07

Spectroscopic control of the energy gap of aluminum-doped vanadium oxide structures

© A.V. Ilinskiy[1], V.A. Klimov[1], A.A. Kononov[2], P.S. Provotorov[2], D.L. Fedorov[3], E.B. Shadrin[1]

[1] Ioffe Institute,
St. Petersburg, Russia
[2] Herzen State Pedagogical University of Russia,
St. Petersburg, Russia
[3] Baltic State Technical University „VOENMEKH“ named after Marshal D.F. Ustinov,
St. Petersburg, Russia

E-mail: shadr.solid@mail.ioffe.ru

Received November 3, 2025
Revised November 10, 2025
Accepted November 11, 2025

It has been shown that doping strongly correlated compounds such as vanadium dioxide and vanadium pentoxide with 5 at.% Al narrows their band gaps and shortens the thermal extension of the Mott component of the complex semiconductor-metal phase transition. This results in a decrease in the semiconductor-metal phase transition temperature in VO_2 from 67 °C to 62 °C. At the same time, for the limiting oxide V_2O_5, the decrease in the thermal extent of the Mott component of the phase transition caused by Al doping is accompanied only by a correlation narrowing of the optical width of the band gap due to the absence of the Peierls component of the complex phase transition in this limiting oxide.

Keywords: dielectric spectroscopy, vanadium dioxide, semiconductor-metal phase transition, VO_2 films, aluminum doping.

DOI: 10.61011/PSS.2025.12.63083.310-25

Introduction

The control of the parameters of the electronic spectrum of materials with phase transitions (PT) remains an urgent task both in scientific and applied terms. The effect of aluminum doping on the band gap width E_g of materials with semiconductor-metal PT such as vanadium dioxide and vanadium pentoxide is studied in this paper to obtain additional information contributing to the development of this scientific topic.

First of all, we point out that for an aluminum atom to replace the base vanadium atom during doping, it is necessary to form the same number of hybrid electron orbitals as the substituted atom, ensuring a stable position of the replacement atom in the crystal lattice. In this case, the number of molecular orbitals formed during doping generally does not coincide with the valence of the atom of the doping impurity [1], just as it is the case for the base atom it replaces. Both form 6 molecular orbitals, delegating 4 electrons to the σ-bond of the oxygen octahedron. Due to the equality of the number of molecular orbitals and the number of delegated electrons, the replacement atom is an isoelectronic (isovalent) impurity relative to the base material. At the same time, being an isoelectronic impurity, the aluminum atom in most cases increases the width E_g of the band gap of the semiconductor in whose crystal lattice it is embedded [1]. The essence of the mechanism of increase of E_g is that the aluminum atom in the table of chemical elements is usually located one row above the chemical element it replaces. For this reason, the ionic radius of the aluminum ion turns out to be significantly smaller than the ionic radius of the substituted element of the same valence (V). For example, the ratio of ion radii is as follows for V^{5+} and Al^{5+} ions: $r = 0.5$ Å (V^{5+}) and $r = 0.3$ Å (Al^{5+}), respectively (the choice of numerical valence value is discussed below). It is also important that aluminum ions, due to the peculiarities of the synthesis process, are randomly located in the crystal lattice of the doped crystal. According to the ideology formulated by N. Mott [2] and confirmed by calculations based on the elements [3], the isoelectronic impurity atoms, being located chaotically in the crystal lattice and forming chaotic electric fields, play the role of acceptors capable of attaching valence band electrons.

Following N. Mott, this principle was developed more broadly in the work [4], according to which, if isoelectronic impurities have a short-range potential, and in the general case not necessarily related to the difference in ionic radii, their properties become similar to the electronic properties of deep charge carrier capture centers, that is, they manifest themselves as electron acceptors, despite the fact that they are isovalent with respect to the base lattice. In both formulations [2–4] of the principle of formation of acceptor properties of an isoelectronic impurity, there is an important point that requires the simultaneous presence of donor impurities in the lattice for the formation of „acceptor properties“ ensuring the formation of a donor-acceptor pair [3,4].

The presence of electron donors in metal oxides is ensured by the occurrence of a high concentration of oxygen vacancies in case of doping of metal oxides with aluminum, which has been experimentally proven for a large number of oxides [5,6].

The introduction of isoelectronic impurities exhibiting acceptor properties into materials with electronic phase transitions usually results in an increase of temperature T_C of PT, which is a consequence of a decrease of the total electron concentration caused by exposure to impurities with acceptor properties. For example, silicon doping of titanium dioxide leads to an increase in the temperature of PT from the anatase phase to the rutile phase [7].

However, contrary to the common situation, aluminum doping of materials with PT such as VO_2 and V_2O_5 is accompanied by a decrease rather than an increase in the T_c of the Mott-Peierls semiconductor-metal PT for VO_2 and the correlation narrowing of the thermal extension of the Mott part of the complex PT for V_2O_5 (the Peierls part of the PT in V_2O_5 is missing, since this oxide is the limiting one in the oxidation range of vanadium [7]). The reason for this phenomenon is that in both vanadium dioxide and vanadium pentoxide, the Al impurity, being isoelectronic with respect to V as a result of the corresponding hybridization of atomic orbitals (presented below), reduces rather than increases the width E_g of the band gap, in contrast to the usual behavior of the acceptor impurity. This circumstance shortens the thermal extent of the Mott part of the complex PT, which reduces the T_C of the thermal PT to VO_2. For V_2O_5, this is manifested in a decrease in the energy width E_g of the optical band gap, since this oxide is a strongly correlated compound like VO_2. Therefore, the temperature-extended Mott part of the process of thermal narrowing of the energy gap (E_g) is preserved in V_2O_5. That is, when the crystal V_2O_5 is doped with an Al atom, the band gap is „shrinks“ in terms of energy, similar to its narrowing in VO_2.

