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Semiconductor-metal phase transition in oxides of Magneli series: VO and V_2O_3

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A comparative analysis of the physical parameters of strongly correlated oxides VO and V_2O_3 has been carried out. It has been established that the semiconductor–metal phase transition in both VO and V_2O_3 has a complex Mott-Peierls character. Namely, as the temperature increases in both oxides, before the Peierls abrupt structural phase transition, the Mott phase transition, which is extended in temperature, take place. It has been discussed the reason for the fact that, despite the stabilization of the semiconductor phase by high-strength π-dimers or σ-dimers, the temperatures of phase transitions are low ($T_c = 126\,\mathrm{K}$ (VO) and $T_c = 140\,\mathrm{K}$ (V_2O_3)).

Keywords: Magnelis series, phase transformations, electron-electron correlations.

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1. Introduction

In this study, a consistent consideration of the physical properties of two oxides of the Magneli series was carried out: vanadium monoxide VO and vanadium sesquioxide V_2O_3. These oxides differ significantly from each other in their physical parameters and have a different structure of the crystal lattice. Nevertheless, they also have common properties, the identification of which is devoted to this article.

Vanadium monoxide (VO) is first considered. It has a face-centered cubic structure, for which a scheme for hybridization of atomic orbitals of vanadium and oxygen ions is formulated, ensuring the stability of the crystal lattice due to σ-bonds between V and O ions. It turns out the possibility of making a phase transition (PT) semiconductor–metal.

Based on the formulated hybridization scheme, there being clarified the mechanisms of formation of such vanadium monoxide parameters, as

1) symmetry of the crystal lattice;

2) mechanisms of electronic and structural PT semiconductor–metal;

3) the atypical course of the temperature dependence of the electronic conductivity of the metallic phase.

After that, the method of hybridization of atomic orbitals is applied to vanadium sesquioxide — V_2O_3, the crystal lattice of which has a lower symmetry (rhombohedral in the metallic phase and monoclinic in the semiconductor phase). It has been shown that vanadium sesquioxide performs a semiconductor–metal PT at a temperature higher than vanadium monoxide.

For both oxides, it has been established that the reason for the existence of atypical properties of both VO and V_2O_3 are the correlation effects inherent in the transition metal oxides — vanadium.

2. Vanadium monoxide

Vanadium monoxide (VO) has a cubic face-centered crystal lattice of the NaCl type. Vanadium and oxygen octahedra are clearly distinguished, in the centers of the bases of which there are vanadium ions (oxygen octahedron) and oxygen ions (vanadium octahedron) (Fig. 1, *a*). All octahedra can be distinguished with the directions of their axes in three mutually perpendicular directions, while having three equivalent bases. The bases of oxygen octahedra in these cases are parallel to the planes xy, xz and yz (Fig. 1, *a*).

All vanadium ions V^{2+} have 6 σ-bonds with oxygen ions O^{2-}, all O^{2-} ions also have 6 σ-bonds with ions V^{2+}.

The following configuration of hybrid atomic orbitals of V^{2+} and O^{2-} ions meets the described situation:

$$[\mathrm{Ne}]3s^2(1)3p_x^2(1)$$

$$\times[3p_y^2(1)3p_z^2(1)3d_{z2}^1(1)3d_{xy}^1(1)4s^2(1)3d_{xz}^0(1)]3d_{yz}^0(1)3d_{x2-y2}^1(1)$$

for V^{2+} and

$$1s^2(1)2s^2(1)[2p_x^1(1)2p_y^1(1)2p_z^2(1)3s^0(1)3p_x^0(1)3p_y^0(1)]$$

for O^{2-}.

