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Thermodynamics of atomic ordering in nonstoichiometric transition metal monoxides

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The XRD studies of structural vacancy redistribution in titanium, vanadium and niobium monoxides undergoing atomic-vacancy ordering or structural vacancy clusterization have shown the necessity of a many-cluster approach to model the free energy function of nonstoichiometric monoxides.

Transition metal monoxides with a cubic (*B*1 type) basic lattice, such as TiO_y, VO_y and NbO_y, show a high (up to 30 at%) concentration of structural vacancies in metal and oxygen sublattices at ambient temperature and pressure. For example, for the stoichiometric monoxides $MO_{1.00}$, the concentrations of vacancies on each sublattice are 16–17 at% for TiO, 12–17 at% for VO and 25 at% for NbO.[1–4] At low temperatures, the high amount of structural vacancies leads either to their ordering or to segregation. These processes should be taken into account when calculating phase diagrams of the compounds.

A phase diagram calculation method for compounds with the high amount of structural vacancies on one of the sublattices of *B*1 type compounds was described in detail elsewhere.[5,6] This order-parameter functional (OPF) method is suitable for nonstoichiometric carbides of Ti, V, Zr, Nb, Hf and Ta because structural vacancies are present on the carbon sublattice and absent from the metal sublattice. This method is not suitable for nonstoichiometric compounds with structural vacancies on both sublattices.

We performed the X-ray diffraction (XRD) analysis of Ti, V and Nb monoxides and proposed a thermodynamic model to describe phase equilibrium in systems with vacancies in metal and nonmetal sublattices.

To calculate the phase diagrams of transition metal monoxides MO_y, it is necessary to solve the following set of equations in the temperature range of interest:[5,6]

$$\frac{\partial F_{\mathrm{dis}}(y,T)}{\partial y} = \frac{\partial F_{\mathrm{ord}}(y,T)}{\partial y}, \tag{1}$$

$$F_{\mathrm{dis}}(y,T) - y\frac{\partial F_{\mathrm{dis}}(y,T)}{\partial y} = F_{\mathrm{ord}}(y,T) - y\frac{\partial F_{\mathrm{ord}}(y,T)}{\partial y}, \tag{2}$$

where y is independent variable in disordered (dis) and ordered (ord) phases, respectively. Free energy F of each phase is determined by its enthalpy H and entropy S

$$F = H - TS. \tag{3}$$

To compute the equilibrium between ordered and disordered phases, the account of configurational contributions to the enthalpy and entropy of a compound dependent on mutual distribution of atoms and vacancies is sufficient. Contributions to the enthalpy and entropy, which are independent of a redistribution of atoms and vacancies on crystal lattice, do not affect the phase diagram. Good approximation for the configurational part of free energy for alloys and solid solutions is suggested in terms of the cluster variation method (CVM).[7–9] The free energy of a solid solution, which consists of N atoms, with a given degree of order can be written as follows:

$$F = N\sum_{s=1}^{n} o^{(s)} \sum_{i\in s} \lambda_i^{(s)} P_i^{(s)} [\varepsilon_i^{(s)} + k_{\mathrm{B}} T \ln P_i^{(s)}]. \tag{4}$$

The number of overlapping figures $(n-1)$, overestimation parameters $o^{(s)}$, multiplicity parameters $\lambda_i^{(s)}$ and energy of clusters $\varepsilon_i^{(s)}$ are constants in the CVM, and they depend on the basic cluster. Thus, at a given temperature, free energy depends exclusively on cluster probabilities $P_i^{(s)}$. Free energy minimization in respect to cluster probabilities determines the degree of order of solid solution at the given temperature.

Thus, in order to elaborate a thermodynamic model for monoxides, it is very important to choose the basic cluster properly. The choice of the basic clusters is based on experimental data on the structure of disordered and ordered phases of titanium, vanadium and niobium monoxides.

