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Structural model of order–order transition state in titanium monoxide $TiO_{1.0}$

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A new class of structures, in which vacancies or other point defects of the crystal lattice occupy the sites of two different superstructures simultaneously, is presented using atomic vacancy ordering in titanium monoxide. One of the superstructures is that of the low temperature phase and the other one is additional superstructure yielding an increase in the configurational entropy of ordered state at high temperatures.

$$\text{Ordered monoclinic } Ti_5O_{5(mon)} \text{ phase} \xrightarrow{\Delta} \text{Transition ordered } Ti_5O_{5(mon)}\text{–}Ti_5O_{5(cub)} \text{ phase} \xrightarrow{\Delta} \text{Disordered cubic phase } TiO_{1.0}$$

Many transition metal compounds feature a high concentration of structural vacancies.[1] Structural vacancy is a crystal lattice site that is not occupied by atom. Depending on the quantity and arrangement of vacancies in the basic crystal structure sites, a variety of phases and modifications can be formed.[1] At the same time, the peculiarities of crystal structures containing vacancies, as well as their effect on the properties have not been completely explained till now. The illustrative example is nonstoichiometric titanium monoxide TiO_y. This compound possesses the basic B1 structure and contains structural vacancies both in the metal and nonmetal sublattices.[2–5] The fraction of vacant sites for the stoichiometric composition ($y = 1$) is about 15% for each sublattice. If there is a deviation from stoichiometry, the concentration of vacancies in one of the sublattices may be as much as 25 at%.[5]

Vacancy ordering in titanium monoxide has been discovered previously.[2–5] The ordered monoclinic phase with $M_5X_{5(mon)}$ superstructure [space group $A2/m$ ($C2/m$)] (Figure 1), which is formed from the disordered cubic phase as a result of annealing at 950 °C for 50 h, has been studied in detail.[2,3] Besides the monoclinic phase, which is in thermodynamic equilibrium below 980 °C, a phase with cubic symmetry, whose space group could not be determined accurately, was also reported.[4] The ordered cubic phase is the equilibrium one in the temperature interval from 980 to 1250 °C. Above 1250 °C the disordered cubic phase is in equilibrium. Its symmetry corresponds to the symmetry of the basic crystal structure B1.

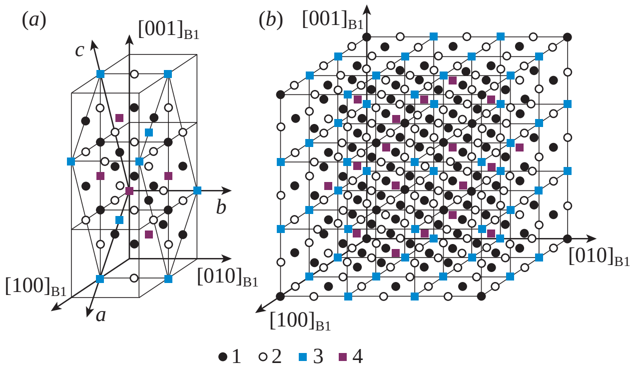

Figure 1 The arrangement of (*a*) monoclinic $M_5X_{5(mon)}$ and (*b*) cubic $M_5X_{5(cub)}$ unit cells in the basic B1 structure: 1 is the position of the titanium atom sublattice, 2 is the position of the oxygen atom sublattice, 3 is the position of the titanium vacancy sublattice, 4 is the position of the oxygen vacancy sublattice. The crystallographic directions of B1 structure and monoclinic superstructure are shown.

