

Conductive properties of Magneli series oxides: VO and V₂O₅

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A comparative analysis of the electrically conductive properties of strongly correlated oxides: vanadium oxide VO and vanadium pentoxide V₂O₅, belonging to opposite ends of the Magneli series, is carried out. It is shown that, despite the radical difference in the symmetry of the crystal lattices of these compounds, these materials have a number of fundamental common properties, the main of which are the dependence of the width of the energy gap (gap band) on the occupation of the conduction band by electrons and the occurrence in both compounds of an electronic Mott transition extended in temperature. It is shown that vanadium pentoxide is a classic Mott insulator.

Keywords: vanadium oxides, phase transition, electronic correlations.

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The paper focuses on physical properties of two oxides of the Magneli series: vanadium oxide — VO and vanadium pentoxide — V₂O₅. These oxides belong to opposite ends of the Magneli series and have a different structure of the crystal lattice. But these oxides have a number of common properties to be revealed in the present article. The set goal is achieved by considering a simple object at the first stage — vanadium oxide (VO), having a face-centered cubic lattice [1]. It will be not difficult to analyze a configuration of hybrid orbitals of ions both of vanadium and oxygen as well. The configuration of the orbitals determines a structure of the crystal lattice and an unusual dependence of the electron metal conductivity of the crystal on the temperature. Analysis of the configuration of the hybrid orbitals clearly explains a fact of the electron and structure phase transition (PT) „semiconductor-metal“ in VO.

At the second stage, the above-described standard analysis method is carried to the vanadium pentoxide (V₂O₅), which has a more complex structure of the crystal lattice. The application of the said method allowed finding out why V₂O₅ (unlike VO) is a semiconductor at all the temperatures up to a crystal melt point, and explaining why there is no structure phase transition in V₂O₅. The authors demonstrated that electric conductivity of V₂O₅ is unusually greatly increases with increase in the temperature (in comparison with typical semiconductors). A fact of great thermal increase in the conductivity indicates that the V₂O₅ is having an electronic Mott phase transition extended in temperature. The V₂O₅ crystal conductivity is close to a metal state, but without changing the symmetry of the crystal lattice. The authors have ascertained that a main reason of the unusual properties of VO and V₂O₅ are correlation effects, which are typical for oxides of a transition metal — vanadium.

Vanadium oxide (VO). Crystal lattice of this material in a highly-conductive metal phase — face-centered (of the NaCl type) — Fig. 1. Base centers of the oxygen octahedrons are occupied by vanadium ions, while base centers of the vanadium octahedrons — oxygen ions. All the edges of the oxygen octahedrons are the same in length, while the octahedron bases are squares, whose plane are mutually orthogonal due to the cubic symmetry. Square diagonals are oriented along crystallographic axes.

In the semiconductor phase, the symmetry of the VO crystal lattice is lower and characterized as a distorted cubic one. There is partial monoclinic distortion of the cube. Complete monoclinic distortion of the cubic lattice would correspond to extension or compression of the cube along the symmetry axis of the fourth order when changing an edge length and changing a value of one of the right angles [1]. There is no such distortion in the VO semiconductor phase. But there is partial monoclinic distortion of the cube, which is reduced to compression or extension of the cube along the diagonal of one of its faces. At this, only one of the three right angles becomes indirect. The other two angles remain right ones and there is still equality of the lengths of all the cube edges. Therefore, in partial monoclinic distortion only two of the six cube faces turn into rhombi [2].

Physically, one of the diagonals of the square cube face shortens due to formation of V–V-dimers along a direction of this diagonal (due to so-called dimerization). The V–V-dimers are formed due to paired approach of the V ions along the diagonal of the square cube face. The approach is provided by overlapping of $3d_{x^2-y^2}^1(1)$ orbitals in the planes of the bases of the oxygen octahedrons, i.e. in the planes of the cube faces. At this, complete σ -bonds are formed inside the V–V-pair, as each $3d_{x^2-y^2}^1(1)$ orbital has one free electron.

