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Vacancy distribution in nonstoichiometric vanadium monoxide

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ABSTRACT

Structural vacancy distribution in the crystal lattice of the tetragonal $V_{52}O_{64}$ superstructure which is formed on the basis of disordered superstoichiometric cubic vanadium monoxide $VO_y \equiv V_xO_z$ is experimentally determined and the presence of significant local atomic displacements and large local microstrains in a crystal lattice of real ordered phase is established. It is shown that the relaxation of local microstrains takes place owing to the basic disordered cubic phase grain refinement and a formation of ordered phase domains. The ordered phase domains grow in the direction from the boundaries to the centre of grains of the disordered basic cubic phase. Isothermal evolution at 970 K of the average domain size $\langle D \rangle$ in ordered $VO_{1.29}$ vanadium monoxide is established. It is shown that the short-range order presents in a metal sublattice of disordered cubic VO_y vanadium monoxide. The character of the short-range order is such that vanadium atoms occupying tetrahedral positions are in the environment of four vacant sites of the vanadium sublattice. This means that the disordered VO_y vanadium monoxide, especially superstoichiometric $VO_{y>1.0}$ monoxide, has a cubic (space group $Fm\bar{3}m$) $D0_3$-type structure differing from the $B1$-type structure typical for most of the strongly nonstoichiometric cubic compounds carbides, nitrides and oxides.

1. Introduction

In a disordered state, the monocarbides and mononitrides MX_y have the cubic structure $B1$ and may contain up to 50% of structural vacancies in the nonmetal sublattice [1–5]. Cubic MO_y ($M_x\blacksquare_{1-x}O_z\square_{1-z} \equiv M_xO_z$; M = Ti, V; $y = z/x$, $\blacksquare$ and $\square$ are structural vacancies in metal and oxygen sublattices, respectively) titanium and vanadium monoxides contain structural vacancies in two sublattices simultaneously [1,2]. At a temperature below the disorder-order phase transformation temperature T_{trans}, the basic cubic structure is unstable and disorder–order phase transformations take place in nonstoichiometric compounds. Ordering leads to the formation of ordered phases with complicated superstructures [1–3,5]. The disorder–order and order–disorder transformations in strongly nonstoichiometric compounds are phase transitions of the first kind [1,2,4,6] with a stepwise change of volume at T_{trans} [1,2,7–9]. As a result of cooling of nonstoichiometric compounds from temperature T, which is higher than T_{trans}, to room temperature or as a result of low-temperature annealing at $T < T_{trans}$, the nonstoichiometric compounds tend to the ordered state. Because of the difference in the lattice constants of the disordered and ordered phases, strains arise in a specimen. With time these strains lead to cracking of crystallites at the interfaces between the disordered and ordered phases.

Cubic (space group $Fm\bar{3}m$) vanadium monoxide VO_y ($V_x\blacksquare_{1-x}O_z\square_{1-z} \equiv V_xO_z$ where $y = z/x$, symbols $\blacksquare$ and $\square$ denote structural vacancies in vanadium and oxygen sublattices, respectively) belongs to the group of strongly nonstoichiometric compounds [1,2]. In the most of strongly nonstoichiometric cubic compounds MX_y (X = C, N, O), structural vacancies are present only in the nonmetal sublattice. On the contrary, cubic vanadium monoxide VO_y contains up to 10–15 at. % of structural vacancies both in oxygen and in vanadium sublattices. At a temperature of 1600 K disordered vanadium monoxide VO_y has a wide homogeneity interval $VO_{0.90}$–$V_{1.30}$ [10]. In a disordered VO_y monoxide vanadium vacancies $\blacksquare$ and V atoms form a substitutional solid solution in the metal sublattice and oxygen vacancies $\square$ and O atoms form a substitutional solid solution in the nonmetal sublattice. High concentration of vacancies in vanadium monoxide is a premise of atomic-vacancy ordering of this nonstoichiometric compound.

The only ordered phase is observed in cubic vanadium monoxide VO_y. This phase possesses tetragonal symmetry [11–14]. According to the data [15], it has a very narrow homogeneity interval and exists at a temperature of 970 K in the region $VO_{1.22}$–$VO_{1.24}$, i.e. is formed in superstoichiometric monoxide V_xO, containing vacancies only in vanadium sublattice. At larger or smaller oxygen content, the samples are two-phase and along with $V_{52}O_{64}$ phase contain either oxide V_2O_3 or disordered monoxide VO_y, respec-

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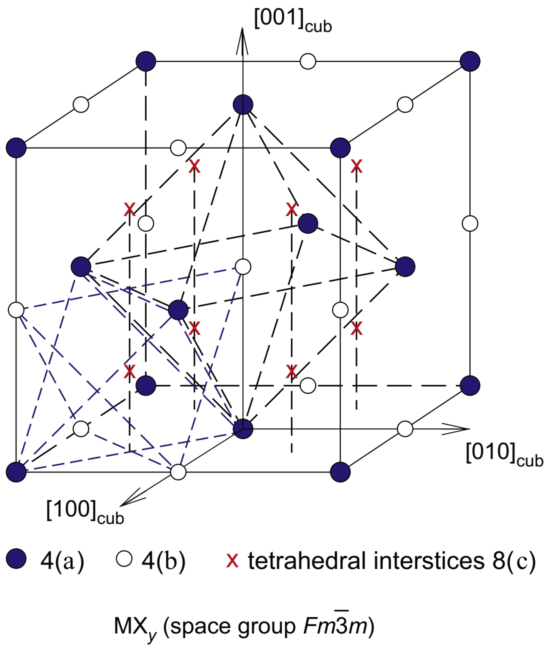

Fig. 1. Unit cell of a disordered nonstoichiometric cubic (space group $Fm\bar{3}m$) compound MX_y (M_xX_z, $y=z/x$): (●) positions 4(*a*), i.e. metal sublattice sites statistically occupied by M atoms; (○) positions 4(*b*), i.e. nonmetal sublattice sites statistically occupied by X atoms; (X) positions 8(*c*) are the centres of tetrahedral interstices. Octahedral interstices formed by six sites of metal sublattice are occupied by nonmetal atoms X. No atoms of any species occupy the tetrahedral interstices formed by four sites of metal sublattice (or four sites of nonmetal sublattice) in a disordered compound MX_y with the *B*1 structure.

tively. The feature of the structure of $V_{52}O_{64}$ is that 4 out of 52 vanadium atoms occupy tetrahedral interstitial sites (interstices) of basic cubic lattice with space group $Fm\bar{3}m$, i.e. 8(*c*) positions, which are unusual for the *B*1-type crystal structure. The nearest environment of these $V^{(t)}$ vanadium atoms is formed by 4 oxygen atoms and four vacant sites of vanadium sublattice, i.e. 4 vacancies ■. In strongly nonstoichiometric compounds MX_y with the *B*1 structure, the M metal atoms occupy 4(*a*) positions with the coordinates (0 0 0), and nonmetal atoms X occupy statistically 4(*b*) positions with the coordinates (1/2 1/2 1/2) [1]. Nonmetal atoms X are located in the octahedral interstices of the face-centred cubic (fcc) metal sublattice. Tetrahedral interstices, i.e. crystallographic positions 8(*c*) with the coordinates (1/4 1/4 1/4), in disordered nonstoichiometric compounds with the *B*1 structure are never occupied by any atoms (Fig. 1). Moreover, in all known superstructures of nonstoichiometric compounds, atoms and vacancies are redistributed only over the 4(*b*) or 4(*a*) positions of the basic disordered lattice, or over the both positions as in superstructure Ti_5O_5 [1,16–18]. For this reason, the question arises whether the disordered V_xO monoxide with vacancies only in the vanadium sublattice has the *B*1 structure or this monoxide has another cubic structure, but with the same space group $Fm\bar{3}m$.

The aims of the present investigation are to determine the atomic displacements in the lattice of the tetragonal $V_{52}O_{64}$ superstructure and to propose some ideas concerning the short-range order in the superstructure studied and in the disordered vanadium monoxide, especially in superstoichiometric monoxide V_xO containing vacancies only in the metal sublattice.