The numbers in parentheses represent the number of orbitals involved in hybridization, the numbers without parentheses indicate the numbers of the electron shells, the superscripts indicate the numbers of electrons fixed in the formation of σ-bonds. For each σ-bond, the V^{2+} ion gives an average of 4/3 electron density, the O^{2-} ion for every σ-bond gives 2/3 electron density. In this scheme,

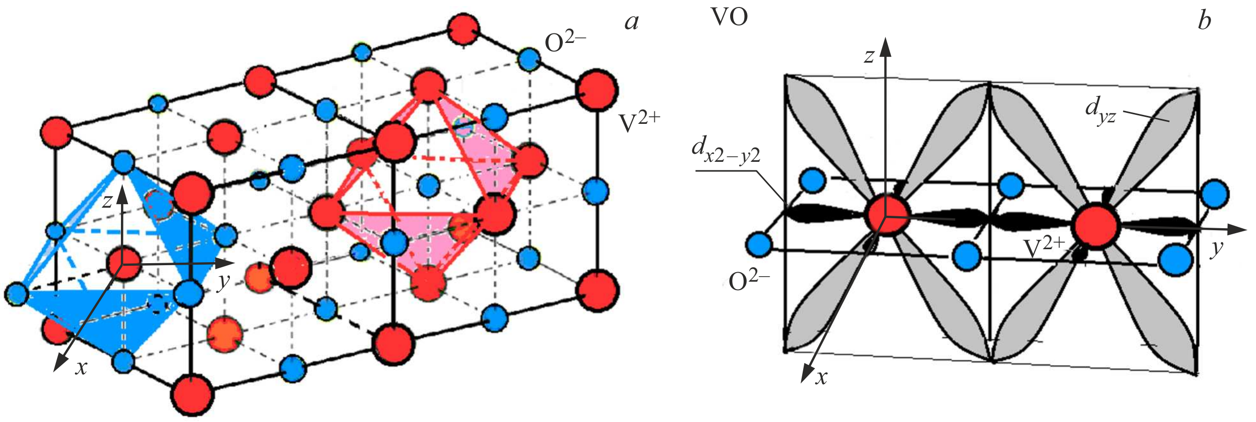

Figure 1. a — fragment of the cubic crystal lattice of VO; b — one of the three orbital arrangements d_{yz} and d_{x2-y2} of the two adjacent ions V^{2+}.

each σ- bond has, as the theory prescribes, $4/3 + 2/3 = 2$ electrons. The configuration formula of orbitals V shows that of the 5 orbitals of $3d$-shell of the V^{2+} ion, two orbitals $3d^0_{yz}(1)$ and $3d^1_{x2-y2}(1)$ do not participate in the formation of σ-bonds. At the same time, in the oxygen ion, all orbitals of $2p$-shell containing electrons participate in the formation of a crystalline framework and therefore cannot form any bonds with free orbitals $3d^0_{yz}$ and $3d^1_{x2-y2}$ of V ion.

In the above configuration, the free orbital $3d^1_{x2-y2}$ contains one electron. Orbital $3d_{yz}$ contains no electrons. But it can be argued that one free electron is equally occupied by the orbital $3d_{yz}$, while the orbital $3d_{x2-y2}$ remains empty. This means that these two orbitals together account for one electron.

As shown in Fig. 1, the cubic crystal structure of VO leaves the possibility for $3d_{yz}$ and $3d_{x2-y2}$ orbitals of V ions to overlap with similar orbitals of the nearest V ions of octahedra located along one of the three mutually orthogonal diagonals of the cube faces. Figure 1, b presents one of the three possible options for overlapping orbitals along the axis y, namely, orbitals $3d_{x2-y2}$ in the plane xy and simultaneously orbitals $3d_{yz}$ in plane yz.

Each pair of such overlapping orbitals is capable of forming chains of σ- or π-bonds along the diagonals of the cubes. However, each bond must contain, according to the rules, two electrons. It follows that only one of the orbitals $3d_{yz}$ or $3d_{x2-y2}$ can participate in the creation of any bonds: real in the semiconductor phase or dynamic in the metallic phase, created and broken during one period of phonon oscillations. Thus, linear chains of bonds directed along the diagonals of the faces of the cubes of elementary cells arise.