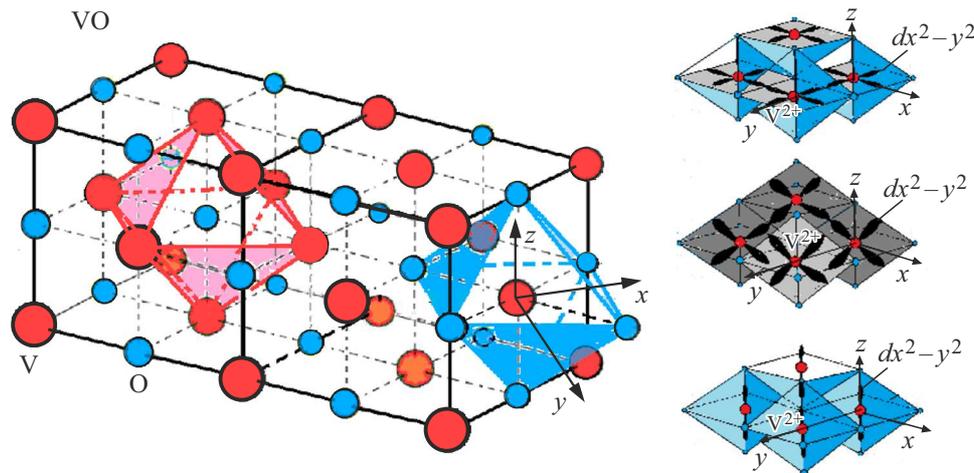


Figure 1. Fragment of the face-centered cubic crystal lattice of VO and diagram of the non-hybridizing orbitals of the $d_{x^2-y^2}$ type of the V^{2+} ion centered in the base of the oxygen octahedron. The orbitals of the d_{xz} type are not shown in the figure.

A dimerization direction is selected based on a direction of a maximum value of a single-axis stress in formation of the martensite plate at the moment of transition into the semiconductor phase. A plate form is determined by minimization of a tensor thermodynamic potential in transition of the VO nanocrystallite into a low-symmetry phase in accordance with a solution of the tensor variation problem [3].

The electron configuration of the hybrid orbitals of the V^{2+} ion takes the following form:

$$[\text{Ne}]3s^2(1)3p_x^2(1)[3p_y^2(2)3p_z^2(2)3d_{z^2}^1(1)3d_{xy}^1(1)4s^2(1)3d_{yz}^0(1)] \\ \times 3d_{xz}^0(1)3d_{x^2-y^2}^1(1).$$

Here, the bracketed numbers show a number of hybridizing orbitals, while the unbracketed numbers show numbers of the electron shells. The upper indices show numbers of electrons occupying specific atomic orbitals. The symbols in square brackets highlight the orbitals, which are needed to form a frame of the crystal lattice.

The two d orbitals of the vanadium ion ($3d_{xz}^0(1)$ and $3d_{x^2-y^2}^1(1)$), one of which has one electron, are non-hybridizing. The V^{2+} ion has 6 σ -bonds with the O^{2-} ions. For each bond, the V atom on average gives off 4/3 of its electron density.

The electron configuration of the hybrid orbitals of the O^{2-} ion takes the following form:

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

The O^{2-} ions form 6 σ -bonds with the vanadium ions. For each bond, the O on average gives off 2/3 of its electron density. Therefore, as a whole each σ -bond is contributed by two electrons.

We underline that the two $3d$ orbitals of the vanadium ion are not involved in the formation of the lattice frame and remain vacant.

As shown in the Fig. 1, the $d_{x^2-y^2}$ orbitals of the adjacent octahedrons are overlapped in the xy plane, while the d_{xz} orbitals are overlapped in the xz plane. As the lattice is symmetrical, these orbitals may be arranged otherwise, as it is shown in the right part of the Fig. 1. However, in any arrangement of the vacant orbitals they are in average contributed only by one free electron. These orbitals form energy bands in the electron spectrum. An energy's lowest zone formed of the orbitals, having only one electron each, is occupied by the electron in half in accordance with the Pauli principle. As a result thereof, at $T > T_c = 126$ K the vanadium oxide has a metal conductivity.

However, when reducing to the temperature to $T < T_c = 126$ K VO implements the metal-semiconductor phase transition [4]. As it is said above, the phase transition occurs due to the V–V-dimerization as the σ -bonds form between adjacent vanadium ions by overlapping their $d_{x^2-y^2}$ orbitals. These orbitals are in the planes of the bases of the oxygen octahedrons and due to the cubic symmetry, with the equal probability are oriented in the three mutually orthogonal crystallographic plane. In other words, when $T < T_c$ the dimers appear to pair formerly free electrons of the $d_{x^2-y^2}$ orbitals. The crystal becomes a semiconductor with reduction of the lattice symmetry, i.e. the structure phase transition happens (the Peierls transition). The VO band gap in the semiconductor phase is $E_g = 0.17$ eV [4]. This phase transition has a thermal hysteresis, i.e. it proceeds at different temperatures $T = T_c + \Delta T$ during the process of heating or cooling the crystal, respectively (ΔT — a half-width of the hysteresis loop).