The stoichiometric transition metal monoxides (y = 1.00) were synthesized by high-temperature (1600 °C) vacuum (0.001 Pa) sintering from metals and corresponding highly oxidized oxides. To achieve the ordered state, which is characteristic of thermodynamically stable monoxides at low temperatures, the specimens were slowly cooled (at a rate of 10 K h^{-1}) in a vacuum from the sintering temperature to ambient temperature. To preserve the state, which is characteristic of thermodynamically equilib-

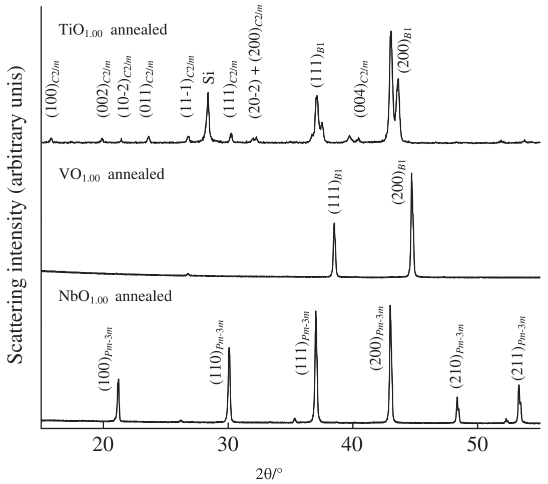

Figure 1 XRD patterns of annealed titanium, vanadium and niobium monoxides. Additional reflection observed at $2\theta = 28.35°$ in the XRD pattern of titanium monoxide TiO_y corresponds to a Si substrate.

rium state at high temperatures, the specimens were quenched at a rate of 200 K s^{-1}.

The XRD analysis demonstrated that the low-temperature state of the titanium and niobium monoxides is close to that with perfect ordering of vacancies as in metal and nonmetal sublattices. In accordance with the position and intensity of superstructural reflections, it can be seen that the Ti_5O_5 phase with space group *C*2/*m* is formed in titanium monoxide (Figure 1). In niobium monoxide (Figure 1), the Nb_3O_3 phase with space group *Pm*-3*m* is formed. In the XRD patterns of slowly cooled specimens of vanadium monoxides (Figure 1), the superstructural reflections were not observed. Such superstructural reflections could point out to the vacancy ordering in this compound at temperatures higher than ambient temperature. In the XRD patterns of TiO_y and VO_y exclusively structural reflections are present. The XRD pattern of quenched NbO_y specimens exhibited superstructural reflections in addition to structural reflections.

Based on the XRD analysis and published data, we suggest the next main defect types present in the transition metal monoxides. In titanium, vanadium and niobium monoxides, those defects are structural vacancies. Moreover, structural vacancies are present on both sublattices simultaneously in all these monoxides.

If the temperature decreases, the equilibrium state of the titanium and niobium monoxides approaches an ordered state. The main feature of an ordered state is that interaction between structural vacancies can be described as repulsive. Segregation or clusterization of vacancies cannot be observed. Structural vacancies are distributed homogeneously in the matrix of the basic crystal lattice. The decreasing of structural vacancy concentration upon decreasing temperature as long as *B*1 type basic lattice exists is not observed in titanium and niobium monoxides.

The behaviour of structural vacancies in vanadium monoxide is different. Upon the decrease of temperature, the structural vacancies in oxygen sublattice tend to form sheets of oxygen vacancies (Figure 2). Such a sheet consists of the squares of vacancies. Structural vacancies in a metal sublattice tend to form three-dimensional vacancy defects. Such defects can be represented as tetrahedral vacancies with an interstitial vanadium atom in the centre (Figure 3). The formation of the latter defect means that the vanadium atom is present in tetrahedral interstitial of basic cubic *B*1 lattice. It means that, in the vanadium monoxide, a new type of defects characteristic of other transition metal compounds appears.

Analysis of the structure of ordered and disordered phases, and the structure of atomic-vacancy defects in the three monoxides enables us to conclude that for an adequate description of any thermodynamic state of monoxides it is necessary to use a multicluster approach. This approach was already used to describe atomic ordering in a fcc solid solution.[10] To describe the thermodynamic state of titanium and niobium monoxide, the multi-cluster approach can be reduced to a two-cluster approach. Two octahedral clusters can be chosen as the basic clusters (Figure 4). The centre of one octahedral has to coincide with the site on nonmetallic sublattice (the upper row of configurations in Figure 4), and the centre of another octahedral has to coincide with the site on metallic sublattice (the lower row of configurations in Figure 4). The octahedral sites in the first basic cluster coincide with the nearest neighbour sites of the metal sublattice. The octahedral sites in second basic cluster coincide with the nearest neighbour sites of the nonmetal sublattice.