The Schrödinger equation for a linear chain of potential peaks with a Hamiltonian, which takes into account the interaction of ions only with the nearest neighbors, allows for an exact solution [1]. In accordance with the theory, when a connected chain of ions is formed, the transformation into an energy zone of a single energy level of an isolated atom occurs in such a way that the energy decreases by the value of the orbital overlap integral and blurs into a zone four integrals wide of electron transfer between neighbors. Electrons of $3d$-orbitals occupy the lowest states and, according to the Pauli principle, occupy half of the levels of the zone. The second half remains free in the same way as it is in ordinary metal. It follows that in the presence of dynamic bonds that break twice in one period of phonon oscillations, the period of potential peaks is equal, by virtue of symmetry, to the distance between the V ions in the chain. In the semiconductor phase, the period is doubled when stable dimers are formed.

For the periodic breaking of the dynamic bonds of the metal phase, it is necessary to exceed the energy of breaking the bonds with thermal energy kT, which is possible only starting from some critical temperature T_C. At this temperature, a structural transition is made from the semiconductor to the metallic phase (when heated) and back (when cooled).

The theory states that the overlapping orbitals of the ions of the linear V chain form an energy zone consisting of the upper and lower Hubbard subzones [2], containing each half of the levels of the entire zone. In the metallic phase (i.e. when $T > T_C$), the subzones are adjacent to each other. The lower subzone according to the Pauli principle (2 electrons at each level) is filled with electrons completely, since the orbital forming the zone contains only one electron, and the number of levels is equal to the number of peaks of the ion chain potential. The upper subzone remains empty. At $T < T_C$, neighboring vanadium ions are combined into pairs (dimers). This corresponds to the structural metal–semiconductor PT. Dimers bind free electrons, and the symmetry of the crystal lattice is reduced to a distorted cubic one by shortening the diagonal of one of the faces of the cube of the unit cell.

The experiment demonstrates the performance of metal–semiconductor PT in VO at $T_c = 126\,\mathrm{K}$, while the E_g of the material is $E_g = 0.17\,\mathrm{eV}$. The simplest calculation shows that at $T_c = 126\,\mathrm{K}$, the thermal energy is much less E_g ($kT_c = 0.01\,\mathrm{eV} \ll E_g$), which should exclude the thermal break of the real σ-bonds of the semiconductor phase dimers. The experiment, however, convinces that the thermal energy $kT_c = 0.01\,\mathrm{eV}$ is sufficient to break the σ-bonds and the emergence of free electrons in the conduction band.

This is because vanadium oxides are highly correlated materials. In such materials, electrons obey not Fermi statistics, but Migdal statistics [3,4], which provides an order of magnitude more efficient thermal transfer of electrons through the energy gap. At the same time, correlation effects narrow the band gap to almost zero in response to an increase in the electron occupancy of the conduction band of the semiconductor, preparing the ground for the commission of structural PT. Thus, there is positive feedback between the increase in the occupancy of the conduction band and the narrowing of the band gap.

According to the theory of molecular orbitals [5], σ-bonds provide a greater energy gap between the binding and loosening orbitals than π-bonds. This means that the binding orbital of σ-bond $3d_{x2-y2}$–$3d_{x2-y2}$ is lower in energy than the binding orbital of π-bond $3d_{yz}$–$3d_{yz}$. Therefore, σ-bond $3d_{x2-y2}$–$3d_{x2-y2}$ occupies the only free electron in the $3d_{x2-y2}$ and $3d_{yz}$ orbitals.

When dimers are formed (both dynamic in the metallic phase and real in the semiconductor phase), the convergence of V ions of neighboring octahedra increases the overlap simultaneously of two branches of neighboring $3d_{x2-y2}$ orbitals, and four branches of neighboring $3d_{yz}$ orbitals, since both orbitals are rigidly bound to V ion. In VO, the energy zone that arose during the expansion of the level of the binding orbital $3d_{yz}$–$3d_{yz}$ of σ-bond is located in energy above the analogous zone of $3d_{x2-y2}$–$3d_{x2-y2}$ of σ-bond, although the gap between them is small. This gap is determined by the uneven overlapping regions of the branches $3d_{yz}$ or $3d_{x2-y2}$ orbitals of V ions of neighboring octahedra [5]. It follows that the binding zone $3d_{yz}$–$3d_{yz}$ of σ-bond, being free of electrons (with accuracy to thermal casting) and located above a similar zone of σ-bond, plays the role of a conduction band of the semiconductor phase of VO. It is separated, as shown by the experiment [6], from the binding orbital $3d_{x2-y2}$–$3d_{x2-y2}$ of σ-bond by a gap 0.17 eV.

