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Patterns of formation of electrically conductive properties of oxides of the Magneli series

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The hybridization of vanadium ions and oxygen ions is considered for four vanadium oxides included in the Magneli series: VO, V_2O_3, VO_2, V_2O_5. Based on the data on hybridization, the details of the structure of the crystal lattice of these oxides are analyzed. For each oxide, the role of electrons not participating in the stabilization of the crystal frame in the process of the semiconductor-metal phase transition was revealed. The complex Mott-Peierls character of the phase transitions in all the listed strongly correlated compounds has been established. It is shown that as the degree of oxidation of the V atom increases, the numerical value of the metallic conductivity of the high-temperature phase naturally decreases and, simultaneously, the temperature of the phase transition from the semiconductor to the metallic state increases.

Keywords: phase transitions, Magneli series, electron correlations, hybridization of atomic orbitals.

1. Introduction

In the series of various metal oxides vanadium oxides hold a specific place. The application demand for these materials is beyond any doubt because of the convenience of their practical use [1]. And their unusualness consists in that these compounds for the Magneli series: VO_x, where x varies from 0.2 (V_5O) to 2.5 (V_2O_5). This series is characterized by a large number of different oxides with varying vanadium mixed valence [2]. In addition, physical and chemical properties of the Magneli series oxides change significantly with temperature with almost all the oxides possessing the thermal phase transition (PT) of a sophisticated complex nature [3]. In this study, we shall be focused on four vanadium oxides (VO — vanadium monoxide, V_2O_3 — vanadium sesquioxide, VO_2 — vanadium dioxide and V_2O_5 — vanadium pentoxide), which are arranged by us in ascending order of the number of oxygen atoms per one vanadium atom.

The above-mentioned unusualness of properties of the vanadium oxides in comparison with oxides of other transition elements is related to the features of filling of atomic energy levels by electrons in the V atom [4]. Electronic configurations of the V atom and its neighboring atoms in the periodic table are presented in Table 1.

According to the presented fragment, potassium (K, 19, $3d^04s^1$) has filled the upper level $4s$ instead of the „expected" filling of the lower energy level $3d$, because this upper level, by accepting an electron, becomes lower in terms of energy that the $3d$-level containing an electron. Only after saturation of the $4s$-level of calcium (Ca, 20, $3d^04s^2$) with two electrons the $3d$-level is filled: by

one electron — in scandium (Sc, 21, $3d^14s^2$), by two electrons — in titanium (Ti, 22, $3d^24s^2$) and by three electrons — in vanadium (V, 23, $3d^34s^2$). However, the sequence of levels filling by electrons chromium (Cr, 24, $3d^54s^1$) is disturbed again: instead of the „expected" four electrons on the $3d$-level there five electrons due to the transfer of one electron from the $4s$ level to the $3d$ level. This suggests that the $3d$-level, being filled with electrons, is lowered in terms of energy below the $4s$ level. In other words, electronic orbitals of these elements are „soft": their energy is strongly dependent on the occupancy of their correspondent energy levels by electrons. Therefore, full theoretical description of the electronic spectrum of these atoms requires a correction to be introduced into the energies of their levels, which is known as correlation

Table 1. Fragment of the periodic table

19 K	[Ne] $3s^2\ 3p^6\ 4s^1$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ $\qquad\qquad\quad\ 2\quad\ \ 8\qquad\quad\ 8$		$4s^1$ $\,1$
20 Ca	[Ne] $3s^2\ 3p^6\ 4s^2$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ $\qquad\qquad\quad\ 2\quad\ \ 8\qquad\quad\ 8$		$4s^2$ $\,2$
21 Sc	[Ne] $3s^2\ 3p^5\ 3d^1\ 4s^2$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5\ 3d^1$ $\qquad\qquad\quad\ 2\quad\ \ 8\qquad\quad\ 9$		$4s^2$ $\,2$
22 Ti	[Ne] $3s^2\ 3p^6\ 3d^2\ 4s^2$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$ $\qquad\qquad\quad\ 2\quad\ \ 8\qquad\quad\ 10$		$4s^2$ $\,2$
23 V	[Ne] $3s^2\ 3p^6\ 3d^3\ 4s^2$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$ $\qquad\qquad\quad\ 2\quad\ \ 8\qquad\quad\ 11$		$4s^2$ $\,2$
24 Cr	[Ne] $3s^2\ 3p^6\ 3d^5\ 4s^1$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$ $\qquad\qquad\quad\ 2\quad\ \ 8\qquad\quad\ 12$		$4s^1$ $\,1$

Table 2. Electronic configuration for neutral V and O atoms, as well as for V and O ions that form the crystal structure of vanadium oxides

Neutral atom atom	V^0	$[Ar]3d_{xz}^0(1)3d_{yz}^0(1)3_{dx2-y2}^1(1)3d_{xy}^1(1)3d_{z2}^1(1)4s^2(1)4p^0(3)$
	O^0	$1s^2(1)2s^2(1)2p_x^1(1)2p_y^1(1)2p_z^2(1)$
VO $x=1$	V^{2+}	$[Ne]3s^2(1)3p_x^2(1)[3p_y^2(2)3p_z^2(2)3d_{z2}^1(1)3d_{xy}^1(1)4s^2(1)3d_{yz}^0(1)]3d_{xz}^0(1)3d_{x2-y2}^1$
	O^{2-}	$1s^2(1)2s^2(1)[2p_x^1(1)2p_y^1(1)2p_z^2(1)3S^0(1)3p_x^0(1)3p_y^0(1)]$
V_2O_3 $x=1.5$	V^{3+}	$[Ar][3d_{xy}^1(1)3d_{z2}^0(1)4s^2(1)4p^0(3)]$
	O^{2-}	$1s^2(1)[2s^2(1)2p_x^1(1)2p_y^1(1)2p_z^2(1)]$
VO_2 $x=2$	V^{4+}	$[Ar]3d_{xz}^0(1)3d_{yz}^0(1)[3d_{xy}^1(1)3d_{z2}^1(1)4s^2(1)4p^0(3)]3d_{x2-y2}^1(1)$
	O^{2-}	$1s^2(1)[2s^2(1)2p_x^1(1)2p_y^1(1)2p_z^2(1)]$
V_2O_5 $x=2.5$	V^{5+}	$[Ar][3d_{xz}^0(1)3d_{yz}^0(1)3d_{x2-y2}^1(1)3d_{xy}^1(1)3d_{z2}^1(1)4s^2(1)]4p^0(3).$
	V^{4+}	$[Ar][3d_{xz}^0(1)3d_{yz}^0(1)3d_{x2-y2}^1(1)3d_{xy}^1(1)3d_{z2}^1(1)]4_s^2(1)4p^0(3).$
	O^{2-}	$2s^2(1)2p^4(3)$

energy. The need for the introduction of correlation correction is due to the strong Coulomb interaction of electrons with each other along with the electron interaction with the atom nucleus, i.e. a great importance is assumed by strong multiparticle electron-electron interactions. These correlation effects are especially strong in transition and rare earth elements [5].

