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Mendeleev Commun., 2019, **29**, 707–709

Mendeleev Communications

Vacancy ordered structures in a nonstoichiometric niobium carbide $NbC_{0.83}$

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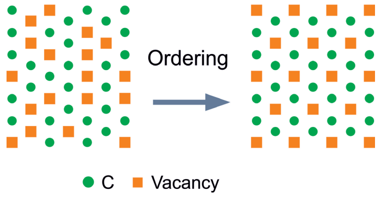
DOI: 10.1016/j.mencom.2019.11.037

Using an evolutionary algorithm for predicting crystal structures, we found the possible ordered phases of a nonstoichiometric niobium carbide $NbC_{0.83}$, a compound with 1/6 vacant sites in the carbon sublattice.



Many binary transition metal compounds with oxygen, nitrogen, carbon and sulfur (FeO, FeS, TiO, VO, NbC, VC, TiN, *etc.*) contain structural vacancies □, *i.e.*, crystal lattice sites that are not occupied by atoms. The concentration of defects of this type can exceed 30 at% regardless of temperature.[1] The effects of nonstoichiometry and short-range and long-range order, resulting in a wide variety of phases and structural modifications,[1–4] are associated with structural vacancies. In addition to ideally ordered states described by superstructures,[2,3] the models of partially ordered modifications that take into account the short-range order[5] and hybrid models that are superpositions of various ordered vacancy sublattices were proposed.[6,7]

The number of possible structural modifications that may occur during atomic-vacancy ordering is not precisely known. The use of standard diffraction methods of analysis and the study of the local environment of defects, in many cases, do not allow one to correctly determine the structure of an ordered phase.[8,9] The stability and the causes of the formation of defect structures remain open questions. For a long time, it was considered that phases with anomalous defects are thermodynamically equilibrium at zero pressure and temperature, and vacancies stabilize the basic crystal structure.[10–13] On the other hand, recent experimental[14] and theoretical[14,15] results for titanium monoxide with 16.7% vacancies indicate the metastability of phases containing structural vacancies.

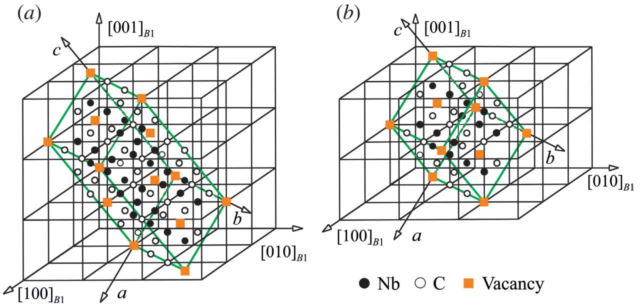


Figure 1 Unit cells of the superstructures with space groups (*a*) *C*2 and (*b*) *C*2/*m* in the basic crystal structure *B*1. The boundaries of the unit cells of *B*1 structure, directions, and crystallographic superstructure axes are shown.

Modern methods for crystal structure prediction can be useful in finding stable structures and determining the sequence of phase transitions during ordering. The evolutionary algorithm for the prediction of crystal structures in the USPEX code[16–18] has a high predictive value. We used this technique to study the nonstoichiometric niobium carbide $NbC_{0.83}$ containing 1/6 vacant sites in the carbon sublattice.

Niobium carbide has a basic *B*1 type crystal structure with vacancies only in the carbon sublattice. The composition of superstructures formed upon atomic-vacancy ordering is close to $NbC_{0.83}$. According to experimental and theoretical data,[1,2] only Nb_6C_5-type superstructures can be formed in the $NbC_{0.83}$ carbide. However, the symmetry and distribution of C atoms and carbon vacancies over the crystal lattice sites for such superstructures may be different. The electron microdiffraction and neutron diffraction data of the ordered phases were interpreted within three ordering models: superstructures with space groups of symmetry $P3_1$,[19] *C*2 [Figure 1(*a*)] and *C*2/*m* [Figure 1(*b*)].[9,19–22] A symmetric group-theoretical analysis of the possible ordering in nonstoichiometric $NbC_{0.83}$ niobium carbide with the determination of disorder–order and order–order transition channels[2,9] showed that the following sequence of transformations most likely occurred with decreasing temperature: cubic (space group $Fm\bar{3}m$) disordered phase $NbC_{0.83}$ – monoclinic (space group *C*2/*m*) ordered phase Nb_6C_5 – monoclinic (space group *C*2) ordered phase Nb_6C_5. The disorder–order transition channels associated with the formation of the Nb_6C_5 type superstructure involves nonequivalent superstructure vectors of three stars $\{k_9\}$, $\{k_4\}$, and $\{k_3\}$.[2] The atomic displacements observed in a superstructure with one or another space group do not affect the possible sequence of phase transformations, and they are not taken into account in symmetry analysis. However, in this study, a search for possible ordered structures and the calculations of the ground state energies of model structures were carried out taking into account atomic displacements (see the CIF-file with crystallographic information in Online Supplementary Materials).

