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Correlational short-range order in superstructures

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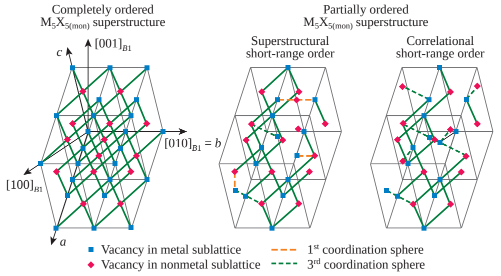
The structural models of an ordered state containing simultaneously long-range order and correlational short-range order have been proposed and examined for $M_5X_{5(mon)}$ (space group $C2/m$), $M_6X_{5(mon)}$ (space group $C2/m$) and $M_4X_{3(tet)}$ (space group $I4/mmm$) superstructures.



Many transition metal compounds contain defects in the crystal structure such as structural vacancies,[1] crystal lattice sites that are not occupied by atoms. Vacancies in the crystal structure can be distributed in an ordered or disordered way. Disordered arrangement of vacancies does not break the basis crystal structure symmetry. As a result of ordering, vacancies are redistributed in the lattice sites giving rise to a long-range order, symmetry reduction and formation of superstructures.[1]

In fully ordered superstructures, all vacancies are on the vacancy sublattices, and atoms, accordingly, are on the atom sublattices. As the long-range order degree decreases, a part of vacancies passes from the vacancy sublattice onto the atom sublattice. When the numbers of vacancies on the atom and vacancy sublattices become equal, these sublattices get indistinguishable again and the structure becomes disordered. As soon as a part of vacancies move onto the atom sublattice, an uncertainty in their arrangement appears, which affects the energy characteristics of the compound and its electronic structure and physicochemical properties. For this reason, the accounting for short-range order becomes so important in the description of disordered and partially ordered states. The short-range order appears due to correlations in the arrangement of vacancies within the first coordination spheres, which, as distinct from a long-range order, do not lead to a crystal structure variation and the formation of superstructures. If in partially ordered modifications the vacancies that passed onto the atom sublattice arrange there independently of other vacancies, then only a superstructural short-range order is present in the structure, which is determined exclusively by long-range order, *i.e.*, by the type of superstructure and the ratio of atoms and vacancies on its sublattices.[1,2] The superstructural short-range order parameters can be calculated analytically from the known long-range order parameters.[3] The partially ordered state with superstructural short-range order corresponds to a mean field approximation,[4] which is widely employed in thermodynamic[5,6] and DFT calculations.[7–9]

The term ‘correlational short-range order’ was proposed[2] as an alternative to superstructural short-range order. The correlational short-range order appears in the structure due to the restriction imposed on the way of mutual arrangement of vacancies located outside their sublattice. This restriction should induce a decrease in the energy of structural modifications with correlational short-range order, as compared with the modifications having superstructural short-range order.

In this work, the possibility of constructing the structural modifications with correlational short-range order was studied by computer simulation using the superstructures $M_5X_{5(mon)}$ (space group $C2/m$),[10–12] $M_6X_{5(mon)}$ (space group $C2/m$)[13] and $M_4X_{3(tet)}$ (space group $I4/mmm$) ($B1$ structure derivatives)[14] as an example. In $M_5X_{5(mon)}$, 1/6 of the metal sublattice sites and 1/6 of the nonmetal sublattice sites are vacant. The superstructures $M_6X_{5(mon)}$ and $M_4X_{3(tet)}$, as distinct from $M_5X_{5(mon)}$, contain vacancies only on the nonmetal sublattice. Their concentrations in $M_6X_{5(mon)}$ and $M_4X_{3(tet)}$ are 1/6 and 1/4, respectively. In $M_5X_{5(mon)}$, correlational short-range order was simulated by forbidding the arrangement of vacancies within the radius of the first coordination sphere from each other. This forbidding was maintained at any possible degree of long-range order down to a zero degree corresponding to a completely disordered structure. In $M_4X_{3(tet)}$, the minimal distance between vacancies is equal to the radius of the fourth coordination sphere, and in the $M_6X_{5(mon)}$ superstructure, to the radius of the sixth coordination sphere. However, the complete exclusion of vacancies within the radius of the second and, the more so, the fourth coordination sphere at such high concentrations of vacancies as in $M_6X_{5(mon)}$ and $M_4X_{3(tet)}$ is possible exclusively for the fully ordered state. Because of disordering, a situation when a part of vacancies is located in the second sphere ($M_4X_{3(tet)}$) or in the second and fourth spheres ($M_6X_{5(mon)}$) becomes inevitable. In this case, correlational short-range order is determined by the ratio of the amounts of correctly and incorrectly located displaced vacancies. That is why during modeling it was controlled that the displaced vacancies are located first only in the positions having no neighboring vacancies at the distances forbidden for $M_6X_{5(mon)}$ and $M_4X_{3(tet)}$. This condition could be violated only when the quantity of unforbidden positions in the atom sublattice was not sufficient to accommodate all the displaced vacancies. As a result, the probability of correct atomic vacancy configurations was higher than that in the framework of the statistical arrangement model, and correlational short-range order appeared in the structure.