The ability to lower the energy of atomic levels with their occupancy by electrons is transferred to compounds of transition elements. In particular, these are vanadium oxides, which are characterized by a strong dependence of energy bands position on their occupancy by electrons [6]. These are the correlation effects in the vanadium atom, that lay behind the possibility of synthesis of a large number of different vanadium oxides that form the Magneli series, as well as the presence of unusual properties in majority of vanadium oxides.

Objectives of this study are:

1. Regularization of the relations between the structure of crystal lattice of vanadium oxides and the hybridization of orbitals of vanadium and oxygen ions in order to gain the information on the presence of electrons not involved in building the lattice framework and responsible for semiconductor properties of the crystal: electrical conductivity, the presence of PT, etc.

2. Discussion, on the basis of the information gained in section 1, of features of the structural and electronic PT in the four vanadium oxides in question.

3. Identification of causes of metal properties weakening in VO_x vanadium oxides with increase in oxidation number of the vanadium atom ($x = 1, 1.5, 2, 2.5$) with simultaneous temperature shift of the semiconductor-metal PT toward higher temperatures.

2. Hybridization of V and O ions in VO_x oxides and their crystal structure

Table 2 shows the electronic configuration for neutral atoms of vanadium and oxygen, as well as the configuration of vanadium and oxygen ions [7] included in the crystal structure of vanadium oxides. Here, figures without brackets show numbers of electron shells, figures in brackets are numbers of orbitals of the given type, superscripts show numbers of electrons on orbitals. [Ar] and [Ne] denote the electronic configuration of neutral atoms of Ar and Ne. Underlined symbols in square brackets highlight the orbitals involved in the hybridization, which are necessary to stabilize the crystal framework of a specific oxide.

2.1. VO_x, $x = 1$ (Vanadium monoxide)

As it is shown in Table 2 [8], in the case of VO the electronic configuration of the V^{2+} ion that includes the hybridization can also be written in the following abbreviated form: $[Ne]sp[sp^2d^3]d^2$ (i.e. without the indication of numbers of electron shells and quantities of electrons on them). Two d-orbitals of the vanadium ion are not involved in the hybridization, one of which is vacant and another contains one electron. The vanadium ion has 6 σ-bonds with oxygen ions. A V atom gives on average 4/3 of its electron density from hybrid orbitals to each bond [9].

The electronic configuration of the O^{2-} ion, that includes the hybridization, can be written in an abbreviated form as follows: $s^2[sp^5]$. All oxygen ions have, as the V^{2+} ion, 6 σ-bonds with vanadium ions. An O atom gives on average 2/3 of its electron density from its hybrid orbitals to each bond.
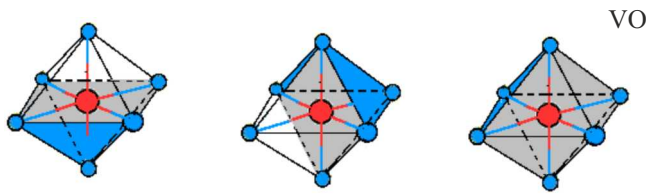
Figure 1. Oxygen octahedra with three identical and mutually orthogonal bases.

Thus, the coordination number of vanadium ion is 6, the coordination number of oxygen ion is 6 as well. At the same time, both ions form six complete σ-bonds with ions of their nearest neighborhood giving in general 2 electrons $[(4/3) + (2/3) = 2]$ per each bond.

All vanadium ions are located in centers of octahedra bases of the octahedral oxygen framework, while all oxygen ions are located in centers of octahedra bases of the octahedral vanadium framework forming a cubic face-centered crystal lattice of NaCl type. Such a lattice is „made-up" of two sublattices (Bravais lattices): a sublattice of vanadium ions and a sublattice of oxygen ions. The sublattices are half-period shifted in relation to each other in three mutually perpendicular directions. Note, that all ribs of octahedra are of the same length, therefore any ion can be adopted either as „nodal" or as located on the octahedron base. Bases of octahedra are squares, and in each octahedron three identical bases can be identified by a symmetry argument (Fig. 1). The bases are mutually orthogonal and arranged in such a way as to have their diagonals directed along the crystallographic axes.

As it was already mentioned before, two $3d$-orbitals (for example, d_{xz} and d_{x2-y2}) of the vanadium atom are not involved in the process of forming the framework of σ-bonds with oxygen ions in octahedron nodes remaining vacant (Fig. 2). At the same time, d_{x2-y2} — orbitals of neighboring octahedra are partly overlapped in the xy plane of their bases, and d_{xz} — orbitals are overlapped in the xz plane normal to the plane of bases (Fig. 2, a). Orbitals of d_{x2-y2} and d_{xz} types can be located in three mutually orthogonal planes (Fig. 2, b, c).
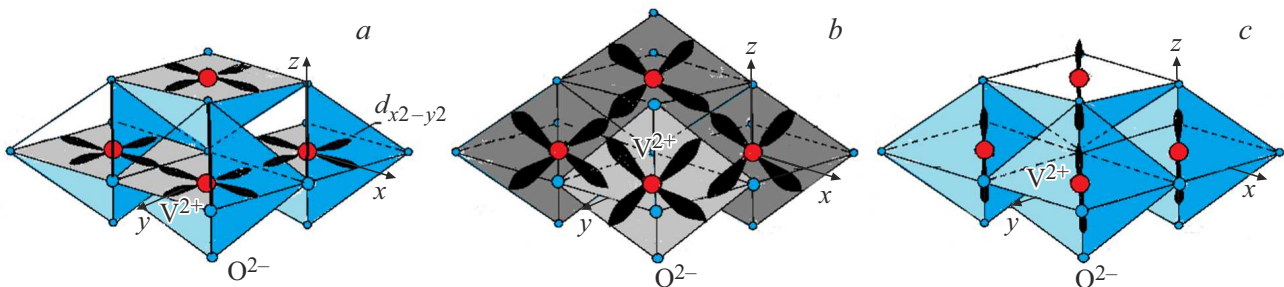
Only one electron on average is accounted for two $3d$-orbitals of the vanadium ion. They form energy bands in the electronic spectrum of the crystal, the lower of which, in accordance with Pauli principle, is half-filled. Therefore, a VO in the described configuration has metallic conductivity at room temperature, which is established experimentally.
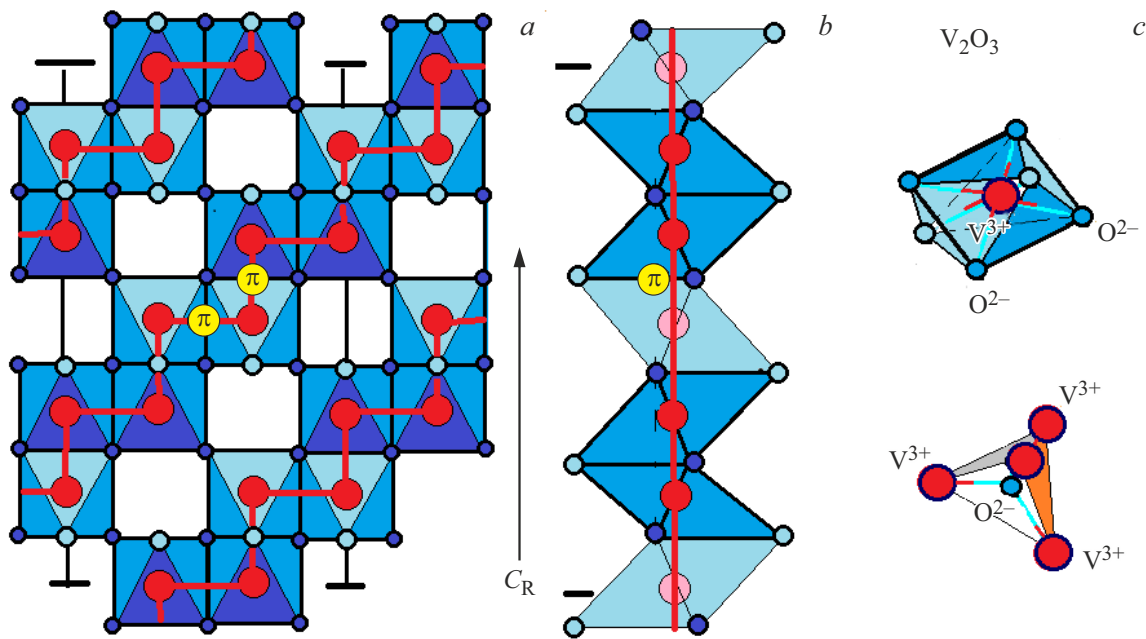
In the described configuration, the $3d^1_{x2-y2}$ orbital contains one electron, and $3d_{yz}$-orbital has no electrons. Or vise versa, one electron not involved in the stabilization of the framework, is occupied by the $3d_{yz}$ orbital, and the $3d_{x2-y2}$ orbital remains empty. However, the choice of preference of the orbital that accepts the only electron nonetheless can be made on the basis of the following considerations.

