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Hybrid $M_{n-i}X_{n-i}$ superstructures in compounds with atomic vacancy ordering

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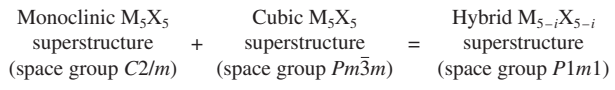
The existence of a special class of $M_{n-i}X_{n-i}$ superstructures (n – integer constant, i – rational variable) formed as a result of incomplete second order equilibrium order–order phase transitions in compounds with atomic vacancy ordering has been theoretically substantiated. The superstructure $M_{5-i}X_{5-i}$ (i = 1; 11/18; 14/18) of the high-temperature ordered titanium monoxide phase β-TiO has been described in detail as an example.



Transition metal compounds with oxygen, carbon, nitrogen and sulfur contain structural vacancies – crystal lattice sites that are not occupied by atoms. The structural vacancies induce nonstoichiometry and ordering giving rise to numerous phases and structural modifications.[1] All possible structures with vacancies are classified as ordered or disordered. The number of possible ordered phases as well as their real structure are not known in details. Here, we suggest a new class of structures to describe high temperature ordered phases.

These structures are based on the partial disordering of vacancies when the temperature is rising. Actually, the position of vacancies can be accurately determined only in ideally ordered systems when all vacancies are located in vacancy sublattice sites, and atoms, accordingly, are in atom sublattice sites. If some vacancies remain in the atom sublattice, the structure determination becomes difficult. An attempt to solve this problem[2–4] yielded two new models of defect structures. In one case,[2,3] vacancies located outside their sublattice formed an energetically favorable short-range order; in the other case,[4] an independent partially disordered superstructure. In the former case, the symmetry of the phase remained unchanged, and two superstructures with different symmetries occurred simultaneously in the compound in the latter case.

Suppose that an ordering binary compound MX forms two or more ordered phases with M_nX_n superstructures, where n is the number of atoms in the metal M or nonmetal X sublattice per vacancy. As an example, let us consider stoichiometric titanium monoxide $TiO_{1.0}$. In titanium monoxide superstructures M_5X_5,[5–9,10] 1/6 of sites of each sublattice is vacant. Most of the familiar superstructures contain vacancies only in the nonmetal sublattice, and they are described by the formula $M_{n+1}X_n$.[1,11] A case when the superstructure sublattices have different numbers of the ordered vacancies is not known. In the framework of each superstructure type, different symmetry variants are possible. For example, for M_5X_5, the existence of the monoclinic superstructure $M_5X_{5(mon)}$ (space group $C2/m$), which occurs in the low-temperature α-TiO phase, has been confirmed experimentally.[5–9] In theoretical works,[12–15] M_5X_5 superstructures with cubic (space group $Pm\bar{3}m$),[12–14] orthorhombic (space group $Pmmm$) and tetragonal (space group $P422$) symmetry[13] were proposed. At the same time, it was shown[12–14] that the cubic $M_5X_{5(cub)}$ superstructure should correspond to the high-temperature ordered β-TiO phase,[9] whose precise position on the phase diagram is not known.[16,17]

According to published data,[12–14] the $M_5X_{5(mon)}$–$M_5X_{5(cub)}$ (α-TiO–β-TiO) order–order phase transition meets the Landau group-theoretical criterion for second-order transitions. When the temperature is varied, the second-order transitions take place with order parameters changing gradually in the whole bulk of the crystal. Namely, with a rise in the temperature, vacancies from the vacancy sublattice of a low-temperature superstructure should gradually move into the vacancy sublattice sites of a high-temperature superstructure. The free energy F of the resulting order–order state is a function of the order parameter η: $F = E(\eta) - TS(\eta)$ (E is internal energy, S is entropy, and T is temperature). Since there should be a unique relation between the order parameters of two different superstructures,[4] the transition process can be characterized by the order parameters of both low-temperature and high-temperature superstructures.

An example of the calculation of thermodynamic functions $E(\eta)$ and $S(\eta)$ was reported.[4] The description of η is given in Online Supplementary Materials. The internal energy was calculated using the simplest point charge model, and a linear $E(\eta)$ function was obtained. In the general case, assume $E(\eta)$ is any monotonic function. If the calculations are carried out with respect to the order parameter of the high-temperature phase, $E(\eta)$ will be an increasing function because the internal energy of the low-temperature phase is smaller than the energy of the high-temperature phase. The configurational component of entropy can be calculated using combinatorial formulas and the Stirling formula if the number of disordered atoms and vacancies for the sublattices or groups of the basis crystal structure sites is known.[4] In the order–order transition structure, the number of groups of sites with vacancy arrangement uncertainty is two if the superstructures have no joint vacancy positions (the case considered in ref. 4) or three if there are joint positions for the initial and final superstructures. Anyhow, owing to the peculiar dependences between the number of vacancies in the groups, the function $S(\eta)$ has only one maximum. Summation of the monotonically increasing function $E(\eta)$ and the function $-TS(\eta)$ having a maximum point gives the functions, whose graphs are depicted in Figure 1. At