The differences between the modifications with correlational short-range order and the modifications with superstructural short-range order are revealed by comparing the dependences of the short-range order parameters on the long-range order parameters calculated based on the modeling results (Figure 1). The long-range order parameter η numerically characterizes the degree of superstructure ordering; in this case, it can be determined through the probability n of finding out an atom in the vacancy sublattice: $\eta = 1 - 6/5n$ (for $M_5X_{5(\mathrm{mon})}$ and $M_6X_{5(\mathrm{mon})}$), $\eta = 1 - 4/3n$ (for $M_4X_{3(\mathrm{tet})}$). At $\eta = 0$, the probability n is equal to the concentration of vacancies in the compound; *i.e.*, the atom and vacancy sublattices are indistinguishable, and the structure is disordered (no superstructure is observed). At $\eta = 1$, all the vacancies are located on the vacancy sublattice, the superstructure is fully ordered, and superstructural short-range order is not distinguished from correlational short-range order.

The short-range order parameter characterizes local correlations, and it can be determined through the probabilities of atom–vacancy or vacancy–vacancy pairs in a specified coordination sphere by the expression[2,3]

$$\alpha^{cs}_{\mathrm{V-A}} = 1 - \frac{P^{cs}_{\mathrm{V-A}}}{C_\mathrm{V} C_\mathrm{A}}, \qquad (1)$$

where V and A are the vacancy type and kind of atom, respectively, C_V and C_A are their concentrations in crystal, and $P^{cs}_{\mathrm{V-A}}$ is the probability of vacancy–atom (or vacancy–vacancy, V–V) pair formation in the coordination sphere with number *cs*. If in the absence of long-range order the vacancies are arranged statistically, $P^{cs}_{\mathrm{V-A}} = C_\mathrm{V}C_\mathrm{A}$ and the parameter $\alpha^{cs}_{\mathrm{V-A}}$ calculated for any coordination sphere is zero. If the considered pair does not exist in the structure, $\alpha^{cs}_{\mathrm{V-A}} = 1$. It can be seen in Figure 1(*a*) that in $M_6X_{5(\mathrm{mon})}$ superstructure without correlational short-range order parameter $\alpha^{\mathrm{IV}}_{\mathrm{VX-VX}}$ increases gradually from 0 to 1 as the long-range order parameter η grows. With allowance for correlational short-range order $\alpha^{\mathrm{IV}}_{\mathrm{VX-VX}}$ at $\eta = 0$ is nonzero. When η grows, the parameter $\alpha^{\mathrm{IV}}_{\mathrm{VX-VX}}$ first decreases insignificantly reaching a minimum at $\eta = 0.2$ and then increases up to 1. If the forbidding in $M_6X_{5(\mathrm{mon})}$ is maintained for all of the long-range order parameters, the parameter $\alpha^{\mathrm{IV}}_{\mathrm{VX-VX}}$ would be always unity, like the parameter $\alpha^{\mathrm{I}}_{\mathrm{VX-VM}}$ calculated for the $M_5X_{5(\mathrm{mon})}$ superstructure [Figure 1(*b*)]. In spite of the presence of extremes, the largest divergence between the short-range order parameters calculated with and without the allowance for correlations is observed at the zero value of the long-range order parameter. As the degree of long-range order increases, the difference in the short-range order parameters decreases.