The anisotropic conductivity properties of nanocrystallites of vanadium oxides near the Fermi level can be described in terms of quantum mechanics using the model of a rigid quasi-one-dimensional chain of atoms or ions having one electron on the outermost electron shell [10]. The expression for electron energy in this case has the following form:

$$E = E_0 - \alpha + 2|\beta_i| \cos(kd), \qquad (1)$$

where E_0 is the energy of ground state of the d_{x2-y2} orbital; α is the integral of overlapping, which is equal to the energy of electron interaction of this atom or ion with electrons of their neighbors; β_i is the integral of transfer, which is proportional to the probability of electron transfer from one node to the neighboring node.

In respect to VO, it means that the semiconductor phase of this material, which is characterized by the presence of V-V-dimers [11], provides a greater integral of overlapping for $3d_{yz}$ orbitals (the OY axis is directed along the linear chain of dimers), because these orbitals are located in the YOZ plane with cruciform branches directed at an angle of 45° to OY and OZ axes. This makes them different from the $3d_{x2-y2}$ orbital, which branches lay in the plane of the base of V-O — octahedron along OX and OY axes. It is clear that the overlapping of two cruciform branches of $3d_{yz}$-orbitals of neighboring octahedra is more effective than the overlapping of one branch of $3d_{x2-y2}$-orbitals. It follows therefrom that the lowering of energy E_0 of the ground state at overlapping of $3d_{yz}$-orbitals is of higher relevance than that for $3d_{x2-y2}$-orbitals. Therefore, the only electron

Figure 2. Scheme of three possible options (a, b, c) for orientation of d_{x2-y2} orbitals of the vanadium ion located in the base of the oxygen octahedron of the VO crystal lattice.

Figure 3. Fragment of the V_3O_2 crystal lattice in the metallic phase. a — The relative position of V^{3+} ions in the „corrugated" layer consisting of oxygen octahedra (σ-dimers are not shown). b — side view of the layer, c — four σ-bonds of oxygen in the crystal framework. The electrical conductivity over the zigzag-shaped is due to the dynamic π-bonds between vanadium ions (a, b).

not used in the building of the crystal framework will be occupied by the $3d_{yz}$-orbital, and not by the $3d_{x2-y2}$-orbital.

2.2. VO_x, $x = 1.5$ (Vanadium sesquioxide)

For the V_2O_3, the situation is more complicated than that for the VO. As it follows from Table 2, each ion of vanadium forms six σ-bonds with six atoms of oxygen, while the ion of oxygen forms four σ-bonds with atoms of vanadium. The coordination number of the vanadium ion is 6, while that of the oxygen ion is 4.

The V^{3+} ion gives 3 electrons for all σ-bonds with oxygen ion octahedron, that is it gives on average 1/2 of its electron density per one bond. The oxygen ion, according to its electronic configuration, gives 6 electrons to hybrid orbitals, i.e. it gives on average 3/2 og its electron density per each σ-bond. Thus, an oxygen ion with 3/2 of electron density, together with 1/2 of electron density of the V^{3+} ion forms complete σ-bonds of the V^{3+} ion with all oxygen ions of the octahedral framework ($3/2 + 1/2 = 2$).

So, as a result of the hybridization each V^{3+} ion forms six σ-bonds with six oxygen atoms, with each oxygen ion having four hybrid orbitals. The rest three nonbonding $3d$-orbitals (d_{xz}, d_{yz} and d_{x2-y2}) of a vanadium atom with one electron belonging to them are not involved in the process of forming the framework of σ-bonds of the oxygen octahedron.

All vanadium atoms are located in centers of oxygen octahedra. However, in the crystal lattice for every two octahedra containing vanadium ions in the base, there is one octahedron that does not contain the vanadium ion.

Octahedra with empty bases are located on either side of a pair of octahedra with filled bases Fig. 3. The V_2O_3 lattice has rhombohedral symmetry at a high temperature [11].

The V^{3+} ion gives one electron from the $3d_{xy}^1$-orbital and two electrons from the $4s^2$ orbital to form σ-bonds of lattice framework with oxygen. Therefore, each V^{3+} ion has two from the five electrons of upper shells not involved in the formation of σ-bonds of the framework.

One of the uninvolved electrons is used to create a strong σ-bond directly between vanadium ions of neighboring octahedra (the formation of dimers from $3d_{x2-y2}$-orbitals of V^{3+} ions) (see Fig. 3, 4). σ-dimers of this kind can not be destroyed by heating up to the room temperature. Their strength is due the fact that each pair of octahedra with V^{3+} ions has adjoining empty octahedra from either side, which excludes „sucking-off" a part of electron density by them.