Thus, despite the fact that aluminum ions must expand E_g, while maintaining their acceptor properties in materials such as VO_2:Al and V_2O_5:Al, the opposite situation occurs, which is experimentally confirmed by the results of this study. Therefore, the question arises of identifying the mechanism of narrowing E_g in these compounds.

It is shown in this paper that the mechanism of this atypical phenomenon can be studied on the basis of a recently developed new theory, positioned as the theory of electron band anti-crossing [7–9].

1. Vanadium dioxide doped with aluminum (VO_2:Al)

1.1. Experimental methods and results

Synthesis of samples. Samples of nanocrystalline vanadium dioxide films doped with Al at a concentration of 5 at.% were synthesized by laser ablation [10, 11] on 40 μ thick optical mica substrates. In this variant of the method, thin polycrystalline films of vanadium dioxide $V_{1-\gamma}Al_\gamma O_2$ were created by simultaneous laser sputtering of targets of metallic V (99.9 %) and metallic Al (99.9 %) in an oxygen atmosphere at a temperature of 750−900 K. The degree of doping (γ) was determined by controlling the numerical value of the ratio of evaporation times of each of the metal targets.

Dielectric measurements were performed using a „Concept-81“ dielectric spectrometer. In this case, the film under study was placed in a spectrometer cell made in the form of a flat capacitor. The capacitance C_0 ($C_0 = \varepsilon_0 S/d$, where S is the electrode area, d is the mica thickness) of the empty cell was 27 pF. The measurements were performed in the frequency range $f = 10^{-1}-10^7$ Hz. The dielectric spectra were studied in the thermal range 55−100 °C at fixed temperatures varying in increments of 5 °C.

Measurement results. Figure 1 shows the frequency dependences of the tangent of the dielectric loss angle of a film sample taken at different temperatures VO_2 both in case of its heating and cooling in the range of 55−100 °C. Figure 1 shows that the resonant frequency corresponding to 0.75-height of the maximum level observed in the frequency spectrum of the function $\mathrm{tg}\,\delta(f)$ increases with increase of temperature, and it decreases with decreasing temperature, but with some temperature lag indicating the presence of temperature hysteresis. The temperature hysteresis loop shown in Figure 1, *c* due to Al doping is shifted as a whole towards low temperatures by 5 °C compared to the PT temperature of $T_C = 67$ °C, characteristic of undoped vanadium dioxide.

1.2. Discussion of the experiment results

The aluminum atom, replacing the vanadium atom during doping and being for this reason an isoelectronic (isovalent) impurity with respect to vanadium, should manifest itself as an acceptor and reduce the concentration of free electrons for the reasons described in the introduction. Thus, an increase in the PT temperature should be expected due to a correlative increase in the energy width E_g of the band gap [12]. Let us point out, for example, that an admixture of copper manifests itself in a similar way, which, when embedded in the crystal lattice of silver iodide AgI:Cu, increases the T_C of the semiconductor-superionic PT, since Cu is an acceptor [13]. However, according to the results obtained in this work, aluminum doping of a nanocrystalline vanadium dioxide film, contrary to expectations, lowers the temperature T_C of the semiconductor-metal PT by 5 °C, as shown in Figure 1, *c*.

To identify the causes of this phenomenon, we have considered the details of the formation of hybrid electron orbitals accompanying the substitution of V^{4+} ion by Al^{4+} ion in an oxygen octahedron in case of the doping of a VO_2 crystal with aluminum atoms.

Thus, in the crystal lattice cell of the tetragonal phase VO_2, a vanadium atom, being hybridized according to the scheme $3d^1_{xy}(1)d^1_{z2}(1)4s^2(1)4p^0(3)$, creates six σ-bonds

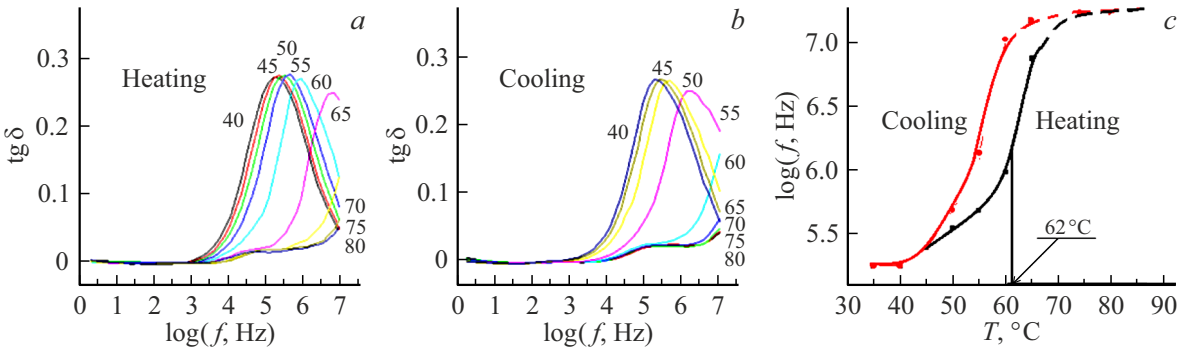

Figure 1. Frequency dependences of the tangent of the dielectric loss angle of the sample VO_2:Al when it is heated (a) and when it is cooled (b). c — thermal hysteresis loop of film VO_2:Al, constructed from dielectric spectroscopy data; it represents the temperature dependence of the frequency position of the ordinate of the function $\mathrm{tg}\,\delta(f)$ at the level of 0.75-the height of the maximum level observed in the frequency spectrum $\mathrm{tg}\,\delta(f)$.

with six oxygen atoms hybridized according to the scheme $s^2(1)p_x^1(1)p_y^1(1)$. Each hybrid orbital of the V^{4+} ion, located in the teragonal phase in the center of the oxygen octahedron, supplies 2/3 of electron density for one σ-bond, and each πhybrid orbital of the O^{3-} ion supplies 4/3 of electron density for the same σ-bond. As a result, each of the six σ-bonds of the octahedron occupies two electrons, ensuring the integrity of the VO_2 crystal lattice.