A similar situation is realized in the crystal V_2O_3 for its semiconductor phase: there is an energy gap between the binding $3d_{xz}$–$3d_{x'z'}$ and $3d_{yz}$–$3d_{yz}$ bands, equal to $E_g = 0.3\,\mathrm{eV}$, with the empty binding $3d_{yz}$–$3d_{yz}$ band acting as a conduction band (see below).

Thus, the PT in VO is complex, consisting in the fact that when the temperature rises, the jump-like structural Peierls PT of the first kind is preceded by the temperature-extended Mott PT of the second kind.

3. Vanadium sesquioxide

Vanadium sesquioxide (V_2O_3) has at room temperature the rhombohedral symmetry of the crystal lattice. Similar to VO, all vanadium ions are located in the base centers of oxygen octahedra. However, in the crystal lattice V_2O_3 for every two oxygen octahedra containing vanadium ions, 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. 2). The figure shows that each V^{3+} ion forms six σ-bonds with six O^{2-} ions, and each O^{2-} ion creates four σ-bonds with V^{3+} ions.

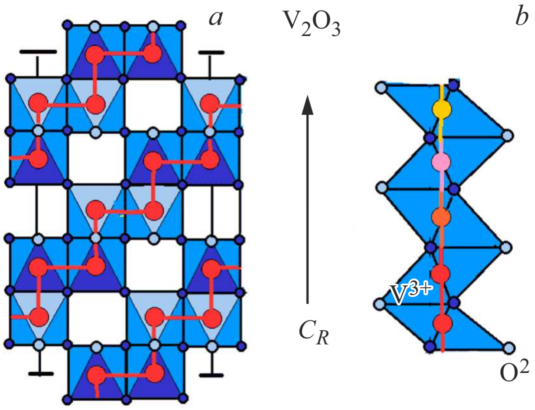

Figure 2. The fragment of the crystal lattice V_2O_3 in the metallic phase. (*a*) The relative position of V^{3+} ions in the „corrugated“ layer consisting of oxygen octahedra (σ-dimers are not shown). The electrical conductivity along the zigzag chain is due to the dynamic σ-bonds between vanadium ions. (*b*) Projection of a zigzag chain on the plane *XZ*.

The following configuration of the hybrid orbitals of the V^{3+} and O^{2-} ion orbitals meets this situation:

$$[\mathrm{Ar}][3d^1_{xy}(1)3d^0_{z2}(1)4s^2(1)4p^0(3)]3d^1_{xz}(1)3d^0_{yz}(1)3d^1_{x2-y2}(1)$$

for V^{3+} and

$$1s^2(1)[2s^2(1)2p^1_x(1)2p^1_y(1)2p^2_z(1)]$$

for O^{2-}.

In square brackets are the orbitals involved in the formation of σ-bonds of the crystal lattice framework. It can be seen that the three orbitals $3d^1_{xz}(1)$, $3d^0_{yz}(1)$ and $3d^1_{x2-y2}(1)$ for the V^{3+} ion do not participate in the formation of σ-bonds. For six σ-bonds of the crystalline framework, the V^{3+} ion gives off 3 electron, that is, 1/2 electron density per one σ-bond. Each V^{3+} ion of the 5 electrons of the upper shells ($3d$ and $4s$) remain unoccupied in the formation of the crystalline framework of the 2 electron. The O^{2-} ion gives all 6 of its electrons of the upper shells (there are no unoccupied ones) to form the framework, that is, 3/2 electron density. Thus, each σ-bond as a whole has, as expected, $1/2 + 3/2 = 2$ electrons.