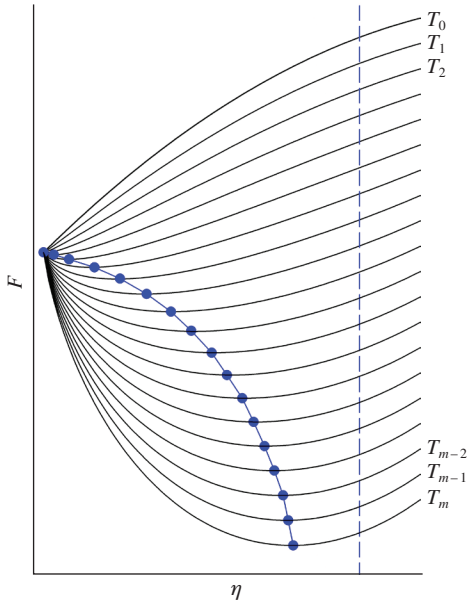


Figure 1 The free energy $F = E - TS$ at different temperatures ($T_0 < T_1 < T_2 ... < T_{m-2} < T_{m-1} < T_m$) *versus* the long-range order parameter η of the high-temperature superstructure M_nX_n. The positions of the minima are shown by a blue line. The asymptote to the minima that corresponds to the configurational energy maximum is plotted by a dashed line.

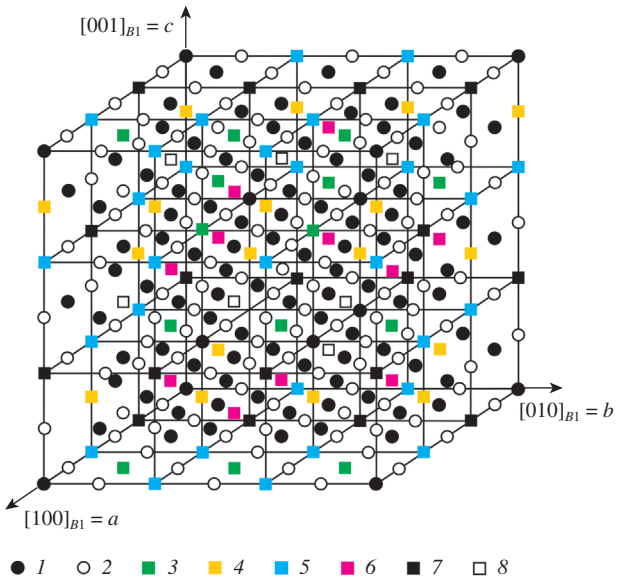


Figure 2 The unit cell of the hybrid $M_{5(11/18)}X_{5(11/18)}$ superstructure (space group $P1m1$): (*1*, *2*) the atoms of metallic M and nonmetallic X sublattices, respectively; (*3*, *4*) the positions of vacancies of metallic and nonmetallic sublattices, respectively, belonging only to the initial low-temperature monoclinic M_5X_5 superstructure (space group $C2/m$); (*5*, *6*) vacancy positions belonging only to the high-temperature cubic superstructure M_5X_5 (space group $Pm\bar{3}m$); (*7*, *8*) the positions of vacancies of metallic and nonmetallic sublattices belonging simultaneously to the monoclinic and cubic M_5X_5 superstructures.

sufficiently low temperatures (T_1, T_2, and T_3 curves in Figure 1), the minimum of free energy is achieved at the minimum values of η, which corresponds to the low-temperature superstructure, whose energy E is minimal. As the temperature is raised further, the free energy minimum gradually shifts towards higher degrees of order of the high-temperature superstructure and, accordingly, smaller degrees of order of the low-temperature superstructure. The minimum point of the free energy asymptotically approaches the minimum point of the configurational entropy.

The above considerations lead to the following conclusions: (a) the vacancy redistribution induced order–order phase transition takes place by the second kind mechanism; (b) the phase transition is not completed, *i. e.*, ideally ordered high-temperature phases cannot be thermodynamically equilibrium phases. Otherwise, the entropy of the system would decrease to zero, which is impossible with rising temperature.

Thus, the structure of the high-temperature ordered β-TiO phases is actually a superposition of the low-temperature superstructure and a certain additional superstructure that increases the entropy of the system at elevated temperatures.