Two $3d$-orbitals $3d_{xz}^0(1)$, $3d_{yz}^0(1)$ of V atoms do not participate in the fixation of the framework of σ-bonds of the oxygen octahedron. These orbitals form donor-acceptor σ-bonds with $2p_z$-orbitals (ligands) of oxygen ions located at the corners of the oxygen octahedron. They create energy levels in the energy space of binding π-orbital and antibinding π^*-orbital. These levels expand into π and π^* energy zones in case of formation of a bulk crystal lattice.

The orbital $3d_{x2-y2}^1(1)$ is located in the plane of the base of the oxygen octahedron. It does not overlap with the orbitals of the ligands and does not participate in the stabilization of the oxygen octahedron, as a result of which it has the lowest energy level compared to other orbitals not involved in the formation of the oxygen octahedron. Therefore, $3d_{x2-y2}^1(1)$-orbital occupies the only one of the three electrons of the $3d$-shell of the atom V not employed in the stabilization of the octahedron. This orbital, having branches along the axes OX and OY (C_R) [13], is capable of overlapping only with the same orbital of ions V of neighboring octahedra fixed along the axis C_R. Therefore, it ensures the formation of one-dimensional chains of vanadium ions parallel to the C_R axis, located in the high-temperature ($T > T_c = 67\,^\circ\mathrm{C}$) tetragonal phase in the centers of oxygen octahedra.

For the sake of certainty, we point out that the numerical value of the valence of an atom inside a compound is determined by the number of electrons delegated by the atom to bond with other chemical elements of the compound. In general, this number does not coincide with the number of molecular orbitals formed during hybridization. So the atom V gives up 4 electrons to 6 hybrid orbitals in the oxygen octahedron.

It should be noted also that an electron with a $3d_{x2-y2}^1(1)$-orbital is given by the atom V to dynamic σ-bonds of a one-dimensional chain only for a short time. It is given to these bonds at the moment the atoms stop V in the process of full-symmetric phonon oscillations, that is, twice per period. This circumstance forces us to attribute fractional valence to the vanadium ion in the tetragonal (metallic) phase. For example, the valence of 4.5+. In the semiconductor phase at $T < T_c = 67\,^\circ\mathrm{C}$, the valence of the vanadium ion is definitely 5+ due to the delegation of the fifth $3d_{x2-y2}^1$-electron to them during the formation of stable V-V dimers along the C_R axis in the monoclinic (semiconductor) phase.

Namely, when the sample temperature decreases below $T_C = 67\,^\circ\mathrm{C}$, the crystal lattice turns from tetragonal to monoclinic due to the pairwise convergence of neighboring V^{4+} ions in the chain. Stable pairs of vanadium ions are formed, designated as V-V dimers. With this pairing, the distance between vanadium ions inside the V-V dimer turns out to be smaller than the distance between the pairs, and the lattice period along the chain doubles in comparison with the initial period.

An energy gap is formed in the electronic spectrum due to the occurrence of such a structural transition, i. e. Peierls PT, as a result of which vanadium dioxide from the metal turns into a Peierls semiconductor with monoclinic lattice symmetry. In this case, the $3d\,\|$-band splits into two Hubbardian subbands ($3d\,\|_{\mathrm{top}}$ and $3d\,\|_{\mathrm{bott}}$) [14], each of which contains half the number of closely spaced levels of the original $3d\,\|$-bands. Experience shows [15] that the energy gap between the subbands is 2.5 eV, i. e. so large that the antibinding π^*-band is located in terms of energy inside the gap between $3d\,\|_{\mathrm{top}}$ and $3d\,\|_{\mathrm{bott}}$ subbands. In this case, the π^*-band is attached at a distance of 0.7 eV from the lower Hubbard $3d\,\|_{\mathrm{bott}}$-subband. The large energy gap of 2.5 eV between the Hubbard subbands leads to the fact that the lower $3d\,\|_{\mathrm{bott}}$-subband becomes completely filled with electrons, while the upper $3d\,\|_{\mathrm{top}}$-subband remains

empty. Therefore, the crystal VO_2 in a scheme with a one-dimensional chain along the C_R axis is a semiconductor with a band gap of 0.7 eV between the lower $3d\,\|_{\text{bot}}$-subband that plays the role of a valence band, and π^*-band that plays the role of a conduction band. This is firmly established by experience [16].

It makes sense to compare the crystal lattice of vanadium dioxide with the lattice of the related material — rutile (TiO_2), since the V atom is directly adjacent to the Ti atom in the Periodic Table of Elements.

Ti atom has the following electronic structure:

$$\text{Ar}3d^1_{z2}(1)3d^1_{xy}(1)3d^0_{xz}(1)3d^0_{yz}(1)3d^0_{x2-y2}(1)4s^2(1).$$

The rutile crystal lattice like crystal lattice of VO_2 has the tetragonal symmetry of the crystal lattice consisting of octahedra of the TiO_6 structure in full accordance with the tetragonal symmetry of the lattice VO_2 [17].