The second of electrons not involved in the formation of the framework is „distributed" between the $3d_{xz}$- and $3d_{yz}$-orbitals, which are overlapped with the same orbitals of neighboring V^{3+} ions forming π-dimers (in contrast to the σ-dimers described above). In this way two different types of dimers arise: σ-dimers and π-dimers located in two different planes inclined in relation to each other with an angle of α. The arising of π-dimers results in lowering of the lattice symmetry (from rhombohedral to monoclinic).

2.3. VO_x, $x = 2$ (vanadium dioxide)

The situation for VO_2 is more complicated than that for VO as well: here a higher valence of the vanadium ion
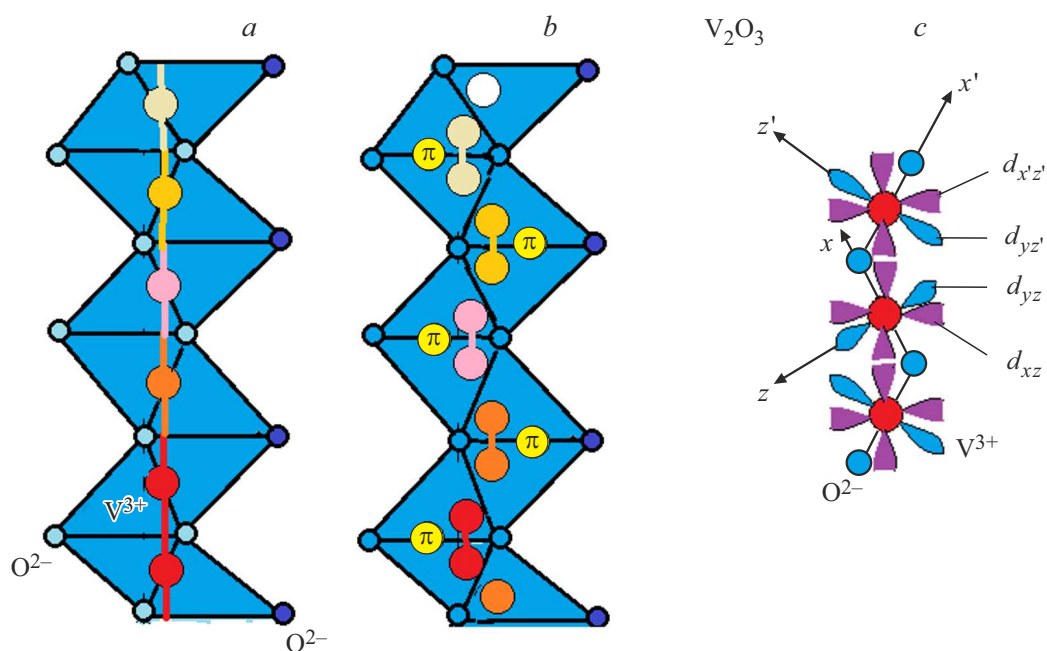
Figure 4. Projection of the zigzag-shaped chain directed along the $\mathbf{C}_R$ axis onto the XZ plane in the metal phase — *a*, in the semiconductor phase — *b*. With $T < T_c$ π-dimers arise, that bind free electrons, and a structural PT takes place. The arising of dimers is due to the overlapping of d_{xz} -orbitals of vanadium ions in the neighboring octahedra — *c*. As a result of formation of π-dimers, vanadium ions leave the base planes of the octahedra and approach each other pairwise — the vanadium ions, which have been „eclipsed" (*a*) on the chain projection before, become „visible" (*b*).
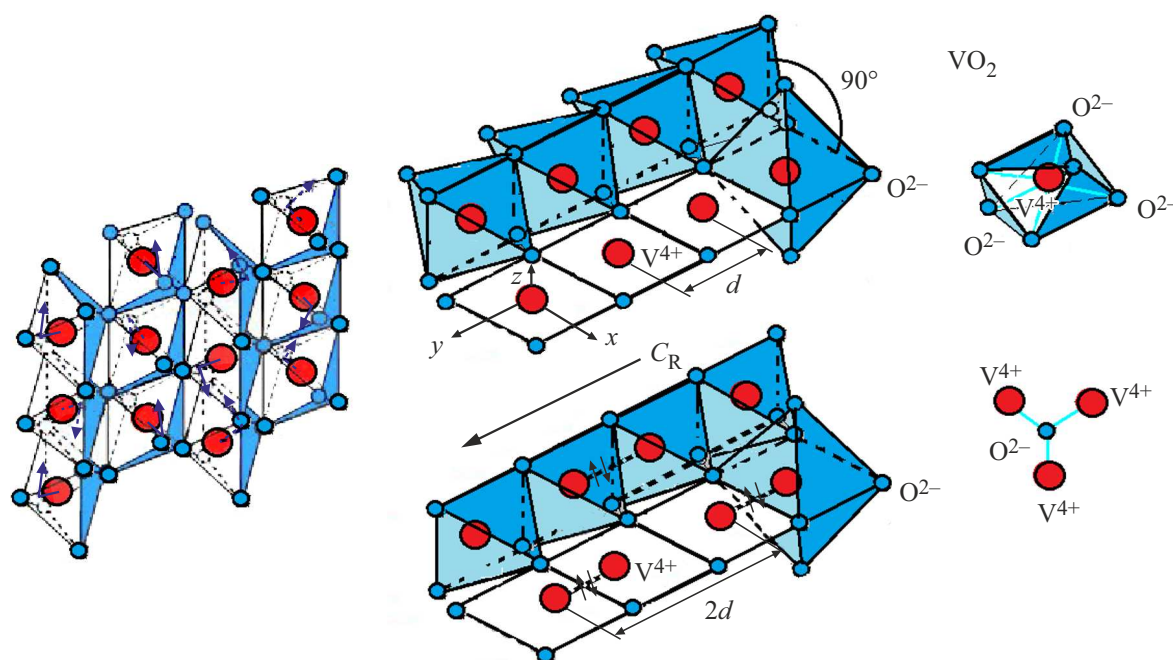
Figure 5. Fragment of crystal lattice of VO_2 in the tetragonal high-temperature metal phase (*a*) and in monoclinic low-temperature semiconductor phase (*b*).

takes place along with a higher coordination number of the oxygen ion and a lower symmetry of the crystal lattice. It follows from Table 2, that a V ion has six σ-bonds with O ions and all O ions have three σ-bonds with V ions. The

coordination number of the vanadium ion is 6, while that of the oxygen ion is 3.