In order to determine the true symmetry of the high-temperature ordered phase, it is necessary to analyze in detail the structure appearing at the superposition of two superstructures with different symmetries in the matrix of a basis crystal structure. Consider this issue using the monoclinic (space group $C2/m$) and cubic (space group $Pm\bar{3}m$) M_5X_5 superstructures of titanium monoxide as an example. According to analysis,[4] three superpositions of these superstructures in the matrix of the basis $B1$ structure are possible: when the number of joint vacancies is 0, 22.23 (4/18) or 38.89% (7/18) of the total number of vacancies. Thorough analysis of the particular superpositions of superstructures shows that, in any case, the resulting structure will have a single point symmetry element – a mirror-reflection plane, which allows one to assign this structure to the space group $P1m1$ of a monoclinic system[18] (see Online Supplementary Materials). On the other hand, in a particular type of superstructure superposition, the minimization of energetically unfavorable correlations should be addressed.[2,19] From this viewpoint, the most acceptable superposition is that in which the number of joint sites in the vacancy sublattices is 7/18. Figure 2 shows the unit cell of a hybrid superstructure, in which different types of vacancy positions are taken into account. Its form and dimensions coincide with those of the unit cell of the cubic M_5X_5 superstructure, *i.e.*, $a = b = c = 3a_{B1}$, $\alpha = \beta = \gamma = 90°$, and the reduction of symmetry from cubic to monoclinic is due to a variation in the arrangement of vacancy positions. In a real structure, residual monoclinic distortions from the low-temperature $M_5X_{5(mon)}$ superstructure should be observed; that is, it should be considered that $\beta \approx 90°$, and the parameters a, b and c are not equal to each other. The coordinates of atoms and vacancies in the unit cell are given in Online Supplementary Materials.

The superstructures of the high-temperature ordered phases produced by the superposition of initial M_nX_n superstructures differ fundamentally from the latter in the fact that the number of sites in their vacancy sublattices is larger than the number of vacancies in the compound. Therefore, the hybrid superstructures can be denoted by the formula $M_{n-i}X_{n-i}$, where the index i assumes discrete values and allows for the vacancy sublattice expansion owing to the superposition of initial M_nX_n superstructures. The value of i is determined by superimposing the superstructures in the basis crystal structure. In the case under study, the values of i are 1, 14/18 and 11/18. Note that the stochastic nature of vacancy distribution in the hybrid superstructures leads to a variety of local atomic displacements, as compared to the initial ordered superstructures in which the displacements are strictly determined by their symmetry.

Why did not Hilti[9] and Gusev[12–14] find a difference between the hybrid superstructure $M_{5-i}X_{5-i}$ with monoclinic symmetry and the cubic superstructure of the M_5X_5 family? The answer to this question is given in Figure 3, where the X-ray diffraction patterns of monoclinic and cubic M_5X_5 and $M_{5-11/18}X_{5-11/18}$ superstructures are depicted. The numbers and positions of superstructure reflections in the X-ray diffraction pattern calculated for $M_{5-11/18}X_{5-11/18}$ are identical to those in the X-ray diffraction pattern of M_5X_5. Theoretically, the $M_{5-11/18}X_{5-11/18}$ and M_5X_5 superstructures can be distinguished by a ratio between the intensities of reflections determined based on the probabilities

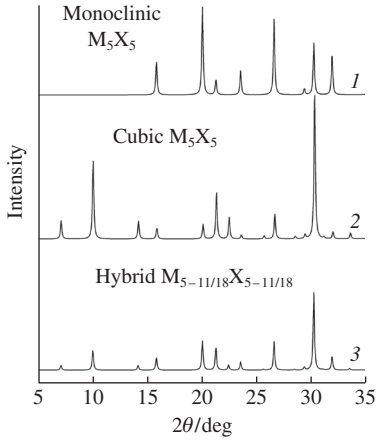


Figure 3 Calculated X-ray diffraction patterns of the (*1*) monoclinic M_5X_5 (space group $C2/m$) and (*2*) cubic (space group $Pm\bar{3}m$) M_5X_5 superstructures and (*3*) the hybrid $M_{5-11/18}X_{5-11/18}$ superstructure (space group $P1m1$). The X-ray diffraction pattern (*3*) is calculated for the case when the probability that a vacancy occupies the initial monoclinic and cubic vacancy positions is 0.5 and joint positions – 1.0. At other ratios of probabilities, the reflection intensities on the X-ray diffraction pattern (*3*) will be different. The basis $B1$ structure spacing is assumed to be 418.2 pm, the X-ray radiation wavelength is λ = 154 pm.

of occupation of different crystallographic positions in the atom and vacancy sublattices by vacancies. However, the problem is almost insoluble considering that the numbers of crystallographic positions in the cubic and hybrid superstructures are 20[12–14] and 144, respectively (see Online Supplementary Materials), and the fact that the experimental reflection intensities differ from the calculated ones due to various reasons. Perhaps, an analysis of local atomic vacancy correlations.[20,21] and the experimental techniques providing information on short-range order[22] could help in the identification of the combined $M_{n-i}X_{n-i}$ superstructures.

In this work, we considered a hybrid superstructure formed by the combination of only two initial simple superstructures. Actually, the number of initial superstructures can be greater. It may be the case that there is a series of high-temperature ordered phases with different types of hybrid superstructures.

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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.2018.01.011.

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