Thus, it can be argued that the lattices of rutile and vanadium dioxide (in the tetragonal phase) are identical to each other, and their difference lies only in the fact that the titanium atom, unlike the V atom, does not have an electron in the $3d^0_{x2-y2}(1)$-orbitals, and therefore Ti-Ti dimers similar to V-V dimers cannot be formed in TiO_2. For this reason, rutile is a good dielectric with a wide band gap and retains the tetragonal lattice structure at any temperature up to the melting point. The width of its band gap is over 3 eV [18].

A degeneration of energy zones is observed in rutile at the Γ-point of the Brillouin zone, since this point is the point of maximum symmetry in the system of energy zones. The specific structure of the rutile zones, including the valence band and the conduction band, is determined by calculations from the first principles, which show that rutile has, as indicated, a wide band gap of more than 3 eV [18].

Returning to vanadium dioxide, we would like to note that in the material studied in this paper VO_2:Al, the ion Al^{4+} replaces the ion V^{4+} in the center of the base of the oxygen octahedron in case of doping a nanocrystalline film of VO_2 with aluminum. It forms 6 hybrid orbitals, thus being an isovalent (isoelectronic) impurity with respect to vanadium ions. In this case, the necessary 6 hybrid orbitals with 4 electrons on them are formed due to the following variant of hybridization of the orbitals of the Al atom: $2p^2_z(1)3s^2(1)3p^0_x(1)3p^0_y(1)3d^0_{z2}(1)3d^0_{xy}(1)$. The $3p^1_x(1)$-orbital of the Al atom with one electron on it, which does not participate in hybridization, allows the formation of one-dimensional metal-type σ-bonds with neighboring V atoms along the C_R axis, similar to the mechanism implemented for vanadium dioxide. In this case, due to the above-mentioned randomness of the introduction of dopant atoms, they can form as Al-V bonds, i.e. σ-bonds of $3p^1_x(1) - 3d^1_{x2-y2}(1)$ type, as well as Al-Al bonds, i.e. σ-bonds of type $3p^1_x(1) - 3p^1_x(1)$.

Thus, doping of vanadium dioxide with aluminum (an isoelectronic impurity) leads to the replacement of the ion V^{4+} with the ion Al^{4+} with the same chemical bonds with oxygen ions as in the undoped material, with the same crystal lattices of tetragonal and monoclinic symmetry in metallic and semiconductor phases and with dimers of the V-V and V-Al types. However, it must be borne in mind that V-Al dimers are more durable than V-V dimers, since the radius of the ion Al^{4+} is significantly smaller than the radius of the ion V^{4+}, i.e. the electron of the ion Al^{4+} at $3p^1_x(1)$-orbital is located much closer to the core, providing a stronger energy effect on the lattice than V^{4+}. Therefore, doping with aluminum reduces the concentration of electrons in the π^*-band compared with undoped vanadium dioxide due to the appearance of acceptor properties in Al due to the stronger bond of the $3p^1_x$-electron with the aluminum core compared with the bond of the $3d^1_{x2-y2}(1)$-electron with the core of vanadium. That is, aluminum, according to the mechanism described in the introduction, acts in VO_2 as a p-type dopant [4].

Doping of rutile with aluminum also leads to the replacement of the Ti^{4+} ion with the Al^{4+} ion with the same chemical bonds with oxygen ions and with the same tetragonal lattice symmetry, but without the possibility of formation of Ti-Ti and Ti-Al dimers due to the absence of an electron on the $3d^0_{x2-y2}(1)$-orbital of the Ti atom. For this reason, an electron not involved in chemical bonds, located on the $3p^1_x$-orbital of the aluminum atom, is thermally thrown into an almost free conduction band. That is, the aluminum atom in the case of rutile acts as an electron donor. We would like to remind that in strongly correlated compounds, such as rutile, the Fermi distribution is replaced by the Migdal distribution [19]. The Migdal distribution includes the correlation energy E_{corr}, which is very high for strongly correlated chemical elements [20]. Replacing the Fermi distribution with the Migdal distribution makes it possible to transfer an electron from the $3p^1_x$ orbital of the Al atom to the conduction band with a deeper occurrence of the donor level in the band gap than the Fermi distribution allows. This circumstance reduces the width of the rutile band gap due to correlation effects.

However, if the doping of a TiO_2 crystal with aluminum takes place at temperatures close to the melting point of crystalline TiO_2 ($T_{\text{melting}} = 1850\,^\circ\text{C}$), Al atoms form Al-Al pairs, located in neighboring crystal cells, which corresponds to the minimum free energy [21]. In this case, the electrons in the $3p^1_x$ orbital of the Al atom do not move into the conduction band. It has been shown that metal atoms and, in particular, Al act as electron traps here, which expands the band gap of rutile and reduces the quantum yield of photoconductivity [22].