So, as a result of the hybridization each V^{4+} ion forms six σ-bonds with six oxygen atoms, with each oxygen
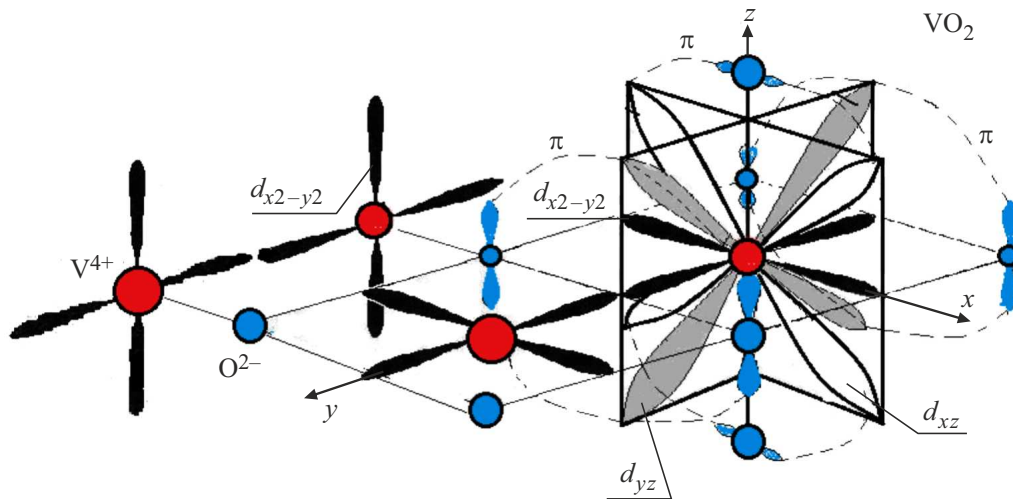
Figure 6. Scheme of not involved in the hybridization d-orbitals of the V^{4+} ion centered in the base of the oxygen octahedron of the VO_2 tetragonal phase.

atom having four hybrid orbitals. All vanadium atoms are located in centers of oxygen octahedra. The rest three $3d$-orbitals (d_{xz}, d_{yz} and d_{x2-y2}) of a vanadium atom with one electron belonging to them are not involved in the process of forming the framework of σ-bonds of the oxygen octahedron. All vanadium ions are located in the center of the octahedral oxygen framework that forms the crystal lattice (see Fig. 5). The lattice has tetragonal symmetry at a high temperature [12].

The only electron not involved in the formation of crystal framework of the V^{4+} ion is located on the d_{x2-y2} orbital (Fig. 4). At a high temperature, free electrons, due to the overlapping of these orbitals, provides for (along the „y" axis in Fig. 5, 6) metallic conductivity of the crystal. The d_{xz} and d_{yz} orbitals are free from electrons because they are higher than the d_{x2-y2}-orbitals in terms of their energy. The interaction of these orbitals with p_z-orbitals of O^{2-} ions creates donor-acceptor (coordination) π-bonds that form π and π^*-bands in the crystal. A π^*-pand in the monoclinic phase at a low temperature has almost no electrons and is separated from the nearest filled band by a gap of 0.7 eV. The π^*-band is a conduction band. d_{x2-y2} orbitals of neighboring V^{4+} ions are overlapped and at low temperatures form V-V-dimers, i.e. strong σ-bonds in a V-V-pair with two electrons with opposite spins. The presence of dimers at low temperatures results in lowering of the lattice symmetry from tetragonal to monoclinic. In the spectrum of VO^2 a $3d \parallel$ -band arises, which is split into two sub-bands at low temperature. The lower sub-band is almost completely filled with electrons and is a valence band of semiconductor, while the upper sub-band is almost empty and located much higher (~ 2.3 eV) than the Fermi level and higher than the π^*-band.

2.4. VO_x, $x = 2.5$ (vanadium pentoxide)

The situation for V_2O_5 is the most complicated one: it is characterized by 2 types of vanadium ions and 3 types of oxygen ions [13].

As can be seen from Table 2, in the case of V^{5+} ion three $4p^0(3)$ orbitals are not involved in the hybridization. This vanadium ion has <u>six</u> bonds with oxygen ions, that is its coordination number is equal to 6.

In the case of V^{4+} ion four $4s^2(1)4p^0(3)$ orbitals are not involved in the hybridization. This vanadium ion has <u>five</u> bonds with oxygen ions, that is its coordination number is equal to 5.

The hybridization of O ion is as follows: $[2s^2(1)2p^4(3)]$, i.e. it has 4 hybrid orbitals. This ion forms either 4 σ-bonds with V ions, or 3, or 2 σ-bonds. In the two latter cases one or two lone pairs are localized on hybrid orbitals of the O ion, which are given by the O ion to appropriate completely vacant orbitals of the V ion (see Fig. 7).

So, in the V_2O_5 crystal lattice near the 6-coordinated V^{5+} ion there is a 4-coordinated O ion bound with it, which, in turn, forms bonds of different types with three other 5-coordinated V^{5+} ions (Fig. 7). In addition, the V^{5+} ion is surrounded by three O ions as well, that form 3 σ-bonds with V^{5+} ions. And finally, this 6-coordinated V^{5+} ion is surrounded by two O ions with 4 hybrid orbitals. Two orbitals of this ion form σ-bonds with V^{5+} ions that do not lay on the same straight line, while the third and the fourth orbitals contain lone electron pairs fixed on them that „hang" in the crystal lattice.

For the 6-coordinated V^{5+} ion, five electrons are accounted for six hybrid orbitals involved in the formation of the crystal lattice framework, so one hybrid orbital remains empty. The electron-containing orbitals of the V^{6+} ion form σ-bonds with oxygen ions. The electron-free orbital accepts a lone electron pair of the oxygen ion forming a
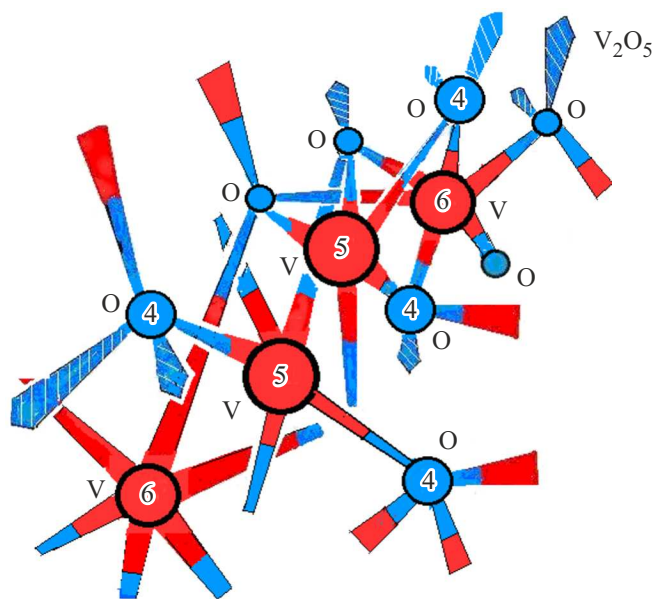
Figure 7. Fragment of the V_2O_5 crystal lattice with lone electron pairs on vacant hybrid orbitals of oxygen ions (shading).

donor-acceptor (coordination) bond. As it is shown above, the oxygen ion has four hybrid orbitals, one of which is the orbital that contains the lone electron pair given to the empty orbital of the V^{6+} ion. The second lone pair of the same oxygen ion is transferred to the empty orbital of the 5-coordinated V^{5+} ion. So, the oxygen ion with 4 orbitals forms two donor-acceptor bonds: one — with the 6-coordinated V^{5+} ion and another — with the 5-coordinated V^{5+} ion.