Note that during heating the VO semiconductor phase to $T_c = 126$ K a value of the thermal energy equal to $kT_c = 10$ meV is not enough for thermally throwing the electrons into the conductivity band and for destroying the V–V-dimers. Nevertheless, there is still the semiconductor-metal phase transition when heating the crystal to $T_c = 126$! It is attributed to the fact that in a greatly correlated material,

to which VO belongs, the electrons comply not to the Fermi statistics, but to the Migdal statistics, which states' „tails“ are in one order higher than the „tails“ of the Fermi distribution for uncorrelated electrons in terms of energy. Moreover, the band gap of the greatly correlated material depends on the electron occupation of the conductivity band [5]. This dependence, which is typical for the greatly correlated compounds, leads to the Mott electron transition in VO with no change in the structure before the Peierls' structure phase transition.

Vanadium pentoxide (V_2O_5). The crystal lattice of this oxide is much more complex: it is characterized by 2 types of the vanadium ions and 3 types of the oxygen ions — Fig. 2. The Fig. 2 shows that the V^{5+} 6-coordinated ion is correlated to the O 4-coordinated ion, which is correlated to the three other V^{5+} 5-coordinated ions. Moreover, the V^{5+} 6-coordinated ion is surrounded with the two O ions with the four σ -bonds with the V^{5+} ions, and the V^{5+} 5-coordinated ion is surrounded with the three O ions, having three σ -bonds with the V^{5+} ions.

The electron configuration of the hybrid orbitals of the V^{5+} 6-coordinated ion takes the following form:

$$[Ar][3d_{xz}^0(1)3d_{yz}^0(1)3d_{x^2-y^2}^1(1)3d_{xy}^1(1)3d_{z^2}^1(1)4s^2(1)]4p^0(3).$$

It means that the three $4p^0(3)$ orbitals are non-hybridizing. The coordination number of this ion is equal to 6. The electron configuration of the hybrid orbitals of the V^{5+} 5-coordinated ion takes the following form:

$$[Ar][3d_{xz}^0(1)3d_{yz}^0(1)3d_{x^2-y^2}^1(1)3d_{xy}^1(1) \times 3d_{z^2}^1(1)]4s^2(1)4p^0(3).$$

It means that the four $4s^2(1)4p^0(3)$ orbitals are non-hybridizing. The coordination number of this ion is equal to 5.

The electron configuration of the hybrid orbitals of the O^{2-} ion takes the following form: $2s^2(1)2p^4(3)$. This

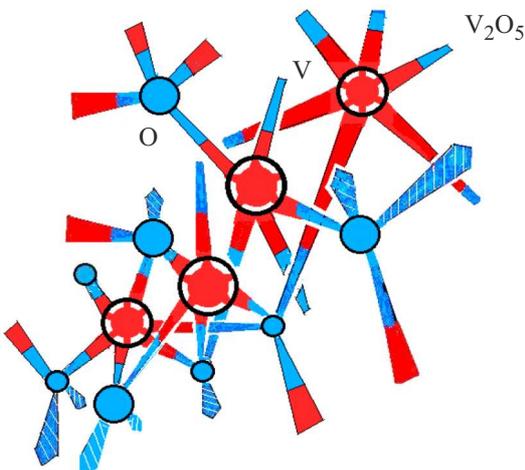


Figure 2. Fragment of the V_2O_5 crystal lattice.

means that it forms either 4 σ -bonds, or 3 bond, or 2 bonds with the V ions. In the two latter cases there is one or two electron lone pairs localized on either one or two hybrid orbitals of the O ion. These electron lone pairs are given off by this O ion to vacant orbitals of the V ion, if the V ion has vacant hybrid orbitals. Thus, donor-acceptor (coordinate) bonds of the V and O ions appear.

For the V^{5+} 6-coordinated ion, there are 5 electrons per 6 hybrid orbitals. The orbitals containing one electron each, form the σ -bonds with the O ions and are involved in formation of a lattice frame. The sixth orbital without the electron accepts the electron lone pair of the O ion by forming the donor-acceptor (coordinate) bond with it. The second lone pair of the same O ion is accepted by a vacant orbital of the V^{5+} 5-coordinated ion. As a result, the O ion with the 4 hybrid orbitals forms 2 donor-acceptor bonds and 2 common σ -bonds with the V ions.