Later on, the experiments on structural vacancy ordering were carried out.[7] The samples of disordered cubic phase were annealed at 1057 °C for 3 h. The structure of annealed samples was described within the same model of monoclinic phase that was proposed earlier.[2,3] However, further studies[8,9] did not confirm the correctness of the monoclinic structure model. One of the possible explanations for the contradictions in the results[7–9] was published,[10–12] where a model of cubic superstructure $M_5X_{5(cub)}$ (space group $Pm\bar{3}m$) was proposed. The model is probably observed in the experiment[4] (see Online Supplementary Materials). This structural model describes satisfactorily the reported results,[8,9] but does not provide a comprehensive interpretation of the experiment.[7]

Evidently, the disagreement in literature[7–9,10–12] appears because the authors considered perfect long-range order in the superstructures, when all the vacancies are located strictly in the sites of vacancy sublattice formed as a result of ordering. In real ordered phases, one can observe the effects associated with a partial disordering, when a part of vacancies remains in the atom sublattice. In particular, it has been found[13] that the energy of the ground state of the compound decreases substantially when correlational short-range order[1] is introduced into the structure of partially ordered modification simultaneously with long-range order.

In this work we propose a structural state, where the vacancies remaining in the atom sublattice are arranged not according to the correlational short-range order type,[1] but so that they occupy the vacancy sublattice sites of an additional superstructure. In this case, two different superstructures coexist in the ordered phase, and the structural modification formed in this way can be considered as a transition state between two ordered phases.

Let us consider the peculiarities of the transition state structure using a combination of $M_5X_{5(mon)}$ and $M_5X_{5(cub)}$ superstructures. As a result of spatial superposition of two superstructures, some vacancy sites will belong only to the vacancy sublattice of monoclinic superstructure, other vacancy sites will belong only to the vacancy sublattice of cubic superstructure, and the rest will be of joint belonging. The degree of vacancy ordering in the superstructure is characterized by long-range order parameter η, which, according to refs. 7,10–12, is related to the fraction of vacancies v in the vacancy sublattice of $M_5X_{5(mon)}$ and $M_5X_{5(cub)}$ superstructures as

$$\eta = \frac{6}{5}v - \frac{1}{5}. \tag{1}$$

The proposed transition structure should be described by two long-range order parameters: η_{mon} calculated for monoclinic structure and η_{cub} calculated for cubic structure. The fraction of vacancies in the vacancy sublattice sites of monoclinic superstructure, which does not include the vacancy sublattice sites of cubic superstructure, is denoted by v_{mon}. Corresponding fraction in cubic superstructure is denoted by v_{cub}, and the fraction of vacancies in common sites for two superstructures is denoted by v_{joint}. The total fraction of vacancies in the vacancy sublattice of monoclinic superstructure will be ($v_{mon} + v_{joint}$). If vacancies occupy only the vacancy sublattice sites, then $v_{mon} + v_{cub} + v_{joint} = 1$. Considering this relation, one can find from expression (1) written separately for monoclinic and cubic superstructures that

$$\eta_{cub} = -\eta_{mon} + \frac{6}{5}v_{joint} + \frac{4}{5}. \tag{2}$$

Thus, the region of admissible relations between the long-range order parameters will be determined by a vertical shift of the line described by equation (2), and the maximal shift value will depend only on quantity of the vacancy sublattice sites that are joint for the two superstructures.

An analysis of possible spatial arrangements of one superstructure relative to another superstructure in the matrix of the basic B1 crystal structure revealed that the number of joint vacancy sublattice sites may be 0, 22.23 or 38.89% of the total number of vacancies. Consequently, there are three options of v_{joint} variation: $v_{joint} = 0$, $0 \leqslant v_{joint} \leqslant 0.2223$, and $0 \leqslant v_{joint} \leqslant 0.3889$. In the first case, the region of admissible values is degenerated into a line. In the other two cases, the region of admissible values will be determined, besides expression (1), by the constraints $\eta_{mon} \geqslant \eta_{mon}^{min}$ and $v_{cub} \geqslant \eta_{cub}^{min}$, because otherwise the number of purely monoclinic or purely cubic vacancy positions will be insufficient to accommodate all the vacancies in the compound. The values of η_{mon}^{min} and η_{cub}^{min} are found from the expression (1) by substitution of $v = 0.2223$ or $v = 0.3889$ to be $\eta_{mon}^{min} = \eta_{cub}^{min} = 0.067$ and $\eta_{mon}^{min} = \eta_{cub}^{min} = 0.2667$, respectively.