2. Experimental details

The $VO_{1.29}$ ($V_{0.775}O$) and $VO_{1.30}$ ($V_{0.77}O$) samples with vacancies only in the vanadium sublattice with the composition close to the upper boundary of the homogeneity interval of cubic vanadium monoxide VO_y are investigated. Synthesis and certification of samples are described in detail earlier [10,14]. To achieve the equilibrium ordered state, the synthesized $VO_{1.29}$ and $VO_{1.30}$ samples are annealed for 1000 h at a temperature of 970 K with subsequent quenching to 300 K. Annealing is performed in quartz ampoules, which are evacuated to a residual pressure of 10^{-5} Pa.

The relative oxygen content is determined by the thermogravimetric analysis in terms of the increase in the weight after the complete oxidation of the samples to the highest oxide V_2O_5. Oxidation is performed in air for 100 h at a temperature of about 820 K. The accuracy of the determination of the oxygen content in the VO_y sample is 0.2 wt.%, which corresponds to an error of 0.01 in the determination of the oxygen index *y*, i.e. $VO_{y\pm0.01}$.

All X-ray diffraction measurements are performed on a DRON-UM1 diffractometer by the Bragg-Brentano method in the $CuK\alpha_{1,2}$ radiation at angles 2θ from 10 to 90 with a step of $\Delta 2\theta = 0.03$ and a scanning time of 10 s at a point. The final refinement of the structure is performed with the use of the X'Pert Plus program [19]. The diffraction reflection profile is modelled as a pseudo-Voigt function. The background is fitted by the Chebyshev fifth-order polynomial.

The average size $\langle D\rangle$ of the ordered phase domains and the value of the microstrains ε in ordered vanadium monoxide are determined by an XRD method from broadening of diffraction reflections [8,9,20]. The diffraction reflection broadening $\beta(2\theta)$ is defined as $\beta(2\theta)=\sqrt{(\mathrm{FWHM}_{\mathrm{exp}})^2-(\mathrm{FWHM}_{\mathrm{R}})^2}$ where $\mathrm{FWHM}_{\mathrm{exp}}$ is the full width at half-maximum of an experimental diffraction reflection and $\mathrm{FWHM}_{\mathrm{R}}$ is the instrumental angular resolution function of the diffractometer. The angular resolution function $\mathrm{FWHM}_R(2\theta)=(u\tan^2\theta+v\tan\theta+w)^{1/2}$ of the DRON-UM1 X-ray diffractometer is determined in a special diffraction experiment with the cubic lanthanum hexaboride LaB_6 (NIST Standard Reference Powder 660a) having the lattice constant $a = 0.41569162$ nm. This angular resolution function $\mathrm{FWHM}_{\mathrm{R}}(2\theta)$ has the following parameters $u = 0.0041$, $v = -0.0021$ and $w = 0.0093$.

Microstructure and phase composition of the VO_y samples are examined by optical microscopy in a Leica DM2500M polarizing microscope. For investigation of a microstructure sintered samples are polished to mirror finish using a Buehler integrated metallographic system. The microstructure of the VO_y samples is also examined by scanning electron microscopy (SEM) in JEOL-JSM LA 6390 electron microscope equipped with EDX analyzer JED-2300.

3. Results and discussion

The XRD data showed that the as-synthesized $VO_{1.29}$ and $VO_{1.30}$ samples contain only cubic (space group $Fm\bar{3}m$) vanadium monoxide VO_y. A cubic lattice constant a_{cub} of these samples are equal to 0.41418 and 0.41388 nm, respectively. The XRD patterns of $VO_{1.29}$

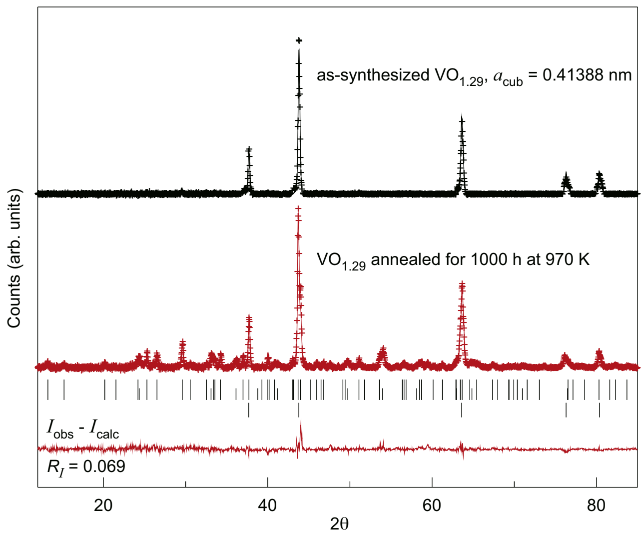

Fig. 2. X-ray diffraction patterns of the as-synthesized $VO_{1.29}$ sample and the same sample after annealing for 1000 h at 970 K: (crosses) experimental data; (solid curves) calculated pattern. As-synthesized $VO_{1.29}$ sample contains only disordered cubic (space group $Fm\bar{3}m$) vanadium monoxide VO_y. The sample upon prolonged annealing at 970 K contains about 85 wt.% of ordered tetragonal (space group $I4_1/amd$) phase of the $V_{52}O_{64}$ type and about 15 wt.% of rhombohedral (space group $R\bar{3}c$) V_2O_3 oxide. Real composition of the ordered phase is $V_{51.6}O_{64}$. Long, medium and short bars show the positions of diffraction reflections of ordered tetragonal $V_{51.6}O_{64}$ phase, disordered cubic $VO_{1.29}$ vanadium monoxide, and rhombohedral V_2O_3 oxide, respectively. The bottom curve shows the difference ($I_{obs} - I_{calc}$) between the experimental and calculated XRD patterns of the annealed sample with ordered $V_{51.6}O_{64}$ phase.

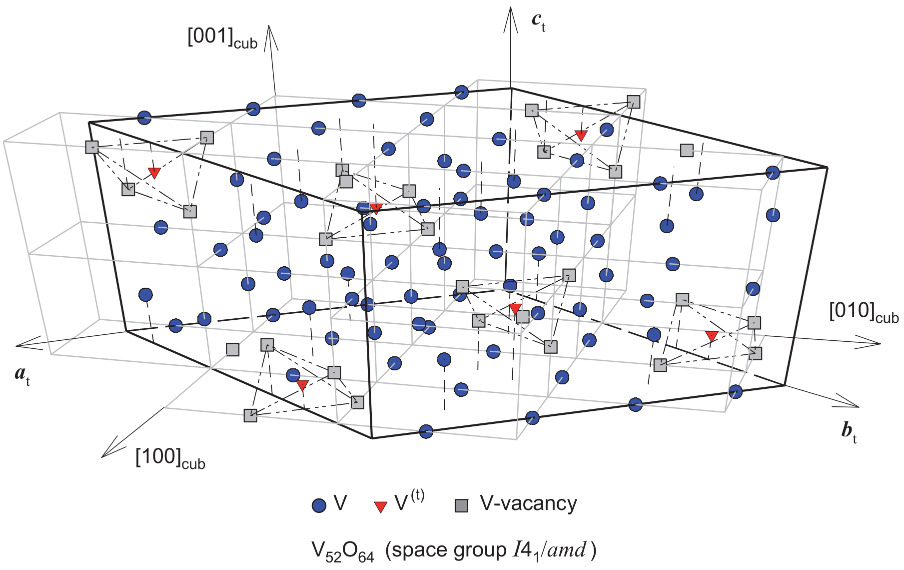

Fig. 3. Position of a unit cell of the perfect tetragonal (space group no. 141, $I4_1/amd$ (D_{4h}^{19})) ordered $V_{52}O_{64}$ (or $V_{52}■_{12}O_{64}$) phase in a basic cubic (space group $Fm\bar{3}m$) lattice: (●) vanadium atoms in octahedral positions, (▼) vanadium atoms in tetrahedral interstices of the basic disordered lattice, and (■) vacant sites of the metal sublattice. Oxygen atoms are not depicted. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

and $VO_{1.30}$ samples annealed for 1000 h at 970 K contain diffraction reflections of ordered tetragonal phase $V_{52}O_{64}$ and rhombohedral V_2O_3 oxide. The XRD patterns of as-synthesized $VO_{1.29}$ and the same sample after annealing for 1000 h at 970 K are shown in Fig. 2 as an example.

