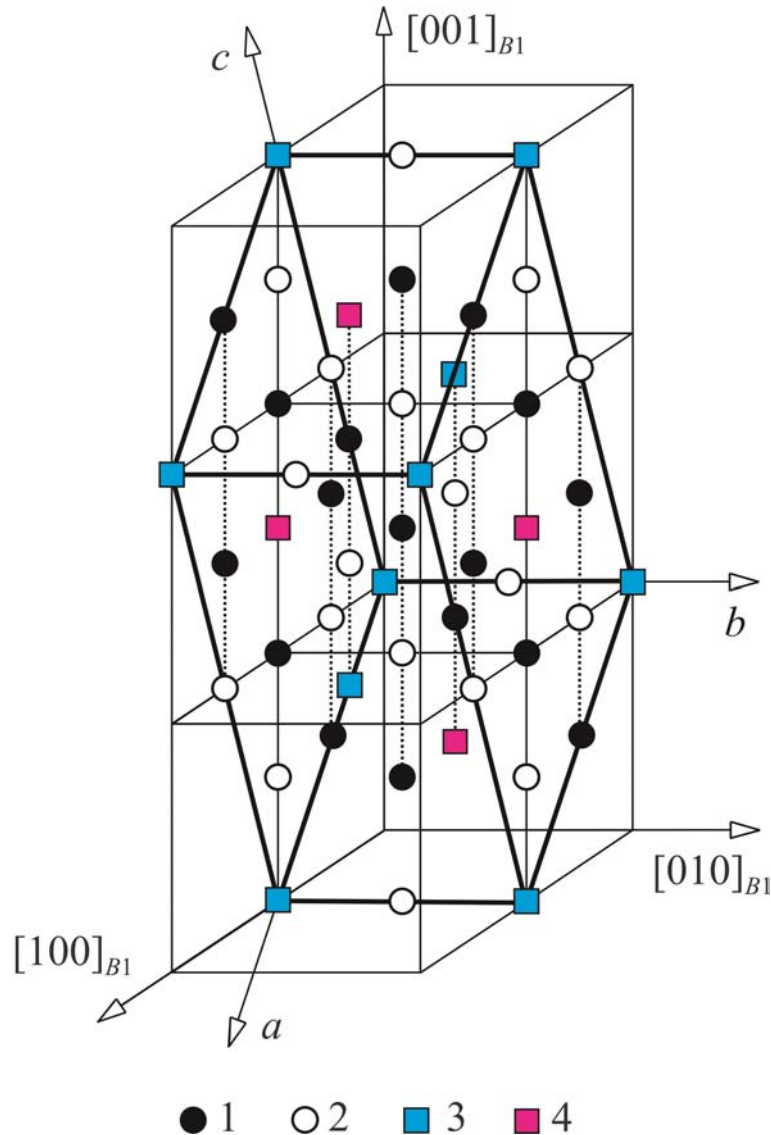


FIG. 1. Position of the monoclinic (space group  $C2/m$  ( $A12/m1$ )) unit cell in the basic  $B1$  structure [4]: 1 – titanium, 2 – oxygen, 3 – titanium vacancy, 4 – oxygen vacancy. The axes  $a$ ,  $b$ ,  $c$  of the superstructure and the crystallographic directions of  $B1$  structure are shown

The fact that the  $Ti-O$  system has an ordered phase with cubic symmetry having a composition of nearly 50 % O was noted in short report by Hilti in 1968 [5]. He pointed out that the phase has threefold lattice constant in comparison with that of  $B1$  and belongs to one of the following possible space groups:  $Fm\bar{3}m$ ,  $F\bar{4}3m$ ,  $F432$ , or  $Fm\bar{3}$ . The atomic model of the cubic structure was not proposed and the distribution of vacancies in the unit cell was unknown. Since then, no attempt has been made to synthesize the cubic modification and identify its structure. The existence of the cubic modification was also ignored in numerous theoretical

studies devoted to the role of vacancies in *B1* structure and mechanism of ordering [6–9]. The experimental data [4, 10, 11] obtained for the samples of ordered phase were always interpreted using the notion of the monoclinic structure only.