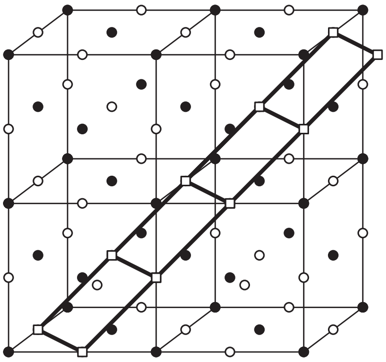

Figure 2 Segregation of oxygen vacancies (□) or sheets of oxygen vacancies in vanadium monoxide VO_y: (○) oxygen atoms O, (●) vanadium atoms V.

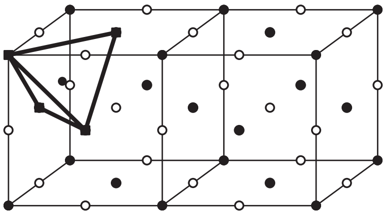

Figure 3 Segregation of vanadium vacancies (■) and interstitial vanadium atom in the centre of tetrahedral in vanadium monoxide VO_y: (○) oxygen atoms O, (●) vanadium atoms V.

For a thermodynamical description of vanadium monoxide in the entire concentration homogeneity region of cubic phase, the third basic cluster has to be used additionally to two basic clusters described above. This third cluster can be a tetrahedron with a vanadium atom in the centre.

For the minimization of free energy (1), the probabilities of clusters might be written as functions of long-range order parameters of ordered phase.[11] Such a representation of probabilities covers both the perfect order and the perfect disorder. In the case of perfect order, all long-range order parameters are equal to unity. In case of perfect disorder, all long-range parameters are zero.

The positions and intensity of superstructural reflections for titanium monoxide (Figure 1) evidence that the crystal structure of ordered phase type Ti_5O_5 with space group *C*2/*m*. For such a phase, the values of distribution function for titanium atom in titanium sublattice with any composition of Ti_xO_z are

$$\begin{aligned} n_1^{\mathrm{Ti}} &= x - \eta_{10}^{\mathrm{Ti}}/6 - \eta_4^{\mathrm{Ti}}/3 - \eta_1^{\mathrm{Ti}}/3, \\ n_2^{\mathrm{Ti}} &= x + \eta_{10}^{\mathrm{Ti}}/6 - \eta_4^{\mathrm{Ti}}/3 + \eta_1^{\mathrm{Ti}}/3, \\ n_3^{\mathrm{Ti}} &= x - \eta_{10}^{\mathrm{Ti}}/6 + \eta_4^{\mathrm{Ti}}/6 + \eta_1^{\mathrm{Ti}}/6, \\ n_4^{\mathrm{Ti}} &= x + \eta_{10}^{\mathrm{Ti}}/6 + \eta_4^{\mathrm{Ti}}/6 - \eta_1^{\mathrm{Ti}}/6, \end{aligned} \tag{5}$$

where η_{10}^{Ti}, η_4^{Ti} and η_1^{Ti} are the long-range order parameters for titanium sublattice. In titanium monoxide, the titanium and oxygen sublattices undergo ordering of the same type. Thus, the distribution functions of oxygen for oxygen sublattice can be written by replacing the superscripts Ti in equation (5) by O.

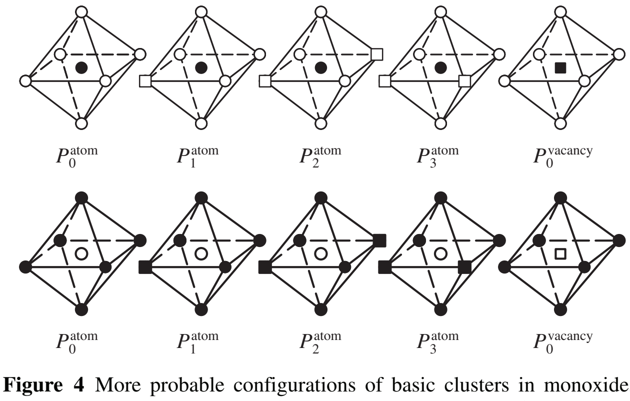

Figure 4 More probable configurations of basic clusters in monoxides: (○) oxygen atoms O, (●) metal atoms, (□) oxygen vacancies, (■) metal vacancies. Upper indices 'atom' and 'vacancy' mean that the centre of cluster is filled by atom or is vacant, respectively.