Annealed $VO_{1.30}$ ($V_{0.77}O$) sample contains about 79 wt.% of a tetragonal (space group $I4_1/amd$ (D_{4h}^{19})) ordered phase of the $V_{52}O_{64}$ type and about 21 wt % of rhombohedral (space group $R\bar{3}c(D_{3d}^{19})$) V_2O_3 oxide. Annealed $VO_{1.29}$ sample contains about 85 wt.% of a tetragonal $V_{52}O_{64}$ ordered phase and about 15 wt.% of rhombohedral V_2O_3 oxide. The presence of the rhombohedral V_2O_3 phase, together with the ordered phase of the $V_{52}O_{64}$ type, indicates that under equilibrium conditions at $T = 970$ K, the $VO_{1.29}$ and $VO_{1.30}$ oxides occur in the two-phase region of ($V_{52}O_{64} + V_2O_3$) near the phase boundary between this region and the region of existence of an ordered $V_{52}O_{64}$ phase.

Table 1
Crystal data, experimental conditions and characteristics of the refinement for the $V_{51.6}O_{64}$ superstructure.

Chemical formula	$V_{51.6}O_{64}$
Formula weight	3652.54
Crystal system	tetragonal
Space group	$I4_1/amd$ (No. 141)
a (nm)	1.1746(1)
b (nm)	1.1746(1)
c (nm)	0.82527(8)
Z	1
V (nm^3)	1.138592
D_{calc} (g cm^{-3})	5.33
Diffractometer	DRON-UM1
Radiation type	X-ray Cu$K\alpha_1$
Wavelength (nm)	0.154056
Temperature (K)	300
2θ Range (°)	10–90
Step-scan (°)	0.03
Counting time (s)	10
Preferred orientation	(1 0 0)
Number of reflections measured	63
R_I (R_{Bragg}) (%)	6.89
R_p (%)	15.26
ωR_p (%)	22.25
R_{exp} (%)	6.70

3.1. Crystal structure of ordered $V_{52}O_{64}$ phase and size of ordered phase domains

Observed I_{obs}, calculated I_{calc} and difference ($I_{obs}–I_{calc}$) values corresponding to the refinement of the XRD pattern for as-synthesized and annealed $VO_{1.29}$ samples are shown in Fig. 2. The refinement of a crystal structure of annealed $VO_{1.29}$ ($V_{0.775}O$) vanadium monoxide using the X'Pert Plus software package [19] provides the following results: the real ordered phase has the composition $V_{51.6}O_{64}$, unit cell parameters are equal to $a_t = b_t = 1.1746(1)$ nm and $c_t = 0.82527(8)$ nm and are in good agreement with the data [11,12]. Details of the structure refinement of the $V_{51.6}O_{64}$ phase are given in Table 1.

The ordered $V_{51.6}O_{64}$ phase corresponds by the composition to the disordered $VO_{1.24}$ vanadium monoxide with a basic cubic lattice constant of $a_{cub} \cong 0.4144$ nm. According to the data [21–23], lattice constant of a disordered cubic $VO_{1.24}$ vanadium monoxide is equal to about 0.413 nm. Thus, the basic cubic lattice constant a_{cub} for $VO_{1.24}$ monoxide increases spasmodically from ~0.413 to 0.4144 nm due to ordering. The stepwise increase in the basic lattice constant specifies that the $VO_y–V_{52}O_{64}$ disorder-order transformation occurs by the mechanism of the first-order phase transition. Taking into account the basic lattice constant a_{cub} of a disordered cubic $VO_{1.24}$ monoxide and the geometry of the perfect tetragonal phase $V_{52}O_{64}$, the translation vectors of the unit cell of the $V_{52}O_{64}$ phase are $a_t = [2\ {-2}\ 0]_{cub}$, $b_t = [2\ 2\ 0]_{cub}$, and $c_t = [0\ 0\ 2]_{cub}$.

In the perfect tetragonal structure $V_{52}O_{64}$, vanadium atoms occupy the 16(h) position with the coordinates (0 1/8 1/4), two 16(f) positions with the coordinates (1/8 0 0) and (5/8 0 0), and the 4(a) position with the coordinates (0 3/4 1/8). Oxygen atoms O are in two 16(h) positions with the coordinates (0 1/8 1/2) and (0 7/8 0) and in the 32(i) position with the coordinates (1/8 0 1/4). The 16(h) position with the coordinates (0 1/8 1/4) in the metallic sublattice is vacant. Fig. 3 shows the position of a unit cell of the perfect tetragonal $V_{52}O_{64}$ superstructure in the basic cubic lattice of vanadium monoxide. It is seen that this superstructure can be described as an ordered arrangement of defect clusters $V^{(t)}■_4$ consisting of one $V^{(t)}$ vanadium interstitial at a tetrahedral position, surrounded by four metal vacancies ■.

The refinement of the crystal structure shows that all of the 16(h) sites with the coordinates (0 5/8 1/4) in the tetragonal $V_{52}O_{64}$

Table 2
Perfect and refined (taking into account the displacements of V and O atoms) structures of the tetragonal (space group no. 141, $I4_1/amd$ (D_{4h}^{19})) ordered $V_{51.6}O_{64}$ phase: $a_t = b_t = 1.1746(1)$, $c_t = 0.82527(8)$ nm.

Atom	Position and multiplicity	Atomic coordinates in the perfect superstructure			Refined structure				
		x/a_t	y/b_t	z/c_t	Atomic coordinates			$B \times 10^{-4}$ (pm^2)	Occupancy
					x/a_t	y/b_t	z/c_t		
V1 (vacancy ■)	16(*h*)	0	0.625	0.25	0	0.625	0.25	–	0
V2	16(*h*)	0	0.125	0.25	0	0.1238	0.25	0.65(7)	1
V3	16(*f*)	0.125	0	0	0.125	0	0	0.93(2)	1
V4	16(*f*)	0.625	0	0	0.6225	0	0	0.65(7)	0.975
V5 ($V^{(t)}$)	[a]4(*a*)	0	0.75	0.125	0	0.75	0.125	1.22(1)	1
O1	16(*h*)	0	0.125	0.5	0	0.1289	0.5	1.09(5)	1
O2	16(*h*)	0	0.875	0	0	0.8818	0	1.34(6)	1
O3	32(*i*)	0.125	0	0.25	0.1298	0.0033	0.25	1.02(4)	1

[a] The tetrahedral interstice is the 8(*c*) position of the basic disordered cubic (space group $Fm\bar{3}m$) structure.

superstructure observed in the annealed $VO_{1.29}$ sample are vacant. Moreover, some 16(*f*) sites of the metallic sublattice with the coordinates (5/8 0 0) are also vacant: the occupancy of these positions in the tetragonal phase of the annealed $VO_{1.29}$ sample is 0.975 (Table 2). These sites in the perfect $V_{52}O_{64}$ superstructure are completely occupied by vanadium atoms. Detailed description of $V_{52}O_{64}$ superstructure is given earlier in [14,15].

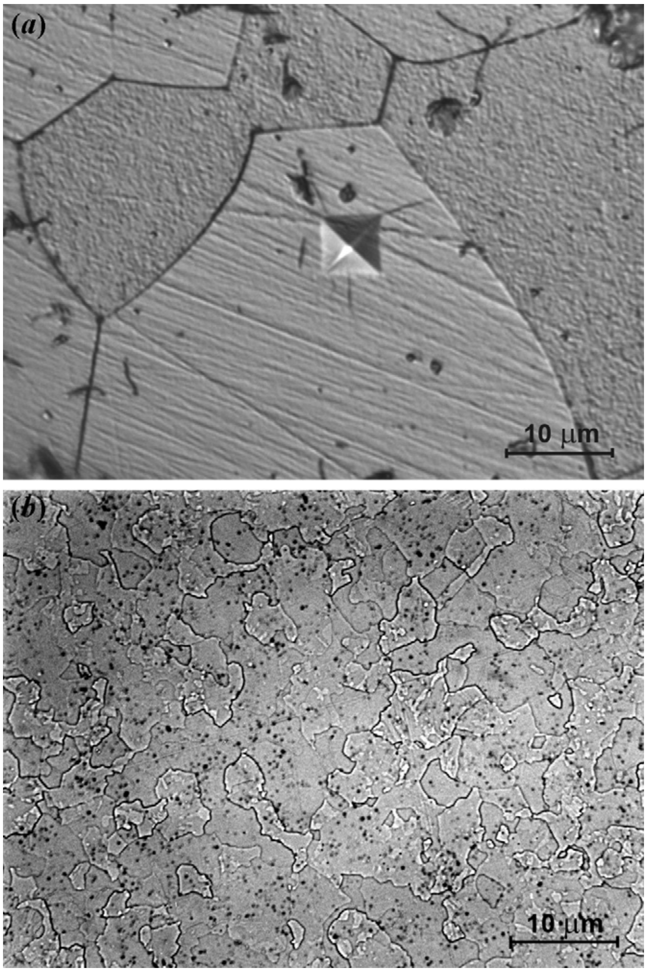

Fig. 4. Microstructure of (*a*) as-synthesized disordered and (*b*) annealed ordered nonstoichiometric $VO_{1.29}$ vanadium monoxide. In disordered cubic $VO_{1.29}$ monoxide coarse grains have sharp and straight boundaries. After annealing of $VO_{1.29}$ monoxide for 1000 h at 970 K grain boundaries of disordered basic cubic phase became broken as a result of the formation and growth of domains of ordered $V_{52}O_{64}$ phase.