Thus, a comparison of the physical properties of VO_2:Al, showing a narrowing of E_g in comparison with E_g of undoped VO_2, with the physical properties of TiO_2:Al, showing an expansion of E_g in comparison with E_g of undoped TiO_2 shows that the identification of the mechanism of narrowing of E_g of vanadium dioxide in case of its doping with an acceptor-like impurity requires special studies. With regard to the implementation of a non-trivial mechanism of reduction of E_g of vanadium dioxide under the impact of the potential of an acceptor-type isoelectronic impurity, it should

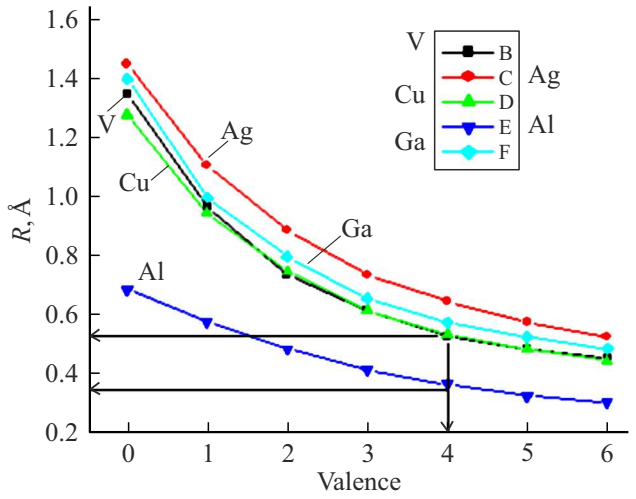

Figure 2. Dependences of ionic radii of a number of chemical elements, such as V, Ag, Cu, Al, Ga, on their valence [17].

be emphasized that there is a sharp difference in the degree of energy effect on the crystal lattice of the replacement element compared with the effect on this lattice of the base ion. For V^{4+} and Al^{4+} ions, the difference is attributable to a sharp difference in their ionic radii, as shown in Figure 2.

To implement the mechanism of reduction of E_g in case of aluminum doping, it is also important that only s- and p-orbitals participate in the hybridization of the orbitals of the Al^{4+} ion. According to the BAC theory (Band Anti-Crossing) [8], this is fundamentally necessary for the implementation of the mechanism of narrowing of E_g as a result of the anti-crossing of electronic zones.

We use this theory for VO_2:Al and briefly present its provisions below. It should be noted that the hybridization of orbitals of V^{4+} ion, in contrast to the hybridization of orbitals of Al^{4+} ion, involves the use of s-, p- and d-orbitals, and not only s- and p-orbitals. This is important because, according to theory, either the substituted or the substituting ion must, as indicated above, use only s- and p-orbitals in case of hybridization.

Back in the 80–90 years, it was shown that hybridization between localized impurity levels and extended band states in crystals with sp^3 bonds gives new localized levels narrowing the band gap [8,23–25]. The BAC (Band Anti-Crossing) theory states that an isoelectronic impurity creates highly localized acceptor-like levels near the bottom of the conduction band. They interact resonantly with the conduction band, removing the degeneracy of this band and forming new hybrid states that form two subbands with minima at $k = 0$ [9]. After removing the degeneracy, the conduction band is divided into an upper narrow subband E^+, formed by highly localized states, and a lower wider subband E^-, formed by delocalized (extended) states. Of course, the implementation of this mechanism requires an initial degeneration of the conduction band in the Γ-point lifted by the action of the potential of the isoelectronic impurity.

Returning to VO_2:Al, it can be argued that the band gap of this material narrows when it is doped with Al according to the concept of anti-overlapping electronic zones described above.

Of course, in order for the Al impurity to split the conduction band VO_2 into two subbands, it is necessary to have at least a twofold degeneracy of the conduction band at the Γ-point, which actually occurs for VO_2 [14].

Thus, the following is necessary according to the BAC theory, to ensure the occurrence of a pronounced effect of anti-crossing of semiconductor energy zones with the introduction of an isoelectronic impurity [9]:

– presence of sp^3-hybridization in either a substitutive or a substitutable chemical element;

– strong lattice distortion due to the difference in the energy of the electronic spectra of the impurity and the element being replaced, which can be achieved, in particular, due to the difference in the energy of the electronic shells involved in the creation of hybrid orbitals. For example, due to the difference in the ionic radii of the impurity and the element being replaced (by at least 0.2 Å) due to the location of the impurity one row higher in the Periodic Table of Chemical Elements. The position of the localized level is determined by the difference in the energy levels of the valence electrons of the impurity atom and the base atom replaced by it, or by a decrease in the lengths of the chemical bonds of the impurity with the matrix.

These considerations reveal the mechanism of narrowing of the band gap of the VO_2 crystal, which occurs due to the influence of the isovalent impurity Al^{4+} on the electronic subsystem of this crystal. We emphasize that numerous experiments [17] have proved the possibility of increasing the degree of oxidation of the Al atom from the widespread value of 3+ to 4+ and even to 5+. The last numerical value of the valence is realized, for example, in the compound $NaAlH_4$.

So, the narrowing of the band gap of the VO_2 crystal reduces the thermal extent of the Mott part of the complex PT, whereas the narrowing itself occurs due to the lifting of the degeneracy of the conduction band at the Γ-point due to the so-called anti-crossing effect of energy bands.

Clarifying the issue of the cause of the degeneration of the conduction band and the details of the mechanism for removing this degeneration is as follows.

The energetic degeneracy of the conduction band occurs due to the fact that the conduction band is an energy-expanded anti-binding π^*-orbital of the coordination bond of the orbitals of the V ion with the orbitals of the O ions, which are not involved in the stabilization of the crystal framework. And the anti-binding orbital itself is, according to the theory of molecular orbitals, a consequence of the formation of coordination σ-bonds between electron-free $3d_{xz}$- and $3d_{yz}$-orbitals of V^{4+} ion and 2_{pz}-orbitals of oxygen ions fixed at the corners of the oxygen octahedron. It is important that there are two empty orbitals $3d_{xz}$ and $3d_{yz}$,

and they are fixed in two mutually perpendicular planes of the coordinate axes (ZOX and ZOY) [13]. At the same time, these orbitals are equally likely to occupy pairs of electrons with $2p_z$-orbitals of oxygen ions [13], which ensures the energy degeneracy of the conduction band □*. That is, there is a geometric difference in the positions of the $3d_{xz}$- and $3d_{yz}$-orbitals when the numerical values of the energy gaps created by them coincide between the binding π and the anti-binding π^* orbitals.