The model of crystal structure for the cubic modification was proposed in 2012 [12, 13]. When analyzing the possible structure, the authors [12, 13] proceeded from two requirements: (a) the lattice constant is three times higher than that of *B1* structure and (b) the concentration of the vacancies equals to 1/6 in every sublattice. It was proved that these conditions cannot be satisfied for the space groups proposed earlier [5]. The only possible space group is  $Pm\bar{3}m$ . For this group, there are 8 variants of vacancy distributions in one of the sublattices, 5 of them implying statistical distribution. From the other 3, the even distribution has been chosen. The unit cell proposed in [12, 13] is shown in fig. 2. It contains 90 titanium atoms, 90 oxygen atoms, 18 titanium and 18 oxygen vacancies. The chemical formula can be written as  $Ti_{90}\blacksquare_{18}O_{90}\square_{18}$ .

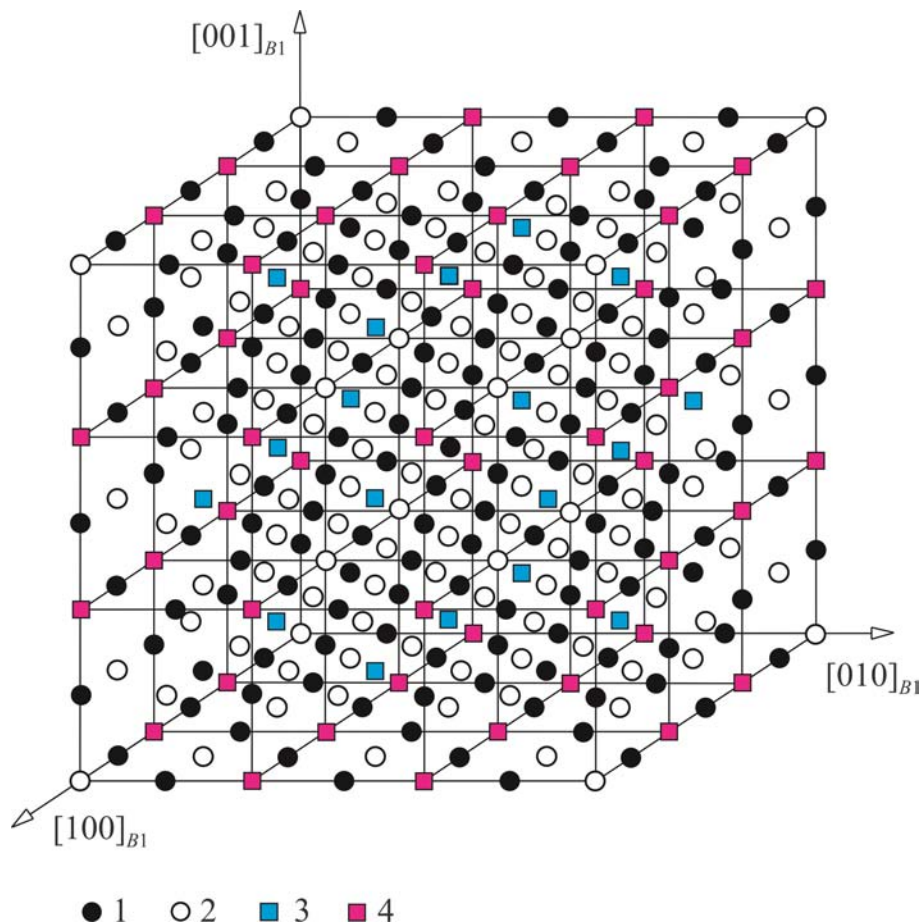


FIG. 2. Unit cell of the cubic superstructure  $Ti_{90}\blacksquare_{18}O_{90}\square_{18}$  (space group  $Pm\bar{3}m$ ) [12, 13]: 1 – titanium, 2 – oxygen, 3 – titanium vacancy, 4 – oxygen vacancy. The crystallographic directions of *B1* structure are shown

The XRD spectrum of the cubic modification resembles one of the monoclinic phase [13]. Two phases can be reliably distinguished only with the reflections at small angles that are not seen in laboratory XRD experiments. The structure of the ordered phase obtained in [4] was identified as monoclinic from the XRD analysis. Later the samples [4] were studied with electron microdiffraction [10]. Only some of the observed superstructure reflections are referred to the monoclinic modification. In [12] it was demonstrated that all the reflections could belong

to the cubic superstructure. So there could be two alternative experimentally confirmed types of vacancy ordering for the composition  $y = 1.0$ .