Fig. 4a shows optical micrograph of the surface of as-synthesized cubic $VO_{1.29}$ vanadium monoxide. The sharp and straight boundaries of coarse grains from 10 to 50 μm in size are clearly visible and the grain shape corresponds to a cubic structure of disordered vanadium monoxide. The ordered phase domain distribution varies with annealing time. After short annealing small separate luminous points appear along the grain boundaries of a cubic matrix structure. According to XRD data, such separate inclusions consist of the ordered tetragonal $V_{52}O_{64}$ phase. After prolonged annealing partial cubic phase grain refinement is observed and grain boundaries of disordered basic cubic phase have become broken as a result of ordering (Fig. 4b). It means that the ordered phase domains grow in the direction from the boundaries to the centre of grains of the disordered basic cubic phase.

A comparison of the XRD patterns of as-synthesized and annealed $VO_{1.29}$ sample (Fig. 2) shows that prolonged annealing of a disordered vanadium monoxide leads not only to the appearance of a set of superstructural diffraction reflections but also to the broadening of the diffraction reflections observed. The diffraction reflection broadening may be due to the small size *D* of particles (grains, crystallites), the presence of microstrains and inhomogeneity, i.e. non-uniform composition of the substance over the volume of the sample [8,9]. The reflection broadening caused by inhomogeneity can be observed for nonstoichiometric compounds and substitutional solid solutions [8,24].

The quantitative analysis of diffraction reflection broadening of ordered $VO_{1.29}$ vanadium monoxide shows that the broadening is caused by both the small size of the ordered phase domains (more correct to say about a size of coherent scattering regions or domains) and the microstrains. Contribution to the reflection broadening through possible inhomogeneity of vanadium monoxide studied is negligibly small.

The size and strain broadening are separated by the Williamson-Hall method [25–27] using the dependence of the reduced broadening $\beta^*(2\theta) = [\beta(2\theta)\cos\theta]/\lambda$ of the reflections ($h\,k\,l$) on the scattering vector $s = (2\sin\theta)/\lambda$. In this case, the average size $\langle D \rangle$ of the coherent scattering domains is calculated by extrapolating the dependence of the reduced broadening $\beta^*(2\theta)$ on the scattering vector s to $s = 0$, i.e. $\langle D \rangle = 1/\beta^*(2\theta) = \lambda/[\cos\theta\,\beta(2\theta)]$ at $\theta = 0$ because $\beta(2\theta)|_{\theta=0} \equiv \beta_d(2\theta)$. The value of the microstrains ε characterizes the relative change of the interplanar spacing. The value of the microstrains in relative units is found from the slope φ of the straight line approximating the s dependence of β^* by the formula $\varepsilon = \{[\beta^*(2\theta)]/2s\} \equiv [(\mathrm{tg}\varphi)/2]$.

The dependence of reduced broadening $\beta^*(2\theta)$ of diffraction reflections of ordered $VO_{1.29}$ vanadium monoxide on the scattering vector s is shown in Fig. 5. According to the estimates performed, the average size $\langle D \rangle$ of the coherent scattering domains in $VO_{1.29}$ monoxide annealed for 1000 h at a temperature of 970 K is equal

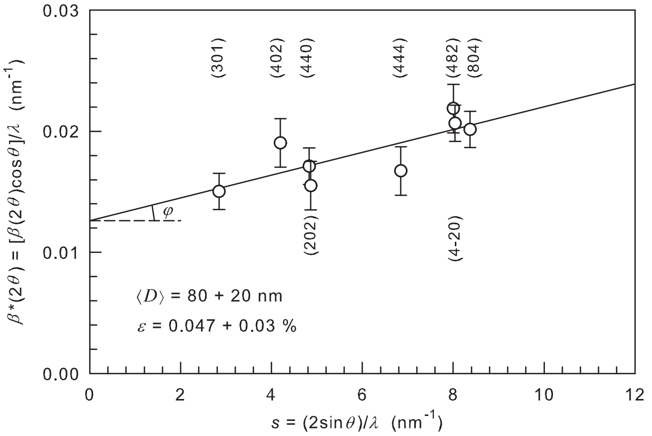

Fig. 5. Dependence of the reduced broadening $\beta^*(2\theta)$ of the XRD reflections on the scattering vector s for annealed $VO_{1.29}$ vanadium monoxide and estimates of the average domain size $\langle D \rangle$ and microstrains ε in ordered $VO_{1.29}$ monoxide.

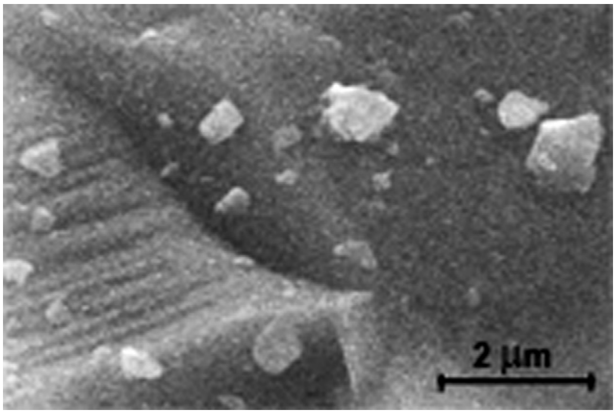

Fig. 7. SEM image of the fracture surface of annealed $VO_{1.29}$ sample: the parallel lines located on the left on a distance of 100–150 nm from each other correspond to the cleavage surface (interfaces) of ordered phase domains with the same orientation of c-axis of tetragonal unit cell of ordered $V_{52}O_{64}$ phase.

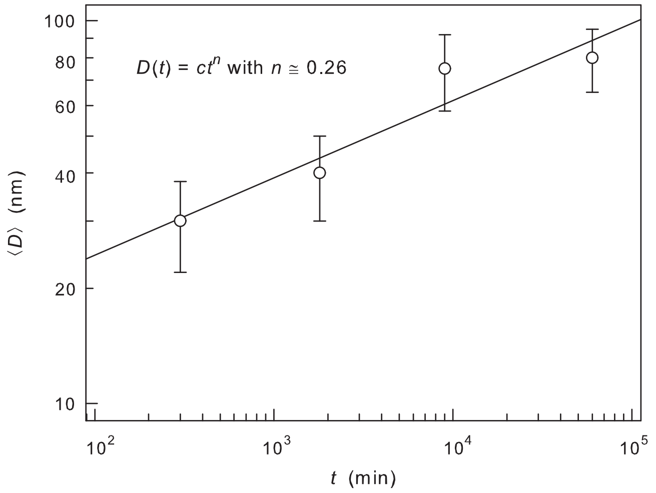

Fig. 6. Isothermal evolution at 970 K of the average domain size $\langle D \rangle$ in ordered $VO_{1.29}$ vanadium monoxide (time t and domain size $\langle D \rangle$ are shown on a logarithmic scale). The continious line represents the fit by expression (1).

to 80 ± 20 nm and the value of the microstrains ε is $0.047 \pm 0.005\%$. According to [12], the average size of ordered domains in $VO_{1.25}$ monoxide annealed for 30 h and 150 h at 970 K is equal to about 40 and 75 nm, respectively.

Large size D of domains of ordered $V_{52}O_{64}$ phase observed after extended annealing is caused by a growth of separate domains and a coarsening process. With taking into account results of [12] and present study the time dependence of the average ordered domain size, $D(t)$, in annealed vanadium monoxide has the form:

$$D(t) = ct^n \tag{1}$$

with $n \approx 0.26$ for $D \geq 20$ nm (Fig. 6).