The V^{5+} 5-coordinated ion gives off only 3 electrons per 5 hybrid orbitals. The orbitals of the V^{5+} ion, which contain one electron, form the σ -bonds with the O ions and are involved in formation of the lattice frame. As said above, one vacant orbital accepts one electron lone pair from the O ion. The second vacant orbital accepts one of the two lone pairs of the O ion, which has 3 hybrid orbitals with one electron each and the fourth orbital with the electron lone pair. The latter lone pair of the O ion „is suspended“ in the V_2O_5 crystal lattice by providing a high photosensitivity of the material. Therefore, no single electron can appear on the hybrid orbitals of the V and O ions. If the single electrons of the V_2O_5 lattice exist and stay on the orbitals unused for frame stabilization, then they would be able to create a metal-like conductivity by expanding into the energy bands. Moreover, they would be able to create conditions for implementing the phase transition from the metal phase into the semiconductor phase.

Thus, all the electrons of the hybrid orbitals of the V and O ions are either involved in stabilization of the lattice frame, or bonded mutually in the electron lone pairs. There is no electron which would be able to create the V–V-dimers. As said above, there is neither any single electrons. That is why, the V_2O_5 is a semiconductor (and not a metal, as might be thought) at any temperature up to a melt point of the material.

Indeed, the experiment shows that at $T = 300$ K the V_2O_5 is a semiconductor with „the optic“ band gap of $E_g = 2.4$ eV [6]. No structure phase transition for V_2O_5 has been found. However, the electron lone pairs create a shoulder of optical absorption in the range of semiconductor transparency, thereby giving the dark yellow V_2O_5 crystal. Therefore, the band gap for light with a low absorption coefficient is less than the above value. Nevertheless, the additional experiments show (Fig. 3) that when the V_2O_5 crystal is heated, then the dark electron conductivity is intensely increased, whose type determines „an electric“ band gap of the semiconductor $E_g = 2k \text{tg } \gamma = 1.4$ eV (Fig. 3). It is almost two time less than the value of the optic band gap of 2.4 eV, but

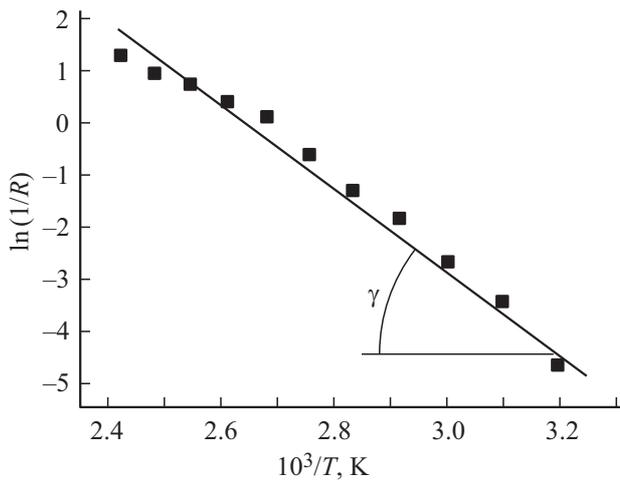


Figure 3. Temperature dependence of the V₂O₅ electric conductivity in the Arrhenius coordinates: Ln(1/R) depending on 1000/T.

still exceeds 1 eV. In order to explain the intense thermal throwing of the electrons into the conductivity band at such a high value E_g , which exceeds $kT = 30$ meV in dozens even at the temperatures 300–450 K, it should be remembered that in V₂O₅ the energy electron distribution complies to the Migdal distribution, which is typical for the greatly correlated materials. As it is said above, with increase in the temperature these materials have the narrower band gap as the occupation of the conductivity band is increased. It means that in such a semiconductor as V₂O₅, with increase in the temperature there is only a purely-electron Mott phase transition of the second order with no change of the lattice symmetry.

Thus, the carried-out study shows that despite a fundamental difference in the structure of the crystal lattice of the studied vanadium oxides VO and V₂O₅ these materials have common properties. They include the high dark electron conductivity of both the oxides and the electron Mott phase transition extended in temperature in them. As it is said in the Introduction, VO may be regarded as a model object due to the high symmetry of the crystal lattice. The V₂O₅ is also the model object, but in another feature: it is „purely“ a Mott insulator, as the electron phase transition is not „masked“ in it by the structural changes of the crystal lattice. It is worth reminding that the Mott insulators (to which the oxides of the transition metals belong) are characterized not only by gapping in the energy spectrum due to strong Coulomb (correlation) interaction of the electrons, but the dependence of the position of the energy bands on the occupation thereof as well [7,8].

Conflict of interest

The authors declare that they have no conflict of interest.

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