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Octahedral clusters in various phases of nonstoichiometric titanium monoxide

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The analytical dependence of cluster configuration probabilities on the vacancy concentrations and the long range order parameters for the TiO_y, Ti_5O_5, Ti_3O_2, Ti_2O_3 and Ti_4O_5 phases of titanium monoxide has been calculated for the first time.

Titanium monoxide (TiO_y) is a strongly nonstoichiometric compound with the $B1$ structure type[1] and a very wide homogeneity region of $y = 0.75$–1.25.[2] Nonstoichiometry in titanium monoxide occurs owing to different concentrations of structural vacancies (unoccupied sites of $B1$ structure) in the titanium and oxygen sublattices. In order to demonstrate the presence of structural vacancies in both sublattices, the composition of titanium monoxide can be written in the form Ti_xO_z or $Ti_x\blacksquare_{1-x}O_z\square_{1-z}$, where x and z are the fractions of atomic positions in titanium and oxygen sublattices, respectively, $\blacksquare$ and $\square$ are the symbols for structural vacancies in these sublattices.[3] In the formula TiO_y, $y = z/x$.

The structural vacancies can be distributed randomly or regularly[3,4] on the sublattice sites depending on the temperature and the heat treatment of the samples. Disordered cubic phase TiO_y and four ordered phases (monoclinic Ti_5O_5, orthorhombic Ti_3O_2 and Ti_2O_3 and tetragonal Ti_4O_5) are reliably known in the region of $y = 0.67$–1.5.[3–6] The values of y and temperature intervals locate position of each phase in the Ti–O phase diagram.

In the case of nonstoichiometric titanium monoxide, a calculated phase diagram will allow us to reveal the reasons for ordering, which are unclear.

The following equation set[1] must be solved for all values of temperature T for calculating the phase diagram:

$$\frac{\partial F(y_1,\eta = 0,T)}{\partial y_1} = \frac{\partial F(y_2,\eta,T)}{\partial y_2}, \tag{1}$$

$$\partial F(y_1,\eta = 0,T) - y_1\frac{\partial F(y_1,\eta = 0,T)}{\partial y_1} = \\ = \partial F(y_2,\eta,T) - y_2\frac{\partial F(y_2,\eta,T)}{\partial y_2}, \tag{2}$$

where F is free energy, η is long range order parameter, y_1 and y_2 are the compositions of disordered and ordered phases, respectively. As generally known, the formula for free energy is

$$F = E - TS, \tag{3}$$

where E is the internal energy of the system, and S is the entropy. If the system is in equilibrium at a particular temperature, the structure corresponds to a free energy minimum.

The entropy of the titanium monoxide can be expressed as a configuration entropy. It occurs because of vacancy disordering. The formula for configuration entropy is[7]

$$S = k_B\ln\left\{\frac{(N/2)!}{(xN/2)!\,[(1-x)N/2]!}\,\frac{(N/2)!}{(zN/2)!\,[(1-z)N/2]!}\right\}, \tag{4}$$

where N is the number of sites in basic $B1$ structure. The main problem of equilibrium structure calculations is to estimate the internal energy. Interaction with energy ε_{ij} occurs between every two atoms. The internal energy itself is a sum of such interaction energies calculated for some i site or sum of interactions for all i sites divided by the number of sites. The way of calculation depends on the crystal symmetry. If interactions between the atoms are short-range, the specific value E/N can be easily found for an infinite crystal. If the interactions are long-range, such as Coulomb ones, specific energy E/N strongly depends on the size of the crystal and calculations become complicated.[7]

The internal energies of cubic $TiO_{1.0}$ phase and monoclinic Ti_5O_5 phase have been calculated.[7] Only the ionic type of chemical bond in titanium monoxide was considered. This approach enabled one to understand the probable reason for the ordering of structural vacancies at low temperatures. The calculated phase transition temperature appeared to be higher than the experimental one by a factor of 10. Therefore, it is necessary to take into account not only Coulomb interactions.

The equilibrium structure of titanium monoxide can be found using a cluster variation method[8–10] if we take into the account only short-range interactions. Basic crystal structure must be presented as a set of clusters and overlap figures. Every cluster S may have i configurations. Constant energy ε_i is attributed to every ith configuration. As the energies of cluster configurations and overlap figures are constant, the free energy depends only on probabilities $P_i^{(S)}$ of ith configurations of cluster S:

$$F = N\sum_{s=1}^{n} o^{(S)} \sum_{i\in s} \lambda_i^{(S)} P_i^{(S)} [\varepsilon_i^{(S)} + k_B T\ln P_i^{(S)}]. \tag{5}$$

The number of overlap figures ($n - 1$), overestimation parameters $o^{(S)}$, multiplicities $\lambda_i^{(S)}$, and energies ε_i of clusters are constant. Therefore, our goals are selection of clusters S, count of probable i configurations of clusters S and calculation of probabilities for all cluster configurations in the ordered and disordered structures of titanium monoxide.