SEM images of fracture surface of annealed $VO_{1.29}$ sample is shown in Fig. 7. The parallel lines located on distance of 100–150 nm from each other are visible on the left side of the fracture surface. Apparently, these lines correspond to the cleavage surface (interfaces) of ordered phase domains having the same orientation of c-axis of tetragonal unit cell of ordered $V_{52}O_{64}$ phase. The distance observed is equal to the linear size of domains. On the whole, the average size of ordered phase domains which is estimated from broadening of the diffraction reflections is in qualitative agreement with the relevant results of the SEM examination. Note that the domain size determined by the XRD method is the smallest because the size estimated by the SEM is a size of grains including some domains rather than a size of separate domains.

3.2. Atomic displacements in ordered $V_{52}O_{64}$ phase

The real structure of the tetragonal (space group $I4_1/amd$) ordered $V_{52}O_{64}$ phase exhibits significant atomic displacements shown in Table 2. The absolute values of the displacements Δ of the oxygen and vanadium atoms are related as $\Delta_{O2} > \Delta_{O3} > \Delta_{O1} > \Delta_{V4} > \Delta_{V2}$; i.e. the oxygen atoms O2 and vanadium atoms V2 undergo the largest and least displacements, respectively.

In perfect (without atomic displacements) ordered $V_{52}O_{64}$ phase with lattice constants $a_t = b_t = (2\sqrt{2})a_{cub}$ and $c_t = 2a_{cub}$ the nearest distances V–V or O–O between the same neighbouring atoms are $a_{cub}/\sqrt{2}$, and a distance $V^{(t)}$–O is equal to $a_{cub}(\sqrt{3}/4)$. As the found basic cubic lattice constant a_{cub} is 0.4144 nm the nearest distances in perfect $V_{52}O_{64}$ phase between the same atoms V–V (except for $V^{(t)}$ atoms) or O–O are 0.29303 nm and $V^{(t)}$–O distance is equal to 0.17944 nm.

Fig. 8 shows the directions of the displacements of the vanadium and oxygen atoms in the $(0\,0\,z)$ planes, where $z = 0$, 1/4, 1/2, and 3/4, of the $V_{52}O_{64}$ superstructure. The lengths of the vectors indicating the displacement directions are proportional to the displacement magnitudes, but are increased by a factor of 20. One can see, the vanadium atoms V2 occupying the 16(h) positions with the coordinates $(0\,y\,z)$, where $y = 1/8$ and $z = 1/4$, in the perfect $V_{52}O_{64}$ structure are shifted in the $(0\,0\,z)$ planes in the real ordered phase from each other to the nearest vanadium vacancy ■. In any $(0\,0\,z)$ plane, where $z = 0$, 1/4, 1/2 and 3/4, the V2–V2 distance increases from 0.29303 nm in the perfect structure to 0.29647 nm in the real structure; the shortest distance between the V2 atoms in the neighbouring planes increases to 0.29414 nm. Vanadium atoms V4 in the 16(f) positions with the coordinates $(x\,0\,0)$, where $x = 5/8$, in the real ordered phase are shifted in the $(0\,0\,z)$ planes towards each other. In any plane $(0\,0\,z)$, the V4–V4 distance decreases from 0.29303 nm in the perfect structure to 0.28778 nm in the real structure; the shortest distance between the same V4 atoms in the neighbouring planes increases to 0.29568 nm. As a result of these correlated displacements, the V2 and V4 atoms form a wave-like chain in the metal sublattice of the real ordered $V_{52}O_{64}$ phase (see Fig. 8). The V3 vanadium atoms in the 16(f) positions with the coordinates $(x\,0\,0)$, where $x = 1/8$, are not shifted according to our data. The V5 ($V^{(t)}$) vanadium atoms that occupy the tetrahedral interstices and are located above and below the $(0\,0\,z)$ planes by $z = 1/8$ are in fixed 4(a) positions of space group $I4_1/amd$.

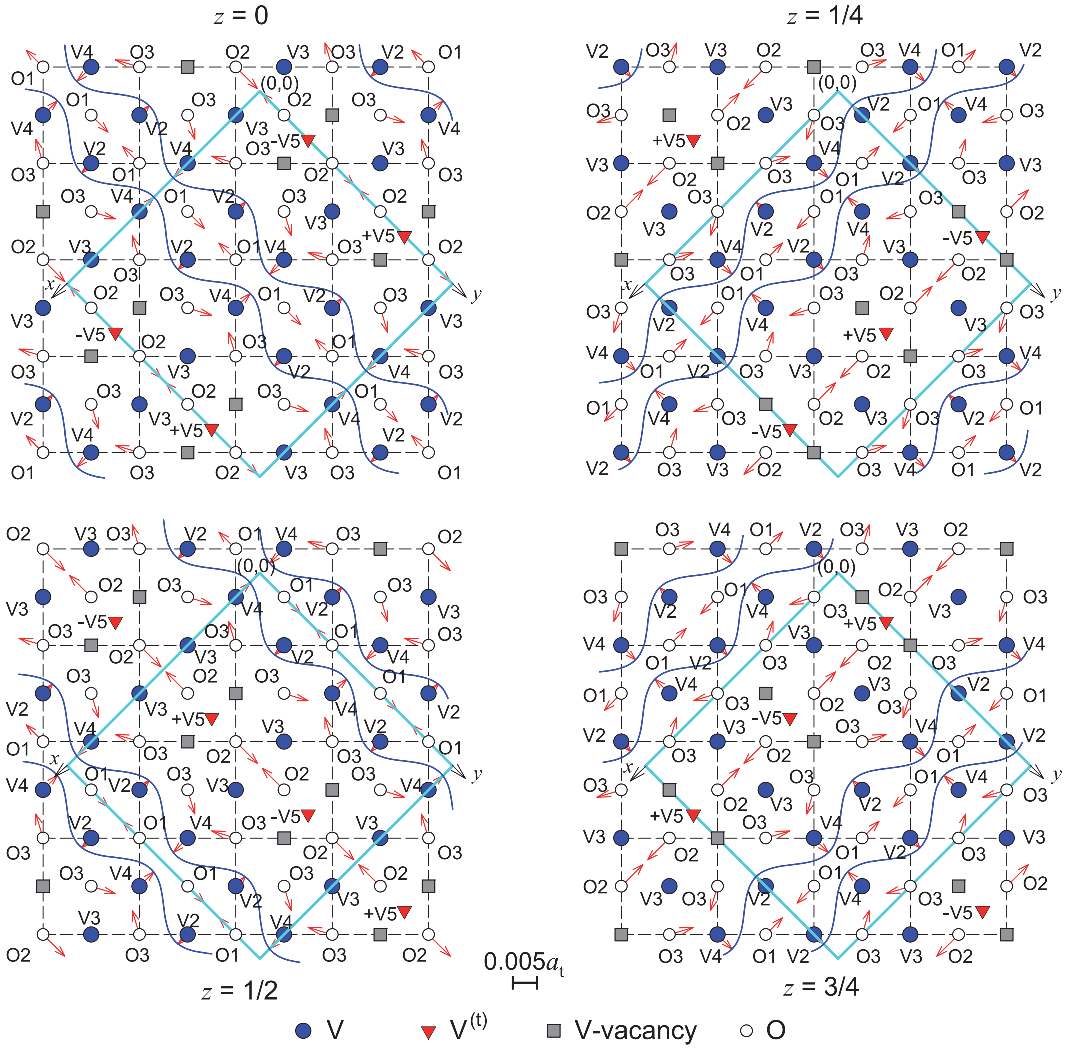

Fig. 8. Directions of the displacements of the vanadium and oxygen atoms in the (0 0 0), (0 0 1/4), (0 0 1/2), and (0 0 3/4) planes of the $V_{52}O_{64}$ superstructure: (●) vanadium V atoms in the 16(h) and 16(f) positions, (▼) vanadium $V^{(t)}$ atoms in the tetrahedral 4(a) positions, (■) vacancies of the vanadium sublattice, and (○) oxygen atoms O. The displacement directions are indicated by arrows; the vector lengths are proportional to the displacement magnitudes and are increased by a factor of 20 (the displacement scale in the units of 0.005a_t is shown below, where a_t is the lattice constant of the unit cell of the tetragonal $V_{52}O_{64}$ superstructure). The contour of the unit cell of the $V_{52}O_{64}$ superstructure is shown by the cyan solid line; and dashed line is the basic cubic lattice. The displacement waves of the V2 and V4 vanadium atoms are shown; displacement waves of oxygen atoms are not shown. The sign + or − in front of the tetrahedral symbols V5 means that the corresponding atom is above or below the plane under consideration by a value of $z = 1/8$. The V and O atoms are enumerated according to Table 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

The distances between the V5 ($V^{(t)}$) atom occupying the tetrahedral 4(a) position of space group $I4_1/amd$ and four nearest O2 oxygen atoms forming tetrahedral environment of V5 atom, increase from 0.17944 nm in the perfect ordered phase to 0.18604 nm in the real phase.