The present work is the next step in the investigation of the recently proposed cubic modification and has as its aim the theoretical study of its electronic structure and stability. Calculations were performed within the density functional theory using the generalized gradient approximation (GGA), as implemented in the PBE [14] form of exchange-correlation potential. The phase was treated with the PWSCF code of the QUANTUM-ESPRESSO package [15] based on plane waves (PW) and pseudo-potentials. Titanium  $3s3p$  semi-core levels were included in the Ti pseudopotential. The lattice constant was assumed to be 417.4 pm [4]. Relaxation of the atomic positions within the cell was realized using quasi-Newton algorithm in PWSCF code. The stability of the phase was estimated by calculating the enthalpy of formation  $\Delta H$  from the following equation:

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

where  $k$  is the coefficient for conversion from eV to kJ/mol,  $E_{\text{TiO}}$  is the full energy of titanium monoxide calculated for one unit cell,  $N_{\text{Ti}}$  and  $N_{\text{O}}$  are the numbers of titanium and oxygen in the cell, respectively,  $E_{\text{Ti}}$  is the energy of titanium in its ground state calculated per one atom,  $E_{\text{O}_2}$  is the energy of an oxygen molecule that includes the effect of spin polarization,  $N$  is the number of Ti-O atomic pairs in the cell.

The density of states for the ordered cubic phase is shown in fig. 3a. For comparison, the results for the ordered monoclinic phase, disordered cubic phase [16], and vacancy-free TiO are presented in figs. 3b, 3c, and 3d respectively. The low energy part of the occupied states region of all the phases generally consists of O  $2p$ . The Ti  $3d$  states are mainly in the high energy part. Vacancy-free TiO and  $\text{Ti}_5\text{O}_{5(\text{mon.})}$  have a distinct  $p$ - $d$  gap between O  $2p$  and Ti  $3d$  peaks. Disordered cubic phase has the states with a very small density in the  $p$ - $d$  gap position [16]. The gap is completely filled in  $\text{Ti}_5\text{O}_{5(\text{cub.})}$ . The existence of the  $p$ - $d$  gap is the main discrepancy between the results of theoretical [6–9, 16, 17] and experimental [11, 17] studies. The calculations predicted the gap for  $\text{Ti}_5\text{O}_{5(\text{mon.})}$ , vacancy-free TiO, disordered cubic  $\text{TiO}_y$  (with a very small density of states in the gap), and also for modeled structures  $\text{Ti}_{10}\blacksquare_2\text{O}_{12}$  and  $\text{Ti}_{12}\text{O}_{10}\square_2$  with vacancies in one of the sublattices. Only the cubic phase is appeared to be out of this regularity. In experiments for  $\text{Ti}_5\text{O}_{5(\text{mon.})}$  [11], vacancy-free TiO [11], and disordered cubic  $\text{TiO}_y$  [17] the  $p$ - $d$  gap was not detected.

The present results for  $\text{Ti}_5\text{O}_{5(\text{cub.})}$  demonstrate that the reason for the disagreement between theoretical and experimental findings is possibly in misconstruction of the real structures of the ordered and disordered phases. The specimens of the ordered titanium monoxide used in [11] were referred to monoclinic phase after XRD analysis. As mentioned above, electron diffraction permits cubic symmetry of ordered structure. Another possible interpretation is that the monoclinic phase [11] had imperfect long-range order. In this case, some number of vacancies out of its native positions in the superstructure could occupy the atomic positions not randomly but with some short-range order. This would lead to the situation when the occupation of the vacancies in the nearest coordination spheres of some atoms is identical to that for some atomic positions of the cubic superstructure. The influence of the gradual disordering on the electronic structure was studied in [18] but the short range order was not accounted for.