For the 5-coordinated V^{5+} ion (in contrast to the 6-coordinated V^{5+}) ion, three electrons are accounted for five hybrid orbitals involved in the formation of the crystal lattice framework, so two orbitals remain empty. One of them, as it is shown above, accepts a lone electron pair from the oxygen ion. The second empty orbital V^{5+} accepts one of the two lone pairs of the oxygen ion, which has 3 hybrid orbitals with one electron each and one orbital with a lone electron pair not involved in the framework formation. The last lone pair „hangs" in the V_2O_5 crystal lattice. These are the lone electron pairs responsible for the high electrical conductivity of vanadium pentoxide (similar to the sillenite crystal [13]). In addition, the presence of such lone electron pairs „hanging" inside the lattice is capable of forming a number of additional unusual optical, electrical and structural properties of the material.

3. The increase in band gap width of VO_x vanadium oxides and PT shift toward high temperatures with increase in x

The comparative analysis performed in this study for the properties of the Magneli series oxides is based on the successive arrangement of vanadium oxides in a series with increasing average number of oxygen atoms per one vanadium atom. In this case the following patterns are observed: the band gap width and critical temperatures of PT are monotonically increase with increase in x (Fig. 8).

Thus, the VO vanadium monoxide at low temperatures has metallic conductivity and transits to the semiconductor phase at a temperature below $T_c = 126$ K (Fig. 8, a), which is the lowest temperature in the above-mentioned series. In the V_2O_3 vanadium sesquioxide the semiconductor-metal PT takes place at a relatively low temperature of $T_c = 140$ K, which is, however, higher than that of VO. In the VO_2 vanadium dioxide the semiconductor-metal PT takes place at a high temperature of $T_c = 340$ K. And finally, the V_2O_5 vanadium pentoxide remains semiconductor with temperature increase for all levels that keep integrity of the crystal framework. For a band gap width E_g the following pattern takes place: for VO $E_g = 0.1$ eV, for V_2O_3 $E_g = 0.2$ eV, for VO_2 $E_g = 0.7$ eV, for V_2O_5 $E_g = 2.4$ eV (Fig. 8, b).

To analyze the described patterns and the weakening of metal properties of VO_x with increase in oxidation number **x**, which is related to them, let us consider details of phase transformations in the listed vanadium oxides.

4. Features of the electronic and structural phase transitions in VO_x ($x = 1, 1.5, 2, 2.5$)

The formation of dimers during synthesis of the crystal considered in section 2 is a prerequisite of the thermal structural PT in all vanadium oxides considered by us. If there are no dimers, the structural PT only takes place in the form of crystal melting at a high temperature, which is identified as the thermal point of phase transition of the material to another physical state. The generalized analysis of features of the phase transitions in VO_x oxides of the $x = 1, 1.5, 2, 2.5$ series should take into account the following well-known circumstances.

The system of energy levels of atoms during synthesis of a periodic crystal lattice is transformed to energy bands, of which the lower bands are filled with electrons in the case of insulator or semiconductor, while upper bands are empty, with an accuracy of the thermal factor. The highest filled band (the valence band) is separated from the nearest empty band (the conduction band) by an energy gap of E_g. With $E_g \rightarrow 0$ the material is approaching metal in terms of its properties, and with $E_g = 0$ the formed band turns to be partly filled with electrons. In principle, the formation of energy structure of both the valence band and the conduction band is contributed not only by energy levels of the crystal framework, but also by levels of the electrons not involved in the formation of the framework. In addition, the thermal and optical filling of bands with electrons in vanadium oxides results in a change of their position on
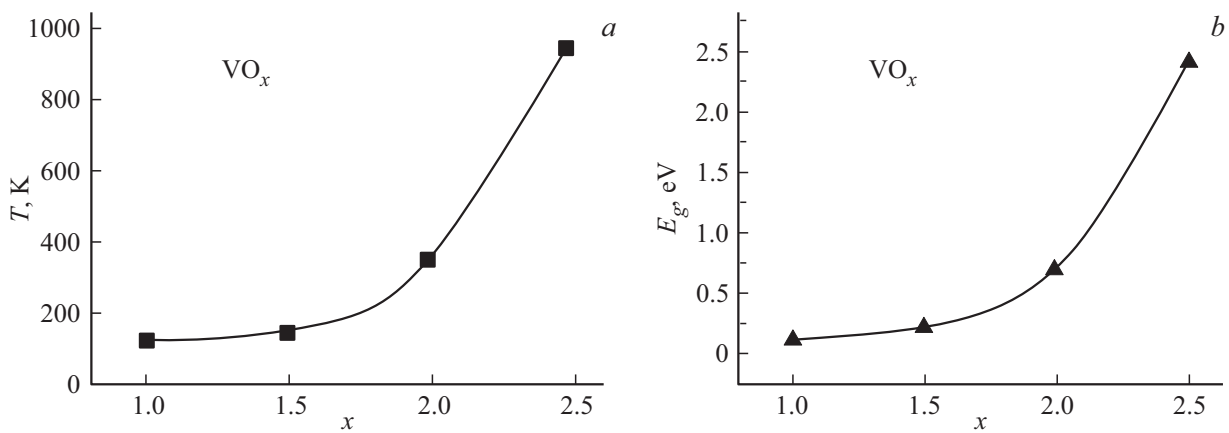
Figure 8. Temperatures of the semiconductor-metal PT (*a*) and widths of the band gap E_g (*b*) for VO$_x$ vanadium oxides ($x = 1$, 1.5, 2, 2.5).

the scale of energies up to $E_g = 0$, that corresponds to occurrence of a purely electronic PT of the second kind.

It is worth to note the Goodenough theory, which is important for the completeness of the analysis [14,15], with the following essential feature. A transition of vanadium oxides to the semiconductor state is accompanied by a step change in symmetry of the crystal lattice at a fixed temperature (PT of the first kind), which results in a drastic change in the band structure. In the vast majority of cases, at higher temperatures a structure with a higher symmetry is found, and at lower temperatures the structure is less symmetrical. Similar to the splitting of electron energy levels of isolated atoms by the crystal field, which is the leading principle of the Goodenough theory, a higher symmetry results in a stronger degeneration of the band structure in comparison to a lower symmetry. At the same time, a band partly filled with electrons at high temperatures (for example, the t_{2g} band for V [16]) forms metal properties of the crystal. Below the PT temperature this band is split into a filled and an empty energy bands. In the case if the filled and empty bands are separated by a nonzero energy gap, then any crystal of VO$_x$, being a metallic conductor at temperatures above the PT, becomes a semiconductor when the temperature is decreased below the PT point.