As for the effect of the doping admixture Al on the energy of PT, it boils down to the following.

It is known that comprehensive mechanical compression, which reduces the volume of crystal cells of VO_2, increases the temperature T_C of the Peierls structural PT [14]. The mechanism of T_C increase is reduced to the difficulty of thermal destruction of V-V dimers during mechanical compression of the crystal. It follows that the reverse effect, that is, mechanical stretching, which increases the volume of crystal cells, can facilitate the thermal destruction of V-V dimers, thereby reducing the T_C of the Peierls PT.

Considering that the ionic radius of the Al impurity replacing V ion in the center of the octahedron base is significantly smaller than the ionic radius of the base element —V (Figure 2), it can be concluded that the σ-bonds of the Al ion with oxygen ions in the octahedron are much shorter than σ-bonds of the base element. This leads to a decrease in the volume of the crystal cell containing Al, inevitably leading to mechanical stretching of the σ-bonds in the crystal cells of VO_2 surrounding it. Remembering that each aluminum ion in such a cell is surrounded by 6 cells with V base ions, it can be stated that 5 % Al doping leads to stretching of 30 % of crystal cells!

And finally, considering that the specified bond stretching of the d_{yz}-orbital of the V ion located in the same plane as the $d_{x2-y2} - d_{x2-y2}$-band of the V-V dimer does not coincide in magnitude with the stretching of the bond of d_{xz}-orbitals of the V ion perpendicular to this plane, it is possible to state the lifting of the energy degeneracy of the conduction band π^*, caused by the difference in the degree of influence on these bonds of the tensile perturbation along the OX and OY axes. The lifting of degeneracy leads to energy splitting of the conduction band into two components, one of which turns out to be higher, and the other turns out to be below the energy of the non-split state [15]. This naturally leads to a narrowing of E_g.

It follows that doping with an isoelectronic impurity modifies the entire process of complex semiconductor-metal PT, affecting the Mot and, through it, the Peierls components!

This proves that the narrowing of the energy width (E_g) of the band gap in VO_2 in case of Al doping finds its consistent explanation within the framework of the theory of energy band anti-crossing, based on the lifting of the energy degeneracy of the conduction band by aluminum. This also provides a basis for the explanation of the decrease of PT temperature by 5 °C determined by a reduction in the thermal extent of the Mott component of the transition, which is accompanied by an easing of the thermal destruction of V-V dimers in the Peierls part of the complex semiconductor-metal PT in VO_2.

2. Aluminum-doped vanadium pentoxide V_2O_5:Al

2.1. Experimental methods and results

Sample synthesis. Nanocrystalline films with a thickness of 80 nm were synthesized on optical mica substrates with a thickness of 40 μ. The undoped films were synthesized by cathode sputtering of the target followed by oxidation of metal vapors in an oxygen stream near a mica substrate. The doped films were synthesized by simultaneous laser evaporation of V and Al in an oxygen atmosphere at a temperature of 750−900 K. The degree of doping of the film corresponded to the ratio of the evaporation times of each target.

Optical transmission spectra were measured in the wavelength range of 200−1000 nm using the SF-2000 spectrophotometer of the interdisciplinary resource Center for Collective Use of the Herzen Russian State Pedagogical University „Modern physico-chemical methods for the formation and research of materials for the needs of industry, science and education“. Since mica has a band gap (7 eV) significantly exceeding the energies corresponding to the optical range of visible light (1.98 eV−3.26 eV [26]), within which this study was conducted, it can be confidently stated that the measured transmission spectra characterize precisely the thin films of vanadium pentoxide. The samples themselves are visually characterized as transparent films of a yellowish hue, which corresponds to the width of the optical band gap of $E_g \approx 2$ eV.

Calculations of the electronic spectrum of V_2O_5 were performed according to density functional theory using the generalized gradient approximation [27]. In addition, the Perdew–Burke–Ernzerhof (PBE) [28] parameterization was used, and ultra-soft pseudopotentials were introduced into the Quantum ESPRESSO software package [29]. When representing wave functions as a system of plane waves, the cutoff was performed at the energy level of 640 eV. Summation over the Brillouin zone was performed by applying a grid mesh structure of k-points with a volume of $4 \times 3 \times 2$ elements. The need to take into account the fact that V_2O_5 is a strongly correlated material forced the use of the DFT+U [30] calculation method with the Hubbard parameter $U = 5.7$ eV in $3d$-shell of the electronic states of the V atom [31]. The DFT+D2 correction made it possible to account for the dispersion interactions [32]. The calculation results are shown in Figure 4.

Measurement results. A narrowing of E_g was also detected in vanadium pentoxide after doping with an p-type admixture of Al, as shown in Figure 3. Namely, Figure 3 shows the dependences of the optical band gap width for indirect (upper graph) and direct (lower graph) transitions

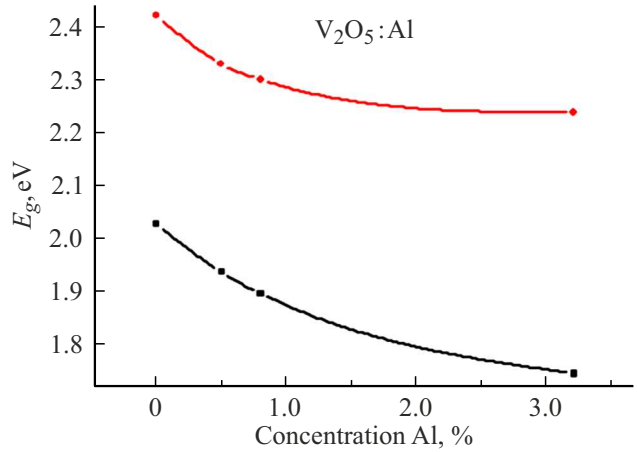

Figure 3. Dependence of the optical band gap width for indirect (upper graph) and direct (lower graph) transitions in V_2O_5, V_2O_5+Al (0.5 %), V_2O_5+Al (0.8 %) and V_2O_5+Al (3.2 %).