Table 1 The cluster probabilities of the ordered and disordered $TiO_{0.96}$ and $TiO_{1.00}$ monoxides.

Atom at the cluster centre	Composition	Monoxide state	P_0^{atom}	P_1^{atom}	P_2^{atom}	P_3^{atom}	P_0^{vacancy}	$\sum P_i$
Titanium	$TiO_{0.96}$	Ordered	0.14	0.62	0.13	0	0.11	1.0
		Disordered	0.34	0.35	0.03	0.12	0.04	0.88
	$TiO_{1.00}$	Ordered	0	0.66	0.17	0	0.17	1.0
		Disordered	0.28	0.34	0.03	0.13	0.06	0.84
Oxygen	$TiO_{0.96}$	Ordered	0.26	0.52	0.07	0	0.15	1.0
		Disordered	0.42	0.31	0.02	0.08	0.07	0.90
	$TiO_{1.00}$	Ordered	0	0.66	0.17	0	0.17	1.0
		Disordered	0.28	0.34	0.03	0.13	0.06	0.84

If all long-range order parameters for each sublattice are equal, *i.e.*, $\eta_{10}^{\mathrm{Ti}} = \eta_4^{\mathrm{Ti}} = \eta_1^{\mathrm{Ti}} = \eta^{\mathrm{Ti}}$ and $\eta_{10}^{\mathrm{O}} = \eta_4^{\mathrm{O}} = \eta_1^{\mathrm{O}} = \eta^{\mathrm{O}}$, the probabilities of clusters with configurations shown in Figure 4 can be written using the distribution functions of titanium atoms n_1 and n_2. The values of n_3 and n_4 in this case are degenerated.

Here the probabilities for the most probable configurations of clusters are presented (Figure 4). For those clusters with a titanium atom in the centre, the probabilities are

$$P_0^{\mathrm{Ti}} = \frac{1}{12}[2n_1^{\mathrm{O}}(n_2^{\mathrm{O}})^6 + 2n_2^{\mathrm{Ti}}(n_1^{\mathrm{O}})^2(n_2^{\mathrm{O}})^4 + 8n_2^{\mathrm{Ti}}(n_1^{\mathrm{O}})(n_2^{\mathrm{O}})^5],$$

$$\begin{aligned} P_1^{\mathrm{Ti}} = \frac{1}{12}\Big\{&2n_1^{\mathrm{Ti}}\Big[\frac{1}{6}6(1 - n_2^{\mathrm{O}})(n_2^{\mathrm{O}})^5\Big] + \\ &+ 2n_2^{\mathrm{Ti}}\Big[\frac{1}{6}[2(1 - n_1^{\mathrm{O}})(n_1^{\mathrm{O}})(n_2^{\mathrm{O}})^4 + 4(1 - n_2^{\mathrm{O}})(n_1^{\mathrm{O}})^2(n_2^{\mathrm{O}})^3]\Big] + \\ &+ 8n_2^{\mathrm{Ti}}\Big[\frac{1}{6}[1(1 - n_1^{\mathrm{O}})(n_2^{\mathrm{O}})^5 + 5(1 - n_2^{\mathrm{O}})(n_2^{\mathrm{O}})^4(n_1^{\mathrm{O}})]\Big]\Big\}, \end{aligned}$$

$$\begin{aligned} P_2^{\mathrm{Ti}} = \frac{1}{12}\Big\{&2n_1^{\mathrm{Ti}}\Big[\frac{1}{3}3(1 - n_2^{\mathrm{O}})^2(n_2^{\mathrm{O}})^4\Big] + \\ &+ 2n_2^{\mathrm{Ti}}\Big[\frac{1}{3}[1(1 - n_1^{\mathrm{O}})^2(n_2^{\mathrm{O}})^4 + 2(1 - n_2^{\mathrm{O}})^2(n_1^{\mathrm{O}})^2(n_2^{\mathrm{O}})^2]\Big] + \\ &+ 8n_2^{\mathrm{Ti}}\Big[\frac{1}{3}[1(1 - n_1^{\mathrm{O}})(1 - n_2^{\mathrm{O}})(n_2^{\mathrm{O}})^4 + 2(1 - n_2^{\mathrm{O}})^2(n_1^{\mathrm{O}})(n_2^{\mathrm{O}})^3]\Big]\Big\}, \end{aligned}$$