According to Goodenough, the preferred mechanism responsible for the crystal transition to a low-symmetry semiconductor state with temperature decrease is the following effect. The interaction with each other of the free electrons fixed at neighboring V atoms equidistant from each other that form metal properties of the material due to the spin correlation (i.e. the interaction of electron spins) disturbs the uniformity of the chain of equidistant atoms, splitting it into pairs of metal atoms bound to each other. A regular alternation of atom pairs with short and long gaps between them arises, which corresponds to doubling of the repetition period of the corresponding one-dimensional thermodynamic potential.

From the above follow non-trivial features of the structural and electronic PT in vanadium oxides. Let us consider

in detail these features for VO$_x$ crystals ($1 < x < 2.5$) in different temperature ranges.

4.1. $x = 1$. The range of low temperatures of the PT

Vanadium monoxide (VO), as it was already mentioned, has metal conductivity at room temperature. $3d_{xy}$ or $3d_{x2-y2}$-orbitals of the V^{2+} ion of neighboring octahedra, not involved in the formation of the crystal framework, have cruciform branches that can be overlapped with each other in a crystal with cubic symmetry of the lattice. Energy levels of each V^{2+} ion with one electron on each level are transformed during the crystal lattice formation to an energy band, which is half-filled with electrons (in accordance with the Pauli principle).

According to the data from literature vanadium monoxide, being a metal at room temperature, does not remain a metal with decrease in temperature, but performs the semiconductor-metal PT at $T_c = 126$ K [17–19].

In the process of building up the model of structural PT mechanism in VO it is reasonable to take as a guide the scheme, according to which, as it was noted above in section 1.1, the decrease in energy E_0 of the ground state with overlapping of $3d_{yz}$-orbitals is more important than that for $3d_{x2-y2}$-orbitals. It follows therefrom that π-dimers are formed in the VO during its transition to the semiconductor phase.

In addition, the height of the potential barrier between elements of the periodic potential of the linear chain (see formula (1)), that determines the transfer integral, with π-overlapping of cruciform branches is considerably lower than that in the case of the σ-overlapping (the barrier is lower — the transfer integral is higher). That is the step change in conductivity for π-dimers at a structural PT to the metal phase should be significantly higher in comparison to the σ-option of the structural PT.

This conclusion is confirmed by the presence of a quite low temperature of the thermal semiconductor-metal PT

in VO ($T_c = 120$ K) as compared to all vanadium oxides discussed in this study. In particular, in comparison to VO$_2$ [$T_c = 340$ K] [20], where formation of σ-dimers takes place with overlapping of d_{x2-y2}-orbitals (and not the π-dimers!). The point is that π-bonds have an order of magnitude lower energy of thermal destruction than σ-bonds [21]. In addition, due to the high conductivity of metal phase, the conductivity step in VO is significantly higher (7 orders of magnitude) than that in VO$_2$ (5 orders of magnitude at $T_c = 340$ K) [12]. The same takes place in V$_2$O$_3$ (7 orders of magnitude at $T_c = 140$ K) [12].

If pairing takes place along one of dedicated directions, then in the course of π-dimers formation a structural PT takes place with a strong lowering of the crystal lattice symmetry due to the one-dimensional nature of the pairing direction [22]. The structural PT in the whole crystal takes place upon achievement of the critical concentration of formed pairs, after which the process of pairing is expanded onto the entire volume of the nanocrystallite due to the collective character of wave functions that describe the behavior of both non-interacting and strongly correlated electrons in the periodic field of the lattice [23]. If in different points of the monocrystal there are one-dimensional stress fields oriented in a chaotic way (for example, near defects in the form of impurities or points of nonstoichiometry), then a formation of separate do-mains with different orientation of dimers is possible in the macroscopic free monocrystal of VO. However, the experiment shows that due to the interaction of stress fields of defects the domains nearly always turn to be oriented in one crystallographic direction. Results of this kind of experiments are presented in scientific literature [24].

It is worth reminding that to realize a PT at $T_c = 126$ K, the $kT_c = 10$ meV energy of phonons turns to be in-sufficient to overcome the gap of $E_g = 0.1$ eV (such an overcoming is necessary to realize a structural PT: $kT_c = 10 \leq E_g = 100$ meV). Therefore, to make the follow-ing step to identify the mechanism of PT process, it is necessary to use the idea of Mott [25], according to which the formation of the PT mechanism model should take into account the multiparticle interaction, i.e. the interaction between electrons themselves — the correlation interaction. The consideration to correlation effects is achieved by in-troducing a correlation energy into the electron distribution function, along with the Fermi energy, therefore instead of the Fermi distribution the Migdal distribution arises [26], which energy „tails" are at least an order of magnitude wider than „tails" of the Fermi distribution, that ensures an effective thermal transfer of electrons over the band gap. Thanks to the correlation effects, the lower Hubbard subband, performing the functions of valence band, pops up, while the upper band (the conduction band) becomes lower in terms of energy with increase in T, zeroing the width of E_g immediately before the structural PT takes place (before the Peierls transition). At the same time the decrease in band gap width is not accompanied by a change in the crystal lattice symmetry.

Thus, a non-trivial feature of the semiconductor-metal PT in VO, as well as in other VO$_x$ oxides, is the complex character of the PT: two transitions take place — an electronic (the second kind) and a structural (the first kind) transitions, with the structural transition initiated by the electronic transition.

4.2. $x = 1.5$. The range of low temperatures of the PT

The vanadium sesquioxide (V$_2$O$_3$) at room temperature also is a metal with a rhombohedral symmetry of the lattice that transits to the semiconductor phase at 140 K. With $T < T_c = 140$ K π-dimers arise, which lower the lattice symmetry from rhombohedral to monoclinic. Since π-dimers have lower energy „strength" than σ-dimers, that present in the crystal lattice of both semiconductor and metal phases, then these are the dimers that are destroyed in the reverse heating process of the semiconductor phase up to a temperature of $T > T_c$, that is a reverse structural PT takes place. As it is shown in Fig. 4, c, π-bonds form along the C_R crystal axis a zigzag-shaped chain, along which the metallic conductivity of rhombohedral phase is formed. The period of chain in the metal phase is d, and in the semiconductor phase it is $2d$. This is a description of the Peierls structural PT, and it explains the fact that PT in the V$_2$O$_3$ takes place at a low temperature ($T_c = 140$ K). However, an explanation is required for the fact that in the above-described VO crystal the PT takes place at a lower temperature (126 K), despite the presence of the above-mentioned V — σ-dimers in the VO crystal.

The cause of this fact consists in that, as known [8], the band gap width of the semiconductor phase of the V$_2$O$_3$ is equal to $E_g = 0.2$ eV, in contrast to the $E_g = 0.1$ eV for the VO. Here, as well as in the VO, the thermal energy of $kT_c = 0.026$ eV, that corresponds to the temperature of 140 K, is insufficient to thermally initiate the structural transition. However, the transition takes place due to the correlation effects and, in particular, the replacement of the Fermi distribution with the Migdal distribution. Thus, the semiconductor-metal PT in the V$_2$O$_3$ compound is of a complicated nature as well: a Mott electronic transition initiates a Peierls structural transition.