The vacancy-free TiO used in [11] is considered in [7] to contain substantial fraction of residual vacancies. The correlation between these vacancies could lead to the formation of short-range order and the filling of the  $p$ - $d$  gap in the occupied states region. Hereby the allowance for the features of the real crystal and atomic structure is the crucial point for

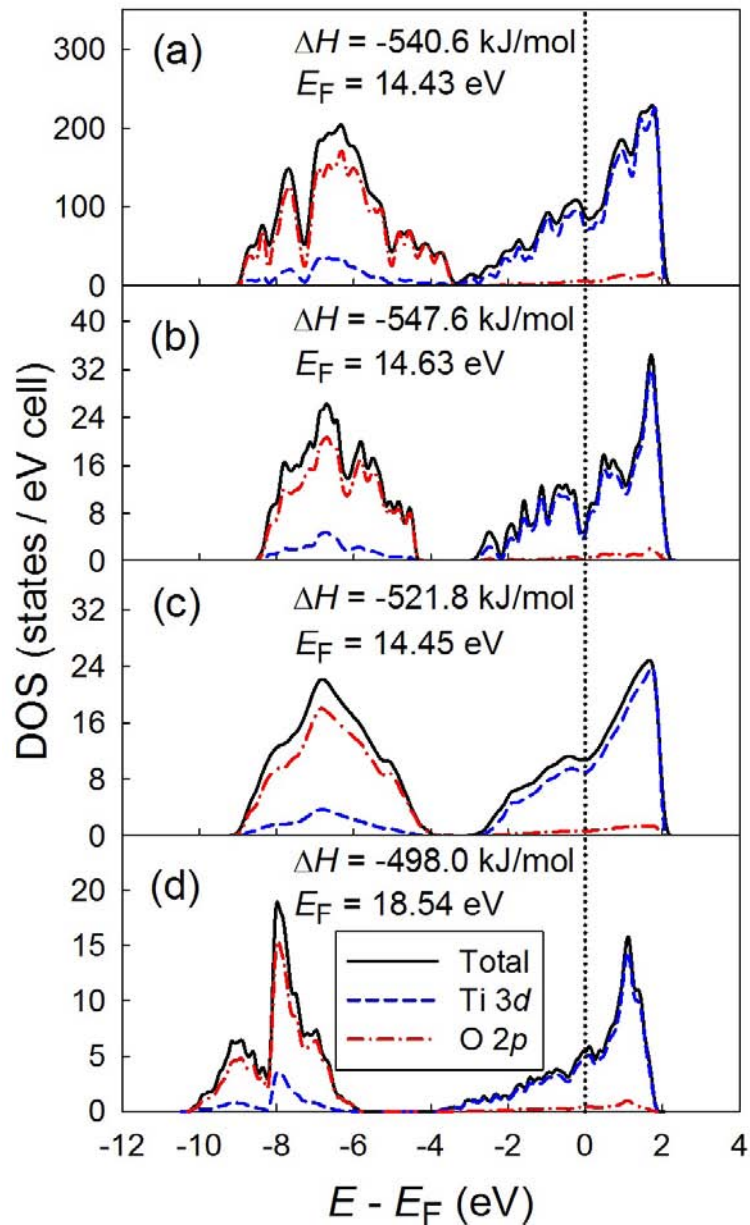


FIG. 3. Density of states calculated for (a) ordered cubic phase, (b) ordered monoclinic phase, (c) disordered cubic phase [16], and (d) vacancy-free TiO. The values of enthalpy of formation and Fermi energy are shown

correct interpretation of the experimental data. The correlations between defects in strongly nonstoichiometric compounds [1] need detailed investigation. First of all this implies modeling of the structures of the disordered and partially ordered modifications with allowance for the short-range order.

As to stability of the cubic ordered phase, the calculation of the enthalpy of formation has demonstrated (fig. 3) that  $\text{Ti}_{90}\blacksquare_{18}\text{O}_{90}\square_{18}$  type of ordering is less advantageous as compared to monoclinic  $\text{Ti}_{10}\blacksquare_2\text{O}_{10}\square_2$  type but preferable as compared to the disordered state. This agrees with the assertions [5, 13] that  $\text{Ti}_{90}\blacksquare_{18}\text{O}_{90}\square_{18}$  is intermediate ordered modification of titanium monoxide. The existence of one more energetically favorable type of ordering in addition to monoclinic one allows us to expect that some new ordered phases of titanium monoxide can be

found. In fact, the sequence of phase transition in titanium-oxygen system is poorly studied. This issue requires additional theoretical and experimental investigations. This is also true for other strongly nonstoichiometric compounds [1], especially for vanadium monoxide  $\text{VO}_y$ , for which no ordered phase for  $\text{VO}_{1.0}$  has yet been found.

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