So, the unoccupied in hybridization orbitals $3d^1_{xz}(1)$, $3d^0_{yz}(1)$ and $3d^1_{x2-y2}(1)$ of V^{3+} ion contain, as indicated above, the remaining two electrons. One of them is located at $3d^1_{x2-y2}(1)$ orbital, the second is distributed between $3d_{xz}$ and $3d_{yz}$ orbitals. The reason for this distribution of electron density is that the electrons of $3d^1_{x2-y2}(1)$ orbitals

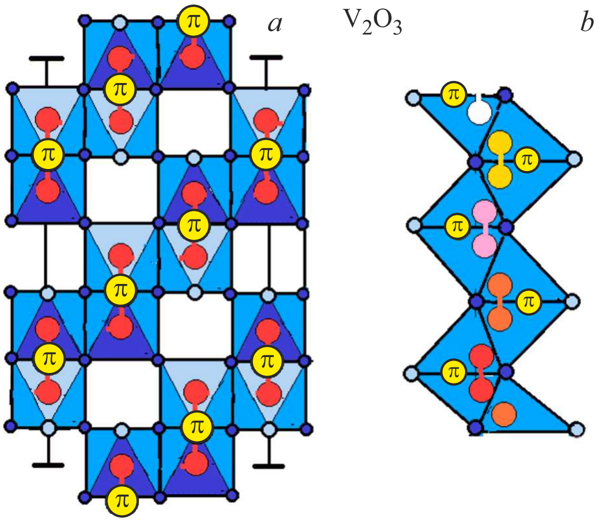

Figure 3. The fragment of the crystal lattice V_2O_3 in the semiconductor phase. When $T < T_c$, π-dimers bind free electrons arise and a structural PT occurs. As a result of the formation of π-dimers, vanadium ions leave the base planes of the octahedra and pairwise converge (a); vanadium ions, previously „obscured“ when the zigzag chain is projected onto the plane XZ, become „visible“ (b).

create a strong σ-bond between two adjacent V^{3+} ions of neighboring oxygen octahedra. This means that the electrons of $3d^1_{x2-y2}$ orbitals form strong σ-dimers from a pair of neighboring V^{3+} ions. Their integrity up to a temperature much higher than $T_c = 140\,K$ is due to the fact that to each pair of oxygen octahedra with V^{3+} ions on both sides there are empty octahedra that do not contain V ions and therefore do not distract $3d^1_{x2-y2}(1)$ orbitals from the creation of dynamic σ-bonds in the metallic phase like the crystal VO_2 [7].

The orbitals $3d_{xz}$ and $3d_{yz}$, which are not used in the formation of the lattice framework, contain the only electron that is additional to $3d^1_{x2-y2}(1)$ orbital. These $3d_{xz}$ and $3d_{yz}$ orbitals overlap with the same orbitals of neighboring vanadium ions, creating dynamic π-bonds in the metallic phase. In the semiconductor phase, there are not dynamic, but full-fledged π-bonds that form π-dimers by analogy with σ-dimers in VO_2 [7]. A zigzag chain of interconnected vanadium ions is formed, according to which, at a temperature exceeding $T_c = 140\,K$, metallic conduction is carried out (Fig. 2), however, when the temperature drops below $T_c = 140\,K$, neighboring vanadium ions are combined into pairs (π-dimers) due to the formation of thermally indestructible π-bonds between them (Fig. 3). This is how a structural metal–semiconductor PT in vanadium sesquioxide is made. Dimers in their formation deprive free electrons of mobility, and the symmetry of the crystal lattice decreases from rhombohedral to monoclinic.

The experiment shows (Fig. 4) that the metal–semiconductor PT is performed at a temperature of $T_c = 140\,K$, and the width of band gap in the semiconductor phase $E_g = 0.3\,eV$. Therefore, at 140 K, the thermal energy $kT = 0.026\,eV$ is a value insufficient for thermal initiation, as in VO, of structural PT due to the transfer of electrons from the valence band to the conduction band (which is accompanied by the destruction of a certain proportion of dimers). Here again, we point out that when interpreting the fact of performing PT, it should be borne in mind that vanadium oxides are highly correlated materials. They are characterized by a strong dependence of the energy position of the zones on the electrons occupancy. In the case of V_2O_3 during thermal colonization of the conduction band with electrons, the band of conduction narrowing occurs, as in VO, by narrowing of the band gap when it is occupied by electrons and raising the energy of the valence band when it is depleted by electrons. In the crystal V_2O_3 electrons obey the statistics of Migdal, „tails“ states of which are at least an order of magnitude higher than those for Fermi statistics. This gives an effective transfer of electrons through the conduction band, ensuring the destruction of the critical proportion of dimers and, thereby, the performing semiconductor–metal PT.