If we suppose short-range interactions to be only in the first coordination sphere, it is convenient to choose an octahedral cluster for the analysis of vacancy ordering in basic $B1$ structure. In this cluster, one site is in the centre and six others are in the vertexes. Central site of the octahedron can be occupied by titanium atom, oxygen atom, titanium vacancy or oxygen one.

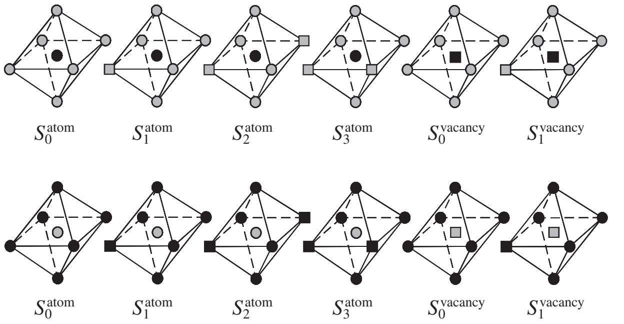

Figure 1 The main configurations of octahedral clusters in titanium monoxide TiO_y. Black circles indicate titanium atoms, grey ones indicate oxygen atoms. Black and grey squares are the symbols for titanium and oxygen vacancies.

Therefore, four types of clusters are possible. The number of vacancies in the vertexes can vary from zero to six.

The probability of appearance of the cluster with m vacancies in the vertexes is $xz^{6-m}(1-z)^m/2$ if we consider a cluster with a titanium atom in the centre. In the case of a titanium vacancy in the centre, the probability is $(1-x)z^{6-m}(1-z)^m/2$. Probabilities for clusters of oxygen sublattice can be calculated from titanium probabilities by replacing symbol x to z and *vice versa*. As vacancy content in every sublattice of titanium monoxide does not exceed 33.3 at%,[4] the probabilities of clusters with three or more vacancies are sufficiently small and such clusters are omitted in this work.

Basic cluster configurations in titanium monoxide are shown in Figure 1. Clusters with two atoms in the vertexes have two probable configurations. The probability of appearance of each configuration can be found by multiplication of probability of cluster appearance with m vacancies in the vertexes to the coefficient considering the number of probable configuration of vacancies on octahedral site. This coefficient equals 1/5 and 4/5 for the S_2^{atom} and S_3^{atom} configurations, respectively.

A redistribution of structural vacancies occurs during the ordering of the structure. The result is that probability n to find out vacancy in random site with coordinates (x_I, y_I, z_I) is not equal to the fraction of vacancies in the sublattice but is equal to the value of distribution function:[3,4]

$$n_{Ti}(x_I, y_I, z_I) = f(x, x_I, y_I, z_I, \eta^{Ti}), \tag{6}$$

$$n_O(x_I, y_I, z_I) = f(z, x_I, y_I, z_I, \eta^{O}), \tag{7}$$

where n_{Ti} and n_O are the probabilities of finding of titanium or oxygen atom, respectively, in the sites of basic $B1$ structure with coordinates (x_I, y_I, z_I), η^{Ti} and η^O are the long range order parameters for titanium and oxygen sublattices. Values of the long range order parameter can vary from zero to their maximum value $\eta_{max} \leqslant 1$. The values of η_{max} depend on the composition y of the compound, *i.e.*, at fixed composition distribution function values cannot be less than zero or more than unity.

If long range order parameter for some of sublattices in basic $B1$ structure equals to zero distribution function value equals to the fraction of atomic positions in that sublattice:

$$n_{Ti}(\eta^{Ti} = 0) = x, \tag{8}$$

$$n_O(\eta^{O} = 0) = z. \tag{9}$$

In this case, the sublattice is completely disordered. If long range order parameters are nonzero, then basic $B1$ structure is divided into four sublattices: titanium atoms, oxygen atoms, titanium vacancies and oxygen vacancies.