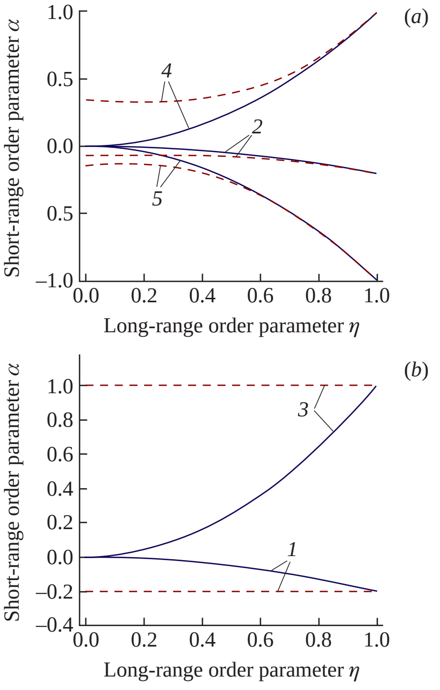


Figure 1 Dependences of the short-range order parameters $\alpha^{\mathrm{I}}_{\mathrm{M-VX}}$ (*1*), $\alpha^{\mathrm{IV}}_{\mathrm{X-VX}}$ (*2*), $\alpha^{\mathrm{I}}_{\mathrm{VX-VM}}$ (*3*), $\alpha^{\mathrm{IV}}_{\mathrm{VX-VX}}$ (*4*), and, $\alpha^{\mathrm{VI}}_{\mathrm{VX-VX}}$ (*5*) on the long-range order parameter calculated for (*a*) $M_6X_{5(\mathrm{mon})}$ or (*b*) $M_5X_{5(\mathrm{mon})}$ superstructure: (solid lines) without and (dashed lines) with allowance for correlational short-range order.

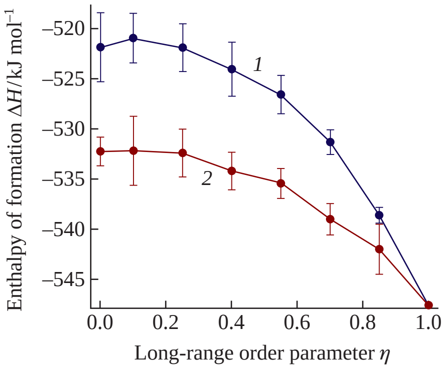


Figure 2 Dependences of the enthalpy of formation ΔH on the long-range order parameter η calculated for the ordered titanium monoxide $Ti_5O_{5(\mathrm{mon})}$ (*1*) without and (*2*) with allowance for correlational short-range order. Different degrees of short- and long-range order in the structure were simulated by a supercell method.[19] Standard deviations calculated for 10 supercells (Figure 1) with different arrangements of vacancies are shown for each point corresponding to a certain degree of the long-range order.

The energy gain from correlational short-range order was established with the use of first-principles DFT calculations.[15] The calculation details and the short- and long-range order modeling were described elsewhere.[16–18] Figure 2 shows the dependences of the enthalpy of formation on the long-range order parameter, which were derived from the data of calculation of the ground state energy using $M_5X_{5(\mathrm{mon})}$ superstructure of ordered titanium monoxide as an example. Thus, in terms of energy, correlational short-range order in partially ordered modifications is advantageous at any values of the long-range order degree. Analogous calculations for the ordered niobium carbide $Nb_6C_{5(\mathrm{mon})}$ and niobium nitride $Nb_4N_{3(\mathrm{mon})}$ showed that the proposed models of correlational short-range order give a considerable energy gain only at small values of the long-range order parameter. As the degree of order increases, the energy difference decreases gradually and disappears when about a half of the vacancies are located on their sublattice.

The principles of correlational short-range order modeling set forth in this work are applicable to the distribution of both structural vacancies and substitutional atoms. For example, local correlations during the formation of superstructures in alloys can be studied in the same way.

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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.2017.03.013.

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