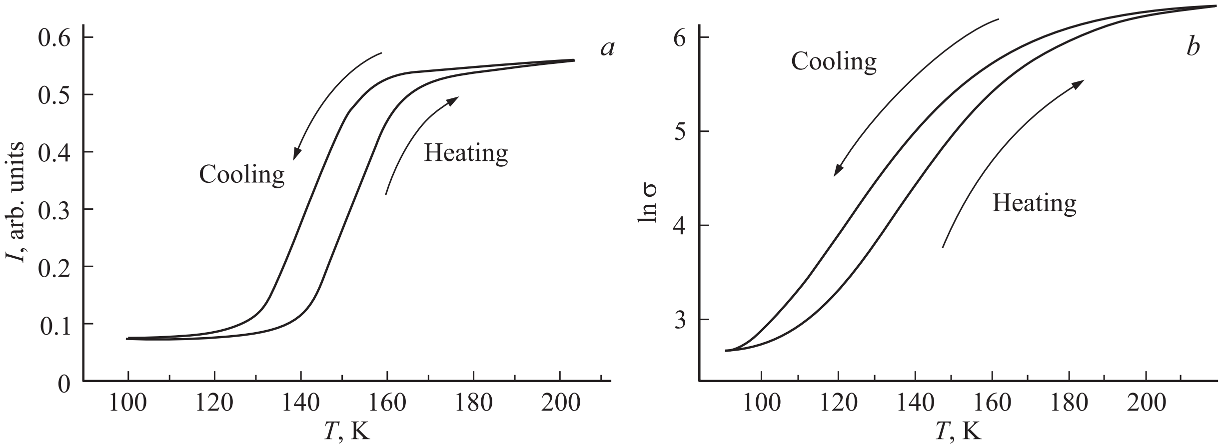

Figure 4. The tapes of thermal hysteresis of transmission I (a) and electrical conductivity σ (b) with semiconductor–metal PT in films V_2O_3.

Thus, the PT in V_2O_3 is, as in VO, complex in nature, consisting in the fact that when the temperature rises, the jump-like structural Peierls PT of the first kind is preceded by the temperature-extended Mott PT of the second kind.

4. Conclusion

Thus, the comparative study shows that, despite the differences in the considered vanadium oxides in the structure of the crystal lattice, they have common parameters that play a fundamentally important role in the algorithm for the formation of the physical properties of the material. These include: the high dark electrical conductivity of both oxides, the presence of a structural Peierls PT in them, as well as the presence of an electron hysteresis-free Mott PT preceding it. Both oxides are characterized by the fact that the metal–semiconductor PT is made at relatively low temperatures ($T_c = 126\,\mathrm{K}$ (VO) and $T_c = 140\,\mathrm{K}$ (V_2O_3)), despite the fact that in both oxides the lattice in a lowly symmetrical state is stabilized by high-strength π-dimers or σ-dimers.

The reason for this situation lies in the fact that, although high-strength dimers form the upper and lower Hubbard subzones, the energy gap between which, according to the theory, is at least $2-2.5\,\mathrm{eV}$ [8], in all vanadium oxides (with the exception of V_2O_5) the upper Hubbard subzone does not play the role of a conduction band. The role of the conduction band is played either by the loosening orbital V-O of π-bond (VO_2) or the binding orbitals V-V of π-bonds (for VO and V_2O_3), which are not related to dimers.

The results obtained show that in both VO and V_2O_3 the semiconductor–metal PT has a complex Mott-Peierls character, consisting in the fact that in both oxides, with an increase in temperature, the discontinuous structural Peierls PT of the first kind is preceded by an extended according to the temperature of Mott PT of the second kind.

Conflict of interest

The authors declare that they have no conflict of interest.

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