Figure 2 depicts the region of admissible values of long-range order parameters for $0 \leqslant v_{joint} \leqslant 0.3889$. In point $A(0.2667, 1.0)$ all purely monoclinic positions of the vacancy sublattice are occupied by atoms; in point $B(1.0, 0.2667)$ an analogous situation is observed for cubic superstructure. The points lying on the *CD* segment characterize the structural states, where the number of vacancies in the joint vacancy positions is equal to zero. Moving along the *BE* segment, vacancies from purely monoclinic and joint positions go with equal probability into the purely cubic vacancy positions. Formally, the structural transition of monoclinic phase into cubic phase can be modeled by motion along any arbitrary path inside the *ABCD* region. Motion along *BA* segment seems reasonable since in this case the least number of vacancy displacements from one superstructure to another is required.

Note that the transition state under investigation needs to be considered as separate phase. Coexistence of two superstructures in a single phase is contradictory to the coexistence of two phases with different structures but with incoherent boundary.[14,15]

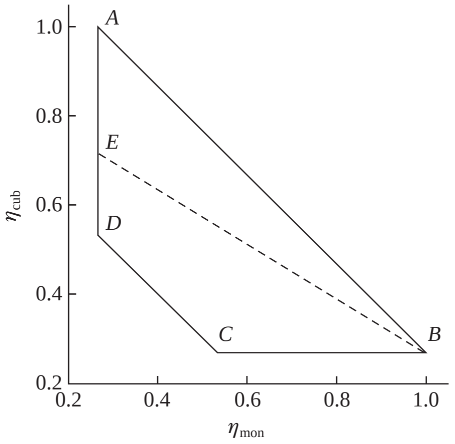

Figure 2 The region of possible values of long-range order parameters of monoclinic and cubic M_5X_5 superstructure for $0 \leqslant v_{joint} \leqslant 0.3889$.

Proposed structural model of the transition state in titanium monoxide can be described as separate superstructure. Its vacancy sublattice is not fully completed with vacancies contrary to the case of $M_5X_{5(mon)}$ and $M_5X_{5(cub)}$ superstructures. The symmetry corresponds to the space group *P*1*m*1. The unit cell coincides with that of $M_5X_{5(cub)}$ but slightly distorted due to the influence of $M_5X_{5(mon)}$. The unit cell basis includes 144 sites, 36 in 1(*a*), 36 in 1(*b*) and 72 in 2(*c*) crystallographic positions. The probabilities of vacancies and atoms in the sites are the functions of η_{mon} or η_{cub}.

Let us consider a thermodynamic validation of the existence of the transition state $M_5X_{5(mon)}$–$M_5X_{5(cub)}$ in titanium monoxide. The equilibrium structural modification corresponds to the free energy minimum $F = E - TS$ at a given temperature T. The dependences of internal energy E and entropy S *versus* order parameters cannot be accurately calculated by first-principle methods at the present. Nevertheless, it is possible to estimate qualitatively the behavior of the system at different temperatures and also to determine the phase transition type with the use of simple models.[16] In this work, the point charge model[16] was used for computing the energy E. The charges of Ti and O are assumed to be +2e and –2e, respectively. Only the configuration component was taken into account in the computation of entropy (see Online Supplementary Materials). The $E(\eta_{cub})$ and $S(\eta_{cub})$ dependences calculated for *AB* path ($v_{joint} = 0.3889$) are presented in Figures 3(*a*) and 3(*b*), respectively. Figure 3(*c*) shows the $F(\eta_{cub})$ dependences calculated at different temperatures. The equilibrium values of long-range order parameter η_{cub} corresponding to the free energy minimum gradually increase with temperature and approach asymptotically the value of 0.6333. Such behavior of the structure parameter is typical of a second-order phase transition. In reality, the maximum possible value of the order parameter will not be achieved since at a certain temperature a state with even greater configuration entropy caused by vacancy disordering both in cubic and monoclinic superstructures will turn out to be advantageous. An order–disorder phase transition will occur giving rise to the disordered cubic phase. Note that the order–order transition does not proceed completely, *i.e.*, the ideally ordered cubic phase $Ti_5O_{5(cub)}$[10–12] is not in thermodynamic equilibrium at any temperatures. Instead, a special structural state is formed, where the vacancies are distributed in the sublattices of two superstructures simultaneously. The sequence of equilibrium phase transitions taking place in titanium monoxide, when the temperature is increased, should be as follows: monoclinic phase $Ti_5O_{5(mon)}$–transition state $Ti_5O_{5(mon)}$–$Ti_5O_{5(cub)}$–disordered cubic phase $TiO_{1.0}$. In the experiment,[7] the low-temperature monoclinic disordered phase