Table 1 Distribution function values for the structures of Ti_5O_5,[3] Ti_3O_2, Ti_2O_3 and Ti_4O_5.[4]

Sub-lattice	Distribution function values for the structures of Ti_xO_z			
	Ti_5O_5	Ti_3O_2	Ti_2O_3	Ti_4O_5
Titanium atoms	$n_{Ti} = x + \eta^{Ti}/6$	$n_{Ti} = x$	$n_{Ti} = x + \eta^{O}/3$	$n_{Ti} = x + \eta^{O}/5$
Titanium vacancies	$n_{Ti} = x - 5\eta^{Ti}/6$	—	$n_{Ti} = x - 2\eta^{O}/3$	$n_{Ti} = x - 4\eta^{O}/5$
Oxygen atoms	$n_O = z + \eta^{O}/6$	$n_O = z + \eta^{O}/3$	$n_O = z$	$n_O = z$
Oxygen vacancies	$n_O = z - 5\eta^{O}/6$	$n_O = z - 2\eta^{O}/3$	—	—

If the structure is completely ordered, the only distinctive configuration can be found in particular position. And if long range order parameter in formulae (6) and (7) is lower than its maximum value, several configurations of clusters can be found in a particular position. The probability of S configuration calculated for all the crystals is the sum of multiplications of the probability of a configuration in particular position and probability of this position in ordered structure. The probabilities were calculated[11] for the main cluster configurations of Ti_5O_5.

As the probabilities of appearance of clusters under consideration depend on the probabilities of appearance of atoms and vacancies in the cluster sites, formulae (6) and (7) allow us to write

$$P_i = f(x, z, \eta^{Ti}, \eta^{O}). \tag{10}$$

If $x = z = 5/6$ and $\eta^{Ti} = \eta^{O} = \eta$, the simple functional dependence can be written as

$$P_i = f(\eta). \tag{11}$$

In this case, the probabilities of cluster configurations in the titanium sublattice are equal to the probabilities of corresponding configurations in the oxygen sublattice.

Monoclinic Ti_5O_5 phase. Distribution function values for Ti_5O_5 are presented in Table 1. Analysis of environment of the sites in the range of first coordination sphere in ordered Ti_5O_5 structure reveals three types of site positions in titanium sublattice and as many again in oxygen sublattice. As ordering in both sublattices occurs identically, the types of site positions in the titanium sublattice are equivalent to those in the oxygen sublattice after replacement of the titanium atoms by oxygen ones and *vice versa* (see Online Supplementary Materials). Calculated dependences (11) are shown in Figure 2. It can be seen that, during the ordering of the structure, the configuration probabilities decrease up to zero and of others increase.

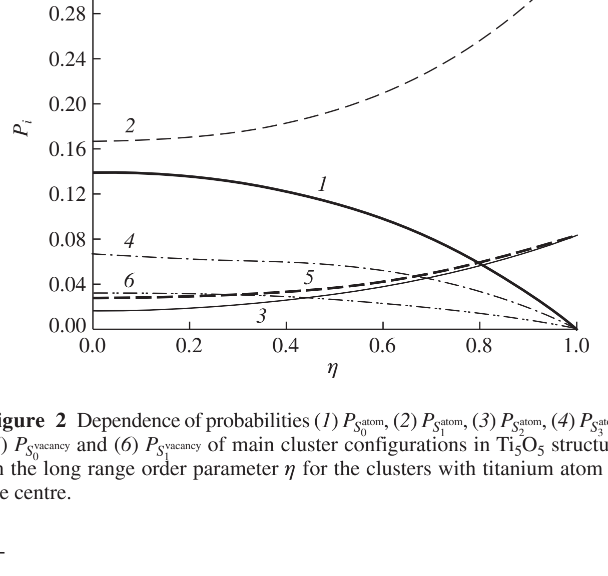

Figure 2 Dependence of probabilities (*1*) $P_{S_0^{atom}}$, (*2*) $P_{S_1^{atom}}$, (*3*) $P_{S_2^{atom}}$, (*4*) $P_{S_3^{atom}}$, (*5*) $P_{S_0^{vacancy}}$ and (*6*) $P_{S_1^{vacancy}}$ of main cluster configurations in Ti_5O_5 structure on the long range order parameter η for the clusters with titanium atom in the centre.

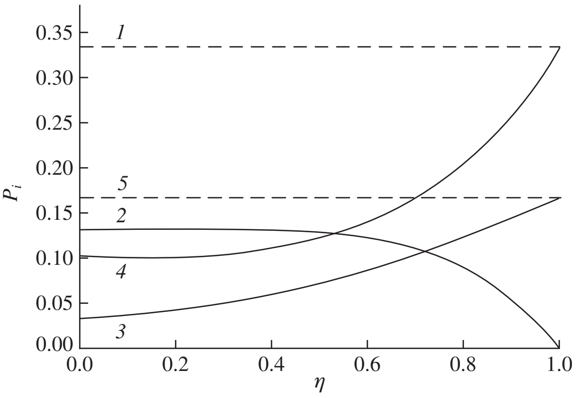

Figure 3 Dependences of probabilities of cluster configurations *(1)* S_0^{atom}, *(2)* S_1^{atom}, *(3)* S_2^{atom}, *(4)* S_3^{atom} and *(5)* S_0^{vacancy} in Ti_3O_2 phase on the long range order parameter η. Solid line indicates plots for the clusters with titanium atom in the centre, dashed line indicates plots for the clusters with oxygen atom in the centre.