The O1 oxygen atoms occupying the 16(h) positions with the coordinates (0 y z), where $y = 1/8$ and $z = 1/2$, are shifted in the (0 0 z) plane towards each other, approaching the V2 vanadium atoms and shifting away from the V4 vanadium atoms. The O2 oxygen atoms occupying the 16(h) positions with the coordinates (0 y 0), where $y = 7/8$, are shifted in the (0 0 z) plane towards each other, moving away from the vanadium vacancy pairs ■–■ and approaching the V3 vanadium atoms. In the planes (0 0 z) under consideration, the O1–O1 and O2–O2 distances between the nearest atoms decrease to 0.28449 and 0.27768 nm, respectively. The distances between the O1 atoms located in the neighbouring (0 0 z) atomic planes decrease to 0.28816 nm and the distances between the nearest O2 atoms located in the neighbouring atomic planes (the edges of the oxygen tetrahedron) increase to 0.30084 nm. The O3 oxygen atoms occupying the 32(i) positions in the real ordered phase are shifted in the (0 0 z) planes towards each other, approaching the nearest V4 atom and moving away from the nearest vanadium vacancy ■ (see Fig. 8). The O3–V4 and O3–O3 distances between the nearest atoms in the (0 0 z) planes decrease to 0.20302 and 0.28238 nm, respectively. Thus, the atomic displacement waves of the O1, O2, and O3 atoms exist in the oxygen sublattice of the real $V_{52}O_{64}$ superstructure.

The found displacement directions of the vanadium and oxygen atoms predominantly coincide with the displacement directions which are determined by authors [32] for $V_{52}O_{64}$ superstructure obtained by annealing of a single crystal $VO_{1.30}$ at temperature of 970 K. However, according to our data in contrast to data [28], the atomic displacements along the z axis are absent.

3.3. *Short-range order and structure of disordered vanadium monoxide*

Each $V^{(t)}$ atom in the perfect $V_{52}O_{64}$ superstructure has the first coordination sphere that consists of four O2 oxygen atoms and four vacancies ■ of the vanadium sublattice (Fig. 9a) and has the radius $R_1 = a_{cub}(\sqrt{3}/4)$, where a_{cub} is the lattice constant of the disordered

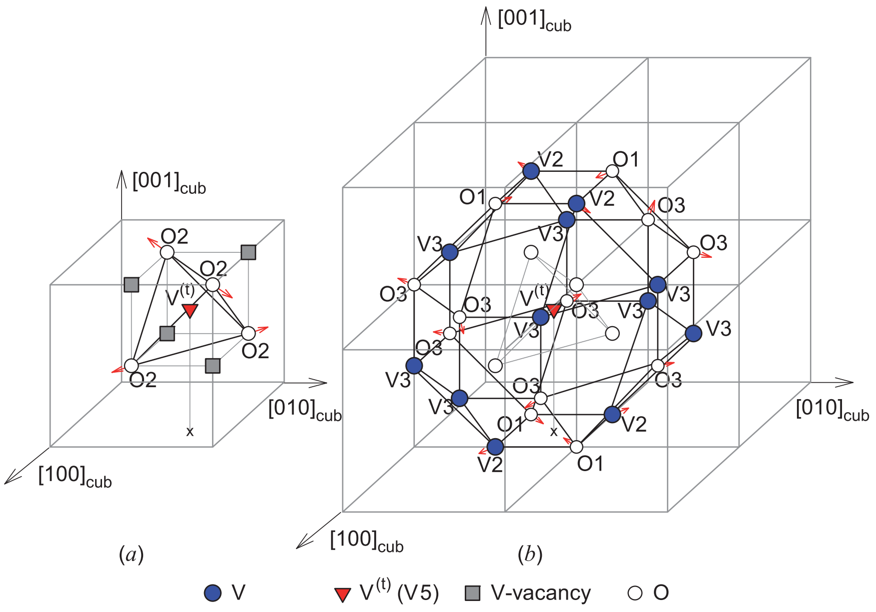

Fig. 9. (a) The first and (b) second coordination spheres of the vanadium atom $V^{(t)}$ (V5) in the $V_{52}O_{64}$ superstructure: (●) vanadium atoms V occupying the 16(h) and 16(f) positions, (▼) $V^{(t)}$ (V5) vanadium atoms in tetrahedral interstices, (■) vacancies of the vanadium sublattice, and (○) oxygen atoms O. The V and O atoms are enumerated according to Table 2 Twenty four O and V atoms forming the 2nd coordination sphere of the $V^{(t)}$ (V5) atom in the perfect $V_{52}O_{64}$ superstructure are in the vertices of the distorted small rhombicuboctahedron, i.e. a convex semiregular Archimedes polyhedron with point symmetry O_h. Owing to the indicated atomic displacements, the 2nd coordination sphere in the real $V_{52}O_{64}$ superstructure is split into four spheres with close radii 0.34060, 0.34315, 0.34414, and 0.34987 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

cubic monoxide. The second coordination sphere with the radius $R_2 = a_{cub}(\sqrt{11}/4) \approx 0.344$ nm consists of 24 atoms: four V2 atoms, eight V3 atoms, four O1 atoms, and eight O3 atoms (Fig. 9b). These 24 atoms in perfect $V_{52}O_{64}$ superstructure are in the vertices of the distorted small rhombicuboctahedron, i.e. a convex semiregular Archimedes polyhedron with point symmetry O_h. The radius of the first coordination sphere in the real $V_{52}O_{64}$ superstructure, i.e. the shortest interatomic distance V5–O2, is 0.18604 nm; it is larger than the same radius for the perfect superstructure. Owing to atomic displacements, the second coordination sphere in the real $V_{52}O_{64}$ superstructure is split into four coordination spheres formed only by the O1, V2, V3, or O3 atoms with close radii 0.34060, 0.34315, 0.34414, and 0.34987 nm, respectively (see Fig. 9b).

Thus, the presence of atomic displacements in the real $V_{52}O_{64}$ superstructure results in the formation of the short-range order of displacements. As a result, the electron diffraction patterns should exhibit extended planar regions of diffusion scattering that do not pass through the structural sites of the reciprocal lattice [29]. This is in agreement with the experimental results reported in [13], where the short-range order in the disordered $VO_{1.23}$ vanadium monoxide was revealed by the diffuse scattering of electrons.

The investigation shows that some V atoms in the $V_{52}O_{64}$ superstructure are regularly located in tetrahedral interstices. What is the probability that vanadium atoms are in tetrahedral interstices of the disordered cubic V_xO_z vanadium monoxide? Is there (i) a second phase with other cubic structure, but with same space group $Fm\bar{3}m$ in the homogeneity interval of a disordered vanadium monoxide along with a known cubic phase with $B1$ structure or (ii) the only cubic (space group $Fm\bar{3}m$) phase, whose structure is not the $B1$-type structure?

Let q be the occupancy of tetrahedral interstices by vanadium atoms. As the number of tetrahedral interstices (positions 8(c)) is twice more than number of the sites of fcc metal sublattice (positions 4(a)), then the relative number of the tetrahedral interstices, occupied by V atoms, is equal to $2q$, and relative number of the sites of fcc metal sublattice, occupied with vanadium atoms, is equal to $(x - 2q)$. Taking into account the presence of vacancies in the positions 4(a) of metal sublattice and in the positions 4(b) of nonmetal sublattice it is possible to present structure of cubic monoxide of vanadium V_xO_z as $V_{x-2q}V^{(t)}_{2q}\blacksquare_{1-x+2q}O_z\square_{1-z}$.