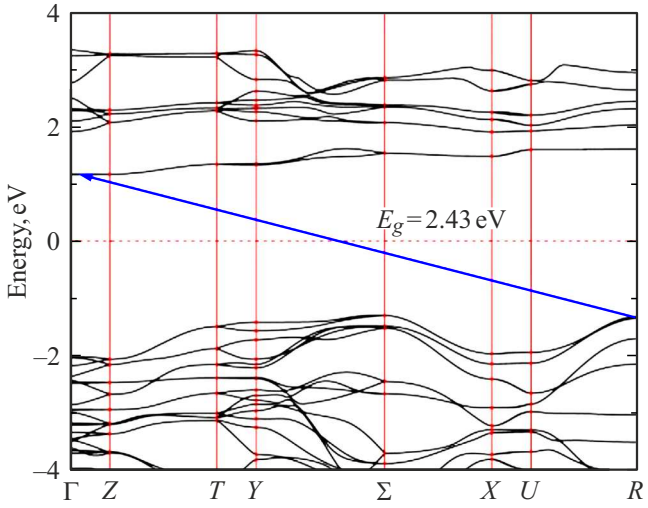

Figure 4. The structure of energy bands of V_2O_5 in K-space according to the calculation in the framework of density functional theory (DFT) performed in this paper using the generalized gradient approximation (GGA).

in V_2O_5 on the degree of doping of films with aluminum: V_2O_5+Al (0.5 %), V_2O_5+Al (0.8 %) and V_2O_5+Al (3.2 %).

2.2. Discussion of the experiment results

Figure 4 shows that the conduction band of V_2O_5 is doubly degenerate at the Γ-point, and this degeneracy is lifted in the presence of an isoelectronic impurity, causing a narrowing of the band gap in the same way as it occurs in VO_2.

The presence of degeneracy makes it possible to apply the Band Anti-Crossing Theory to explain the narrowing of E_g of V_2O_5 crystal when an admixture of Al is introduced into it.

Let us consider in more detail the structure of the crystal lattice of V_2O_5 for clarifying other conditions necessary for the application of the theory of electron band anti-crossing.

According to Ref. [33] the vanadium ion V^{5+} forms five hybrid orbitals in the crystal lattice of V_2O_5, each of which is linked to one of the three hybrid orbitals of the oxygen ion.

In general, the situation with the crystal lattice structure is complicated for V_2O_5: it is characterized by 2 types of vanadium ions (V^{5+} and V^{4+}) and 3 types of oxygen ions [34]. The ion V^{5+} has three orbitals $4p^0(3)$ and does not participate in hybridization. This vanadium ion, being 5-valent, has six bonds with oxygen ions. The specific hybridization option for this case is presented in the table 2 in Ref. [35]. Four orbitals $4s^2(1)4p^0(3)$ do not participate in hybridization for the V^{4+} ion. This vanadium ion has five bonds with oxygen ions. Three electrons account for the five hybrid orbitals for the V^{5+} ion involved in the formation of the crystal lattice framework, and two empty orbitals remain. One of them accepts one of the two lone pairs of electrons from the oxygen ion. The second empty orbital of the V^{5+} ion accepts another unoccupied pair of oxygen ions, which has 3 hybrid orbitals with one electron each and one orbital with an unoccupied pair of electrons in the construction of the skeleton.

The hybridization of ion O is as follows: $[2s^2(1)2p^4(3)]$, that is, it has 4 hybrid orbitals. This ion is capable of forming 4σ-bonds with V^{4+} ions. In this case, the oxygen ion with 4 orbitals forms two donor-acceptor bonds: one with the 6-coordinated ion V^{5+} and the other with the 5-coordinated ion V^{4+}.

As for the doping impurity Al, it is an isovalent (isoelectronic) impurity with respect to vanadium ions. In the process of doping of V_2O_5 crystal aluminum ion replaces the 5-valence 6-coordinated ion V^{5+}. In this case, the necessary 6 hybrid orbitals with 4 electrons are formed on them, as in the case of VO_2, due to the following variant of hybridization of the orbitals of the Al atom: $2p_z^2(1)3s^2(1)3p^0(2)3d^0(2)$. It should be especially noted that such oxygen ion hybridization is shown above, that it is capable of, in contrast to the case of VO_2:Al, delegate not 4, but 6 electrons to the 5-valence, but 6-coordinated, ion of V^{5+}, introducing one of its vacant pairs into one of the vacant orbitals of the 6-coordinated ion V^{5+}.

Thus, in the case of V_2O_5:Al, all the conditions for the formation of electron band anti-crossing are fulfilled: the presence of an energy degeneracy of the conduction band at the Γ-point, the presence of acceptor properties of the dopant, as isovalent with respect to V^{5+}, as well as the sharp difference in the ionic radii of the impurity and the element it replaces, shown above in Figure 2 in the section on VO_2:Al. This determines the applicability of the theory of electron band anti-crossing to materials such as V_2O_5:Al, and explains it within the framework of the theory of band anti-crossing, as in the case of VO_2:Al, narrowing of the band gap of vanadium pentoxide during its doping with an admixture of aluminum. This narrowing can be clearly seen

in the graphs obtained in this work of the dependence of the widths of the optical band gap on the concentration of the doping impurity Al for both indirect and direct electronic transitions.