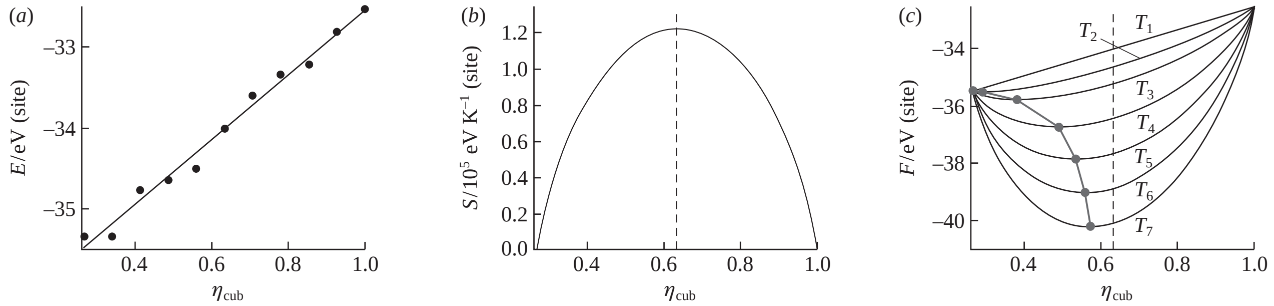

Figure 3 (*a*) The internal energy, (*b*) configuration entropy and (*c*) free energy at different temperatures ($T_1 < T_2 < T_3 < T_4 < T_5 < T_6 < T_7$) *versus* long-range order parameter of cubic superstructure $Ti_5O_{5(\text{cub})}$. The free energy minima are marked with points. The asymptote to the minima, which corresponds to the entropy maximum, is shown as a dashed line. The internal energy was calculated by supercomputer modeling for a crystal of cubic shape and size 200 × 200 × 200 sites of B1 structure with the use of the point charge model. See detailed calculations of $S(\eta_{\text{cub}})$ in Online Supplementary Materials.

was not obtained since the higher temperatures and smaller annealing time were used as compared with the original works.[2,3]

Thus, in this work we have proposed a new model for distribution of structural vacancies in ordered phases. This model is fundamentally different from the previous models since the transformation from ordered state into disordered one proceeds *via* partial formation of the special order–order transition state representing superposition of two superstructures. One of them is superstructure of the low-temperature ordered phase and another one is the high-temperature superstructure, which is not in equilibrium, but acts as additional structures necessary for the enhancement of entropy contribution to the free energy of the ordered phase during temperature rise. The structural peculiarities of the transition states in compounds with atomic-vacancy ordering,[1] as well as their effect on the electronic structure and physical properties require further theoretical and experimental investigations. The redistribution of substitutional or interstitial atoms can be considered by analogy with structural vacancies. It is also important to examine the possibility of the formation of transition states in alloys and solid solutions, for which low-temperature and high-temperature ordered phases are known. Many high-temperature ordered phases are possibly a combination of two or more superstructures, because the elevation of temperature implies certain disorder resulting from the configuration entropy contribution growth.

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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.2017.05.011.

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