The problem of the second cubic phase has already arisen in published works. In particular, Vol'f et al. [30] reported on the stepwise change in the lattice constant of VO_y near the composition $VO_{1.05}$–$VO_{1.06}$, which can be attributed to the presence of the phase boundary between two cubic phases close in structure in this place of phase diagram. Reuther and Brauer [31] arrived at a similar conclusion on the presence of two similar cubic phases in the region $VO_{0.970}$–$VO_{1.011}$, but they did not propose the structures of the phases. Pointing to the non-monotonic variation of the lattice constant, density, and defect content in the oxygen and vanadium sublattices of the VO_y vanadium monoxide near the equiatomic composition VO, Davydov and Rempel [21] also mentioned the possibility of the existence of two cubic phases.

According to [32–35], important feature of the cubic phase structure are the non-vacancy defects, namely, vanadium atoms, which are present in a small amount in the tetrahedral interstices of the cubic lattice. For example, the occupancy q of tetrahedral interstices by vanadium atoms in the disordered monoxide $VO_{1.23}$ which was produced by annealing at a temperature of 1070 K, amounts from ~0.016 to ~0.029 (or from 2.0 to 3.7 tetrahedral $V^{(t)}$ atoms on an unit cell of $V_{52}O_{64}$ superstructure) [32]. Watanabe et al. [33] established that the occupancy q of interstitial tetrahedral sites by $V^{(t)}$ atoms in disordered $VO_{0.82}$ and $VO_{1.20}$ vanadium monoxides is equal to 0.004 ± 0.003 and 0.026 ± 0.005, respectively. By results of X-ray diffraction [34], occupancy of tetrahedral positions 8(c) by vanadium atoms in disordered VO_y monoxide varies from 0.004 ± 0.004 and 0.008 ± 0.006 in $VO_{0.80}$ and $VO_{0.98}$ to 0.015, 0.022 and 0.028 in $VO_{1.01}$, $VO_{1.11}$ and $VO_{1.25}$, respectively.

Andersson et al. [35] assumed that the superstoichiometric $VO_{>1.0}$ vanadium monoxide contains tetrahedral clusters of the vacancies of the metallic sublattice; the vanadium $V^{(t)}$ atoms located in the tetrahedral interstices of the cubic lattice are the centres of these clusters $V^{(t)}\blacksquare_4$. Using the electron diffraction

Table 3

Crystal structure of the $D0_3$-type of cubic (space group $Fm\bar{3}m$) vanadium monoxide $(\mathrm{V}_x\mathrm{O}_z = \mathrm{V}_{x-2q}\mathrm{V}^{(t)}_{2q}\blacksquare_{1-x+2q}\mathrm{O}_z\square_{1-z})$ $(z > x)$.

Atom	Position and multiplicity	Atomic coordinates			Occupancy
		x/a_{cub}	y/a_{cub}	z/a_{cub}	
V1	4(*a*)	0	0	0	$x - 2q$
V2 ($\mathrm{V}^{(t)}$)	8(*c*)	1/4	1/4	1/4	q
O	4(*b*)	1/2	1/2	1/2	z

method, Andersson [36] demonstrated that the disordered $\mathrm{VO}_{1.23}$ vanadium monoxide has not only the short-range order of the substitution type (or substitutional disorder, in termin [37]), but also significant atomic displacements. Local atomic distribution which corresponds to these displacements, it is possible to interpret as existence of defect tetrahedrons $\mathrm{V}^{(t)}\blacksquare_4$ in a disordered vanadium monoxide [36]. Strong diffraction evidence for the existence of tetrahedral defect clusters in disordered $\mathrm{VO}_{1.23}$ was presented by Andersson et al. [13]. In the ^{51}V NMR spectrum of the $\mathrm{VO}_{1.25}$ monoxide at a temperature below 5 K, Takagi et al. [38] detected a line corresponding to the V^{3+} ions occupying tetrahedral interstices.

The above background makes it possible to suppose that $\mathrm{V}^{(t)}$ vanadium atoms in the tetrahedral environment, i.e. in the environment consisting of four sites of the oxygen sublattice and four sites of the vanadium sublattice, appear in a disordered cubic vanadium monoxides in addition to V atoms in 4(*a*) positions surrounded by six sites of the oxygen sublattice. Moreover, very small quantity of $\mathrm{V}^{(t)}$ atoms is present in a disordered substoichiometric vanadium monoxide VO_y with $y < 1.0$. It means that the structure of a disordered $\mathrm{VO}_y \equiv \mathrm{V}_x\mathrm{O}_z$ vanadium monoxide is not the *B*1-type structure in which there are no atoms in 8(*c*) positions. The vanadium monoxide VO_y is stated by the authors [22,23] to have the structure of type *B*1, but this conclusion has been made without detailed crystallographic analysis by analogy to cubic titanium monoxide TiO_y. In the subsequent investigations [32–38,38], the vanadium atoms occupying tetrahedral positions 8(*c*), which are unusual for the *B*1-type crystal structure, were found in a lattice of a disordered VO_y vanadium monoxide. One might think that a disordered $\mathrm{VO}_y \equiv \mathrm{V}_x\mathrm{O}_z$ vanadium monoxide has a cubic (space group $Fm\bar{3}m$) crystal structure $D0_3$-type with partial filling of positions 8(*c*) by V atoms in all homogeneity interval. This structure and the *B*1-type structure belong to the same space group $Fm\bar{3}m$ and have an identical set of diffraction reflections. At small degree of filling of 8(*c*) positions by V atoms, the intensities of diffraction reflections for the $D0_3$ structure differ slightly from the reflection intensities for the *B*1 structure. Therefore exact determination of a crystal structure of a disordered $\mathrm{VO}_y \equiv \mathrm{V}_x\mathrm{O}_z$ vanadium monoxide is possible only by means of the careful analysis of the reflection intensities and values of atomic displacements.

If the occupancy of tetrahedral interstices by vanadium atoms is equal to q then the composition of cubic $\mathrm{V}_x\mathrm{O}_z$ vanadium monoxide can be represented as $\mathrm{V}_{x-2q}\mathrm{V}^{(t)}_{2q}\blacksquare_{1-x+2q}\mathrm{O}_z\square_{1-z}$ taking into account the presence of vacancies in metal and nonmetal sublattices. According to [34], occupancy q of the tetrahedral 8(*c*) positions with $\mathrm{V}^{(t)}$ atoms varies from 0.015 for $\mathrm{VO}_{1.01}$ to 0.028 for $\mathrm{VO}_{1.25}$. Analysis of the data [34] has shown that the dependence of occupancy q on the composition of VO_y monoxide with $y \geq 0.8$ can be described as a first approximation by function $q(y) = -0.0428 + 0.0569y$.

Each $\mathrm{V}^{(t)}$ atom in the disordered VO_y $(\mathrm{V}_x\mathrm{O}_z = \mathrm{V}_{x-2q}\mathrm{V}^{(t)}_{2q}\blacksquare_{1-x+2q}\mathrm{O}_z\square_{1-z})$ monoxide has the nearest environment consisting of four sites of the vanadium sublattice and four sites of the oxygen sublattice; each site can be occupied by an atom of its own species or can be vacant. For the statistical distribution of the atoms and vacancies, the probability $P_{n\mathrm{V}/m\mathrm{O}}$ that the nearest environment of the $\mathrm{V}^{(t)}$ atom contains n vacancies of the vanadium sublattice and m vacancies of the oxygen sublattice is given by the expression:

$$P_{nV/mO} = C_4^n C_4^m (x-2q)^{4-n}(1-x+2q)^n z^{4-m}(1-z)^m \tag{2}$$

The disordered cubic monoxide corresponding to the $\mathrm{V}_{52}\mathrm{O}_{64}$ superstructure does not contain oxygen vacancies and has the composition $\sim\mathrm{V}_{0.8}\mathrm{O}$ ($\mathrm{V}_{13/16}\mathrm{O}$). Formula (2) with $z = 1$ and $m = 0$ has the form:

$$P_{nV/0O} = C_4^n (x-2q)^{4-n}(1-x+2q)^n \tag{3}$$

As follows from the Eq. (3), the largest probability at $1 > x > 0.7$ and $q \ll x$ is the probability $P_{0\mathrm{V}/0\mathrm{O}}$, i.e. $n = 0$. In other words, the environment consisting of four vanadium atoms should formally be the most probable nearest environment of the $\mathrm{V}^{(t)}$ atoms in the completely disordered $\sim\mathrm{V}_{0.8}\mathrm{O}$ monoxide. However, this is physically excluded, because the radius of the tetrahedral interstice formed by the vanadium atoms is given by the expression $R_{\mathrm{tetrV}} = a_{\mathrm{cub}}(\sqrt{3}/4) - R_{\mathrm{V}(6)} \ll R_{\mathrm{V}(4)}$ and is much smaller than the vanadium atomic radius $R_{\mathrm{V}(4)} = 0.118$ nm. Indeed, the vanadium atomic radius $R_{\mathrm{V}(12)}$ is equal to 0.134 nm for the coordination number 12. With allowance for the correction on the coordination numbers 4 and 6, vanadium atomic radii are equal to $R_{\mathrm{V}(4)} = 0.88R_{\mathrm{V}(12)} = 0.118$ nm and $R_{\mathrm{V}(6)} = 0.96R_{\mathrm{V}(12)} = 0.129$ nm for the tetrahedral and octahedral environments, respectively [39]. Thus, the probability $P_{0\mathrm{V}/0\mathrm{O}}$ is equal to 0 due to the size of the vanadium atoms. The oxygen atomic radius R_{O} is equal to 0.066 nm [39] therefore the radius of the tetrahedral interstice formed by four oxygen atoms is given by the expression $R_{\mathrm{tetrO}} = a_{\mathrm{cub}}(\sqrt{3}/4) - R_{\mathrm{O}} \leq R_{\mathrm{V}(4)}$, which is close to the vanadium atomic radius $R_{\mathrm{V}(4)}$. Hence, the vanadium atom can take places in a tetrahedral interstice of four oxygen atoms. The same conclusions can be received using the ion radii for V^{2+} and O^{2-} ions [39].

In the absence of the long-range order in cubic monoxide $\mathrm{V}_x\mathrm{O}$ the probability $P_{0\mathrm{V}/0\mathrm{O}}$ can be equal to zero only in the case when there is a short-range order at least in the first coordination sphere of $\mathrm{V}^{(t)}$ atoms formed by the sites of the vanadium sublattice. In the presence of short-range order, the number of vacant sites of the vanadium sublattice in the first coordination sphere of any $\mathrm{V}^{(t)}$ atom is equal

$$n = z_1(1-\alpha_1)(1-x), \tag{4}$$

where α_1 and $z_1 = 4$ are the short-range order parameter and the coordination number of the first coordination sphere of $\mathrm{V}^{(t)}$ atom, respectively. While considering the metal sublattice, the $\mathrm{V}^{(t)}$ atom in the disordered $\mathrm{V}_x\mathrm{O}$ monoxide can only be in the environment of four vacancies of the vanadium sublattice formed tetrahedral cluster $\mathrm{V}^{(t)}\blacksquare_4$, i.e. $n = 4$. It follows from equation (4) that the short-range order parameter for disordered vanadium monoxide $\mathrm{V}_x\mathrm{O}$ with $x < 1.0$ at $n = 4$ and $z_1 = 4$ is

$$\alpha_1 = \frac{-x}{1-x} \tag{5}$$

The analysis performed allows to conclude that the disordered $\mathrm{V}_x\mathrm{O}$ vanadium monoxide with vacancies only in the vanadium sublattice has a cubic (space group $Fm\bar{3}m$) $D0_3$-type structure with partial filling of tetrahedral 8(*c*) positions by vanadium atoms (Table 3) and with displacements of oxygen atoms surrounding $\mathrm{V}^{(t)}$ atoms. This structure is characterized by the presence of short-range order of displacements in the oxygen sublattice and short-range order of substitution in the metal sublattice. The short-range order of displacement is caused by the local displacements of O2 oxygen atoms forming tetrahedral environment of $V^{(t)}$ atoms. These oxygen atoms displace from $V^{(t)}$ atoms. The short-range order of substitution appears because vanadium atoms in the 8(*c*) positions are always in the environment of four vacancies $\blacksquare$ of the vanadium sublattice. Tetrahedral clusters $V^{(t)}\blacksquare_4$ and separate vacancies $\blacksquare$ are located statistically in the crystal lattice of a disordered cubic vanadium monoxide and only in condition of temperature decreasing they arrange in ordered manner forming tetragonal superstructure $V_{52}O_{64}$. Taking into account the literature data, one can assume that the disordered vanadium monoxide V_xO_z ($V_x\blacksquare_{1-x}O_z\square_{1-z}$, $z>x$) with the minimum content of oxygen vacancies $\square$ and the disordered V_xO_z vanadium monoxide with $z\cong x$, i.e. with approximately the same contents of oxygen and metal vacancies, has the same short-range order in the metal sublattice. Relative content of $V^{(t)}$ atoms in a disordered V_xO_z ($z<x$) vanadium monoxide with large concentration of oxygen vacancies $\square$ is as small as the experimental error [33,34].

The presence of local atomic displacements in a disordered V_xO_z vanadium monoxide which transform to atomic displacement waves in ordered $V_{52}O_{64}$ phase means that the microstrains occur in crystal lattice of ordered vanadium monoxide. The quantity $\varepsilon=\Delta l/l\equiv\Delta d/d$ is the lattice microstrain which characterizes the uniform strain averaged out with respect to the crystal volume, i.e. relative change Δd of interplanar or interatomic distances d in comparison with perfect crystal. Interatomic distances for perfect and real crystal structures of ordered vanadium monoxide are given in Section 3.2. Value of the local microstrains can be estimated using these interatomic distances. For example, the nearest distance between the V2 atoms in the neighbouring atomic planes $(0\,0\,z)$, where $z=0$, 1/4, 1/2 and 3/4, increases from 0.29303 nm in the perfect ordered structure to 0.29414 nm in the real ordered structure. In this case $\Delta d=0.00111$ nm and $\varepsilon\sim 0.38\%$. Relaxation of sufficiently large local microstrains takes place owing to the grain refinement of a basic cubic phase and formation of a nanostructure which represents a set of domains of an ordered tetragonal $V_{52}O_{64}$ phase. Indeed, performed analysis of the diffraction reflection broadening of annealed nanostructured ordered vanadium monoxide (see Section 3.1) has shown that the value of the microstrains ε is equal to $0.047\pm0.005\%$. Thus, occurrence of a nanostructure at ordering of nonstoichiometric vanadium monoxide is caused by the basic cubic phase grain refinement that promotes a relaxation of local microstrains.

4. Conclusion

Investigation of atomic-vacancy ordering of nonstoichiometric cubic $VO_{1.29}$ ($V_{0.775}O$) vanadium monoxide shows that ordering is accompanied an appearance of local atomic displacements, local microstrains, stepwise increasing of a basic cubic lattice constant and the formation of a nanostructure which represents a set of domains of an ordered tetragonal phase of the $V_{52}O_{64}$ type. After prolonged annealing for 1000 h at 970 K the size of domains is equal to ~80 nm and value of microstrains is ~0.047%. Determination of a real crystal structure of ordered vanadium monoxide phase finds out that this phase has a composition $V_{51.6}O_{64}$ and its crystal lattice contains significant local atomic displacements and, consequently, large local microstrains. The results of the present work prove that the ordering process can be applied for creation of a nanostructure in nonstoichiometric vanadium monoxide.

Study of the structure of ordered tetragonal phase $V_{52}O_{64}$ and disordered cubic vanadium monoxide V_xO_z indicates that a certain fraction of V atoms in these phases are located in tetrahedral positions. The nearest environment of these $V^{(t)}$ vanadium atoms is formed by four sites of oxygen sublattice and four vacant sites of vanadium sublattice. Both structures are characterized by the presence of short-range order of displacements in the oxygen sublattice and short-range order of substitution in the metal sublattice. The short-range order of displacement is caused by the local displacements of O atoms from $V^{(t)}$ atoms. The short-range order of substitution appears because vanadium atoms in the tetrahedral positions are always in the environment of four vacancies $\blacksquare$ of the vanadium sublattice. Tetrahedral clusters $V^{(t)}\blacksquare_4$ and separate vacancies $\blacksquare$ are located statistically in the crystal lattice of a disordered cubic vanadium monoxide with $D0_3$-type structure and they arrange in ordered manner in tetragonal $V_{52}O_{64}$ superstructure.

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