The aim of this theoretical study was, first, to search for an ideally ordered superstructure in equilibrium at zero pressure and temperature; second, to determine the number of possible polymorphic modifications that can be formed in atomic-vacancy experiments; and, third, to check the availability of alternative stable defect-free structures by analogy with a new polymorphous modification of titanium monoxide.[14,15]

The search for structures using an evolutionary algorithm was carried out for primitive cells containing one and two formula units Nb_6C_5. The ground state energies of model structures were calculated using the VASP code[23] with PAW potentials[24] and an exchange-correlation approximation of the PBE version.[25]

For primitive cells with one formula unit, a monoclinic superstructure with space group *C*2/*m*[22] and two new models, an alternative arrangement of vacancies within the symmetry *C*2/*m* [Figure 2(*b*)] and an orthorhombic superstructure with space group *Cmmm,* were found. For primitive cells with two formula units, a triclinic superstructure with space group $P\bar{1}$ [Figure 2(*a*)] and one more superstructure with space group *C*2/*m* [Figure 2(*a*)] were revealed. The superstructure described earlier[1] with space group *C*2 was not found.

The predicted energetically favorable crystal structures of niobium carbide[16–18] were derived from the *B*1 structure, and they contained 1/6 vacancies in the carbon sublattice. A stable defect-free phase was not found. For the predicted models of atomic-vacancy ordering, the calculations of a ground state energy with an enhanced accuracy of relaxation of atomic positions and unit cell parameters were carried out. The algorithm[16–18] is effective only with sufficiently small numbers of atoms in a primitive cell (in this case, it is one formula unit Nb_6C_5); therefore, the known superstructures with space groups *C*2 (two formula units) and $P3_1$ (three formula units) were calculated additionally. According to the calculations, the ordered monoclinic phases with space groups *C*2 and *C*2/*m* (see Figure 1) have the lowest energy. In this case, the arrangement of vacancies in the superstructure with space groups *C*2 gives a slightly lower energy compared to the superstructure with space group *C*2/*m*. Other ordering models are significantly less favorable. In Figure 2, they are arranged in an order of increasing their energy. Ordering vacancies with the trigonal superstructure formation with space group $P3_1$[19–21] are not energetically beneficial (not shown in Figure 2). The appearance of this superstructure in atomic-vacancy ordering experiments is doubtful.

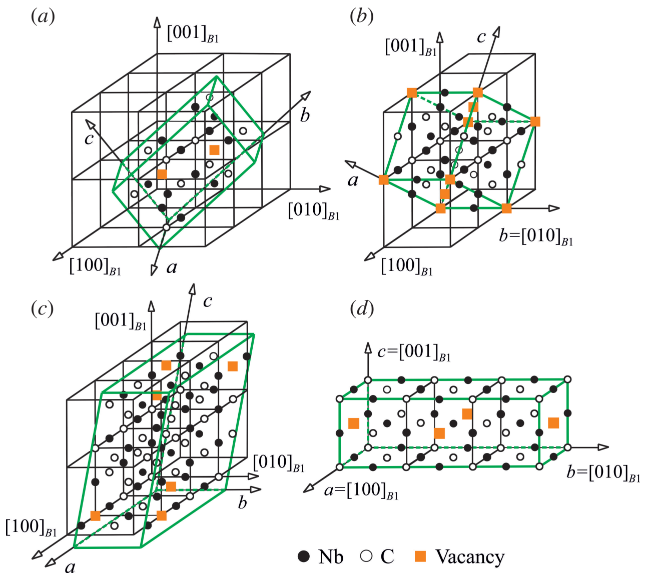


Figure 2 Alternative models of vacancy ordering in the carbon sublattice of niobium carbide $NbC_{0.83}$: (*a*) triclinic superstructure with space group $P\bar{1}$, (*b*) monoclinic superstructure (space group *C*2/*m*), (*c*) another monoclinic model with the same space group, and (*d*) the orthorhombic superstructure (space group *Cmmm*). The boundaries of the unit cells of the basic structure, its directions, and crystallographic superstructure axes are shown.

Gusev[9] experimentally examined the superstructure of Nb_6C_5 in detail and found that a superstructure with space group *C*2/*m* could be erroneously interpreted as a superstructure with space group $P3_1$ due to the similarity of their diffraction spectra and microdiffraction patterns. According to Wu *et al.*,[26] the trigonal superstructure has a lower energy than that of the monoclinic one. Our calculations suggest the opposite: the model with space group $P3_1$ is unfavorable compared to the *C*2/*m* structure.

Among the ordering models considered in this paper, only the monoclinic superstructure with space group *C*2/*m* [see Figure 1(*a*)] was apparently observed experimentally.[22] We expect that the phase with space group *C*2 [see Figure 1(*b*)] will be found in the subsequent experiments. Note that the superstructure with higher ground state energy (see Figure 2) could describe the structure of high-temperature ordered phases. For example, for titanium monoxide with 1/6 vacant sites in the metal and nonmetal sublattices, the low-temperature ordered phase with space group *C*2/*m* (*A*2/*m*)[27,28] and the high-temperature phase with space group *Pm*-3*m*[29] or *P*1*m*1[7] were observed experimentally. The phase diagram of the Nb–C system calculated taking into account the ordering of niobium carbide by an order parameter functional (OPF) method[1,30] in the region of $NbC_{0.83}$ carbide at temperatures below 1594 K contains only one ordered Nb_6C_5 phase, but its symmetry cannot be determined by the OPF method. A simulation performed using an evolutionary algorithm and the calculation of the ground state energy made it possible to estimate the sequence in which the Nb_6C_5 model superstructures should appear when the disordered $NbC_{0.83}$ carbide is cooled.

This work was supported by the Russian Science Foundation (grant no. 19-73-20012) and performed at the Institute of Solid State Chemistry of the Ural Branch of the Russian Academy of Sciences. We are grateful to Professor A. I. Gusev for his valuable comments and discussions.

Online Supplementary Materials

Supplementary data (crystallographic information in CIF format) associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.11.037.

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Received: 13th May 2019; Com. 19/5922