Orthorhombic Ti_3O_2 and Ti_2O_3 phases. As opposite to the monoclinic Ti_5O_5 phase, ordering in the orthorhombic Ti_3O_2 and Ti_2O_3 phases[4] occurs only in one of the sublattices. Distribution function values for the sites of those structures are shown in Table 1. Basic *B*1 structure in this case can be described by three sublattices.

For the types of site positions in Ti_3O_2 and Ti_2O_3 structures, see Online Supplementary Materials. Plots of the calculated dependence of probability functions on the long range order parameter $\eta^{\text{Ti}} = \eta^{\text{O}} = \eta$ for certain cluster configurations in Ti_3O_2 structure are shown in Figure 3. Calculations were taken for the case of $x = 1$ and $z = 2/3$. It results from the symmetry of Ti_3O_2 and Ti_2O_3 structures (see Online Supplementary Materials) that the probabilities of cluster configurations with central site of titanium sublattice in basic *B*1 structure of Ti_3O_2 should correspond to the probabilities of configurations in Ti_2O_3 with oxygen site in the centre of octahedron.

Vacancies in the titanium sublattice of Ti_3O_2 are absent if $x = 1$. Therefore, the probabilities of S_0^{atom} and S_2^{vacancy} configurations in the oxygen sublattice for any value of long range order parameter equal to the probabilities of types of corresponding positions in ordered structure. In contrast to Ti_5O_5, ordering in Ti_3O_2 and Ti_2O_3 results in increasing the probability of S_3^{atom} configuration with two contiguous vacancies. It is because of higher vacancy concentration in one of the sublattices of these structures (33.3 at%) in comparison with that in Ti_5O_5 (16.7 at%). Probabilities of all other configurations unconsidered become lower up to zero if the value of long range order parameter increases up to its maximum.

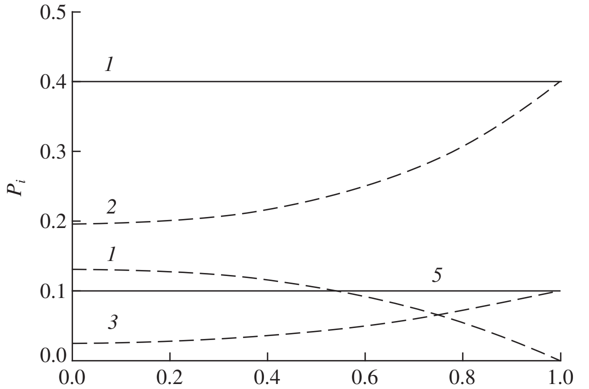

Figure 4 Dependences of probabilities of cluster configurations *(1)* S_0^{atom}, *(2)* S_1^{atom}, *(3)* S_2^{atom} and *(5)* S_0^{vacancy} in Ti_4O_5 phase on the long range order parameter η. Solid line indicates plots for the clusters with titanium atom in the centre, dot line indicates plots for the clusters with oxygen atom in the centre.

Tetragonal Ti_4O_5 phase. Ordering of structural vacancies in the Ti_4O_5 phase occurs as well as in Ti_2O_3 phase only in the titanium sublattice[4,5] (Table 1). If the structure is completely ordered and $y = 1.25$, there are no vacancies in the oxygen sublattice. In the titanium sublattice, the fraction of structural vacancies is 20 at%. This is less than that in Ti_2O_3. Therefore, there is no type of site position in ordered structure, which is equal to S_3^{atom} configuration (see Online Supplementary Materials). Dependences of probabilities of certain configurations on the long range order parameter are presented in Figure 4. Calculations were performed for the case of $x = 4/5$, $z = 1$. Probabilities of appearance of S_1^{atom} and S_2^{atom} configurations in the oxygen sublattice increase during the ordering. Probabilities of appearance of all other configurations in the sublattice decrease up to zero. In the titanium sublattice only S_0^{atom} and S_3^{vacancy} configurations can exist for all values of long range order parameter.

The calculations demonstrate the unique dependence of the probabilities of configurations of octahedral clusters in various phases of titanium monoxide on the long range order parameter and the fractions of atomic positions in sublattices of basic *B*1 structure. Vacancies are situated in the sites so that their maximum value in the first coordination sphere is 2. If the vacancy content of sublattices is sufficiently small, these two vacancies are only in the opposite vertexes of the octahedron. The probability of S_3^{atom} configuration decreases up to zero during ordering. If structure is ordered only Ti_3O_2 and Ti_2O_3 phases can have vacancies situated in the next sites because of its high vacancy content (33.3 at%). In this case, the cluster configuration with a single vacancy in the vertexes is impossible.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2012.09.005.

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