4.3. $x = 2$. The range of medium temperatures of the PT

The vanadium dioxide (VO$_2$) at room temperature is a semiconductor with a band gap width of $E_g = 0.7$ eV. The only electron not involved in the formation of the crystal framework is located in the VO$_2$ on the d_{x2-y2}-orbital, that has cruciform branches in the plane of the V-O octahedron base. These orbitals promote the arising of metal type bonds in the one-dimensional chain of vanadium atoms along the C_R tetragonal axis. The metallic conductivity remains at temperatures of $T \geq 340$ K (67°C). However, at

a temperature of $T < T_c = 340$ K the vanadium dioxide becomes a semiconductor with a monoclinic symmetry of the lattice, because at $T < T_c = 340$ K V-V-dimers are formed due to the formation of σ-bonds between d_{x2-y2}-orbitals of V ions of neighboring octahedra. Therefore, the model of physical properties of the one-dimensional V-V chain becomes more complicated with the idea of σ-bonds formation at $T < T_c = 340$ K. These are the bonds that lower the symmetry of the crystal lattice from tetragonal to monoclinic. The period of lattice along the chain is doubled, i.e. a structural PT (a Peierls transition) takes place with the $3d \parallel$ -band split into two subbands, and in the energy spectrum a gap of $E_g = 0.7$ eV forms (the band gap). The lower subband is completely filled with electrons, the upper subband is almost empty (with an accuracy of thermal transfer of electrons over the band gap). The experiment confirms the fact that at $T > T_c$ a PT from semiconductor to metal state takes place despite the phonon energy close to kT is insufficient at $T_c = 340$ K to overcome the gap of $E_g = 0.7$ eV, which is necessary for destruction of dimers. At this stage it is necessary, as in the cases of VO_2 and V_2O_3, to use the idea of Mott [25], which stipulates the need to take into account the multiparticle interaction (the consideration to correlation effects). In this case, as before, instead of the Fermi distribution the Migdal distribution is used, which, in addition to the Fermi energy, includes the correlation energy and has its „tails" at least an order of magnitude wider that „tails" of the Fermi distribution. This ensures an effective transfer of electrons over the band gap. The ab initio calculations for VO_2 [27] have shown that the correlation effects cause make lower the conduction band as it is filling with electrons, and at $T = 340$ K a collapse of the band gap takes place, i.e. it becomes $E_g = 0$. The decrease in E_g promotes the destruction of V-V-dimers. Thus, a Mott electronic transition initiates a Peierls transition. It should be noted that the Mott electronic transition determines the superfast (100 fs) response of vanadium dioxide to the optical transfer of electrons from the valence band to the conduction band in the experiments of femtosecond spectroscopy. The structural transition takes place over a longer time of about several picoseconds [28]. Different response times make it possible to identify the pure electronic component of the PT and unambiguously confirm the need for consideration to the correlation effects when building up the model of phase transition mechanism in oxides of strongly correlated compounds.

4.4. $x = 2.5$. The range of high temperatures of the PT

The vanadium pentoxide (V_2O_5) at room temperature is a semiconductor with an „optical" band gap width of $E_g = 2.4$ eV. No structural PT for this oxide has been found. However, a large number of lone electron pairs accounted for a lattice cell forms an absorption shoulder in the transparency region of the crystal. Transmission spectra demonstrate [29] the presence of such a shoulder, which

causes the dark-yellow color of the oxide. In addition, the high sensitivity of methods used to measure the electrical conductivity of the crystal made it possible to report a E_g less than it was assumed before. It follows from this that the width of „electrical" band gap or „optical" band gap for the light with low absorption coefficient k is less the presented value of $E_g = 2.4$ eV [13,30]. Nevertheless, this value is greater than one eV. The experiment shows the presence on an intensive transfer of electrons to the conduction band even at relatively low temperatures $(300-450$ K), that can be only explained by the replacement of Fermi distribution with Migdal distribution. And since the vanadium pentoxide (V_2O_5) is an oxide of strongly correlated element (V), then in this case an increase in temperature also causes a narrowing of the semiconductor band gap, as it is expected for a compound of strongly correlated element. Thus, in the V_2O_5 with increase in temperature a pure Mott electronic PT takes place as well, however without achievement of collapse of the semiconductor band gap [31].

Summarizing this section, it is worth to note that as the numerical value of the x index grows, the oxygen ions in the structural formula of VO_x „bind" ever-growing portion of the electron density of vanadium ions, specifically the electrons that are free from the stabilization of the lattice framework and that provide the metal phase conductivity. This makes difficult, as x increases, the arising of metallic conductivity with temperature growth for the members of the above-mentioned series, finally excluding at all the presence of electrical conductivity in the ground state at $x = 2.5$ (V_2O_5). Indeed, at temperatures above T_c for VO the electrical conductivity is possible in all crystallographic directions, for V_2O_3 — along the zigzag-shaped chain, for VO_2 — only along the linear chain, for V_2O_5 it is impossible at all. All the described features are caused by the structure of the crystal lattice, as it follows from the above discussion.

It is worth to note that the crystal lattice structure of V_2O_5, the ultimate vanadium oxide $(x = 2.5)$, is such that all electrons not involved in the stabilization of the crystal framework are paired and at any configuration they do not create conditions for formation of a half-vacant energy band, which could provide the arising of metallic conductivity.

5. Conclusions

The presented analysis makes it possible to conclude the following.

1. The identification of the connection between the hybridization of atom orbitals of vanadium and oxygen ions and the structure of the VO_x crystal lattice made it possible to establish the presence of orbitals that contain electrons not involved in the formation of the crystal framework, but responsible for both the metal phase conductivity and the formation of dimers of the semiconductor phase arising after the structural PT.

2. Vanadium oxides inherit the correlation properties of the oxydated chemical element — vanadium, specifically

the circumstance that the energy position of electron bands in crystals is strongly dependent on the degree of filling of these bands with electrons. This dependence is manifested not only in the presence of the superfast anhysteretic Mott transition, which is a pure electronic PT, but also in the fact that this transition initiates realization of a more inertial Peierls transition, which is a structural PT and has a thermal hysteresis.

3. As the degree of vanadium oxidation increases in VO_x compounds (growth of the x index from 1 to 2.5) metal properties of oxides become weaker, which is accompanied by an increase in width of the band gap and a growth of the semiconductor-metal PT temperature.

4. In VO and V_2O_3, with the transition to the semiconductor phase the formation of π-dimers takes place, which strength is approximately an order of magnitude lower than that of σ-dimers in VO_2 arising here with the transition to the semiconductor phase. Therefore, PT temperatures in VO and V_2O_3 (120 and 140 K) are lower than in VO_2 (340 K).

Conflict of interest

The authors declare that they have no conflict of interest.

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