$$\begin{aligned} P_3^{\mathrm{Ti}} = \frac{1}{12}\Big\{&2n_1^{\mathrm{Ti}}\Big[\frac{1}{12}12(1 - n_2^{\mathrm{O}})^2(n_2^{\mathrm{O}})^4\Big] + \\ &+ 2n_2^{\mathrm{Ti}}\Big[\frac{1}{12}[8(1 - n_1^{\mathrm{O}})(1 - n_2^{\mathrm{O}})(n_1^{\mathrm{O}})(n_2^{\mathrm{O}})^3 + 4(1 - n_2^{\mathrm{O}})^2(n_1^{\mathrm{O}})^2(n_2^{\mathrm{O}})^2]\Big] + \\ &+ 8n_2^{\mathrm{Ti}}\Big[\frac{1}{12}[4(1 - n_1^{\mathrm{O}})(1 - n_2^{\mathrm{O}})(n_2^{\mathrm{O}})^4 + 8(1 - n_2^{\mathrm{O}})^2(n_1^{\mathrm{O}})(n_2^{\mathrm{O}})^3]\Big]\Big\}. \end{aligned}$$

The probability of the most probable configuration of cluster with titanium vacancy in the centre is

$$P_0^{\mathrm{Ti}} = \frac{1}{12}[2(1 - n_1^{\mathrm{Ti}})(n_2^{\mathrm{O}})^6 + 2(1 - n_2^{\mathrm{Ti}})(n_1^{\mathrm{O}})^2(n_2^{\mathrm{O}})^4 + 8(1 - n_2^{\mathrm{Ti}})(n_1^{\mathrm{O}})(n_2^{\mathrm{O}})^5].$$

The most probable cluster configurations with the oxygen atom (P_0, P_1, P_2, P_3) or oxygen vacancy (P_0) at their centres are shown in Figure 4 (lower row). Due to the identity of ordering in titanium and oxygen sublattices the probabilities of such configurations of cluster can be written by replacing the superscripts Ti by O and O by Ti. For example, the probability of cluster with oxygen vacancy in the centre can be written as follows:

$$P_0^{\mathrm{O}} = \frac{1}{12}[2(1 - n_1^{\mathrm{O}})(n_2^{\mathrm{Ti}})^6 + 2(1 - n_2^{\mathrm{O}})(n_1^{\mathrm{Ti}})^2(n_2^{\mathrm{Ti}})^4 + 8(1 - n_2^{\mathrm{O}})(n_1^{\mathrm{Ti}})(n_2^{\mathrm{Ti}})^5].$$

When determining the cluster probabilities for the disordered titanium monoxide, the probabilities from P_0 to P_9 should be calculated using the atomic distribution functions with a zero long-range order parameter η. The corresponding values are x for titanium and z for oxygen. The cluster probabilities calculated for the ordered and disordered $TiO_{0.96}$ ($Ti_{0.888}O_{0.854}$) monoxides are given in Table 1. The cluster probabilities for the ordered and disordered stoichiometric titanium monoxide $TiO_{1.00}$ ($Ti_{0.833}O_{0.833}$) are shown for comparison. Table 1 indicates that the cluster with one vacancy in the coordination shell has the highest probability P_1 for both the titanium and oxygen sublattices and different compositions. Calculations show that the maximal number of vacancies in the first coordination sphere of the ordered monoxide is two. Note that these two vacancies can occupy only the opposite sites of the coordination octahedron, while the probability P_3 to find clusters with two neighbouring vacancies is zero. Table 1 indicates that the most probable clusters for disordered titanium monoxides are P_0 and P_1.

The above scheme can be used to calculate cluster probabilities in ordered vanadium and niobium monoxides.

Based on the analysis of the defect structure of titanium, vanadium and niobium monoxides, we proposed a thermodynamic model suitable for calculating the phase diagrams of compounds with structural vacancies on the few sublattices. The main feature of this model is a multi-cluster approach, which can extend the well-known cluster variation method. For titanium and niobium monoxides, the two-cluster approach and the three-cluster approach for vanadium monoxide were suggested.

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