Conclusion

In summary, we would like to point out the following results of this paper:

1) Dielectric spectra of nanocrystalline VO_2:A films have been studied, which allowed obtaining new experimental material on a decrease in T_C AF with an increase in the degree of Al doping, which indicates a narrowing of E_g under the influence of an isoelectronic doping impurity.

2) Optical transmission spectra of nanocrystalline V_2O_5:Al films have been studied, which showed a shift of the edge of intrinsic optical absorption to the long-wavelength side of the spectrum with an increase in the degree of doping of Al, that is, a narrowing of E_g for both indirect and direct transitions.

3) Calculations of the electronic spectrum of V_2O_5 were performed showing the presence of a double degeneracy of the conduction band at the Γ-point of the Brillouin zone.

4) The fact of the shortening, with an increase in the Al doping level, of the energy extent of the Mott part of the PT in the VO_2:Al and V_2O_5:Al compounds has been established.

5) Based on the analysis of the full set of experimental data, it is concluded that the mechanism of electron band anti-crossing is implemented, which defines the narrowing of the band gap both of VO_2:Al, and V_2O_5:Al under the influence of the potential of an isovalent doping impurity Al.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] V.K. Kazimova, Z.M. Zahrabekova, M. Zeynalova, G.H. Azhdarov. Rost kristallov **51**, 192 (2007) (in Russian).
[2] N.F. Mott, E.A. Devis. Electron processis in noncristalline materials. Oxford (1971). 472 p.
[3] E.M. Conwell. Phys. Rev. **103**, 51 (1956).
[4] S. Iizuka, T. Nakayama. Jap. J. Appl. Phys. **55**, 101301, (2016).
[5] P. Kofstad. Otklonenie ot stekhiometrii, diffuziya i elektroprovodnost v prostykh okislakh metallov. Mir, M. (1975). p. 396 (in Russian).
[6] A. Markose, D.D.P. Ravindran. Mater. Adv. **4**, 3399 (2023).
[7] W. Shan, W. Walukiewicz, J.W. Ager III, E.E. Haller. Phys. Rev. Lett. **82**, *6*, 1221 (1999).
[8] W. Shan, K.M. Yu, W. Walukiewicz. Appl. Phys. Lett. **75**, *10*, 1410 (1999).
[9] N.K. Morozova. Izoelektronnye primesi v poluprovodnikah v svete teorii antiperesekayushchihsya zon. Uch. pos. (2019). p. 202 (in Russian).
[10] M.H.P. Eshfold, F. Claisens, G.M. Fuedj. Chem. Soc. Rev. **33**, 23 (2004).
[11] V.N. Andreev, V.A. Klimov, M.E. Kompan. FTT **67**, *6*. 998 (2025) (in Russian).
[12] A.V. Ilyinsky, R.A. Castro, V.A. Klimov, A.A. Kononov, I.O. Popova, E.B. Shadrin. FTT **66**, *12*, 2092 (2024) (in Russian).
[13] A.V. Ilinskiy, O.E. Kvashenkina, E.B. Shadrin. FTP **46**, *4*, 439, (2012) (in Russian).
[14] W. Bruckner, H. Operman, W. Reichelt, E.I. Terukow, A.F. Tschudnovskii, E. Wolf. Vanadiumoxide. A-V, Berlin (1983). 252 s.
[15] C. Parker, W. Geiser. J. Am. Cerom. Soc., **73**, [II], 3206 (1990).
[16] J.B. Goodenough. Solid State Chemistry **3**, *4*, 490 (1971).
[17] Himicheskaya enciklopediya v 5 t. Izd-vo „Bol'shaya rossijskaya enciklopediya", M. V. 5, p. 783 (1998) (in Russian).
[18] A. G.Thomas, W.R. Flavell, A.K. Mallick. Phys. Rev. B **75**, 035105 (2007).
[19] V.V. Valkov, D.M. Dzebisashvili. FTT **51**, *5*, 833 (2009) (in Russian).
[20] R. Sakuma, T. Miyake, F. Aryasetiawan. Phys. Rev. B **78**, *8*, 075106 (2008).
[21] A.A. Minnekhanov. Fotoelektronnye processy v nanostrukturirovannyh materialah na osnove dioksida titana s paramagnitnymi tsentrami. Avtoref. diss. kand. f.-m.n. MGU im. M.V. Lomonosova, M. (2018). P. 134 (in Russian).
[22] W. Choi, A. Termin, M.R. Hoffann. J. Phys. Chemistry **98**, *51*, 13669 (1994).
[23] H.P. Hjalmarson, P. Vogl, D.J. Wolford, J.D. Dow. Phys. Rev. Lett. **44**, *12*, 810 (1980).
[24] M. Weyers, M. Sato, H. Ando. Jpn. J. Appl. Phys. **31**, L853 (1992).
[25] J. Wu, W. Shan, W. Walukiewicz. Semicond. Sci. Technol. **17**, 860 (2002).
[26] J.L. Bishop, M.D. Lane, M.D. Dyar, A.J. Brown. Clay Minerals **43**, 35 (2008).
[27] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais. Phys. Rev. B **46**, *11*, 6671 (1992).
[28] J.P. Perdew, K. Burke, M. Ernzerhof. Phys. Rev. Lett. **77**, *18*, 3865 (1996).
[29] B.M. Glinsky. Problemy informatiki **3**, 72 (2013) (in Russian).
[30] M. Cococcioni. The LDA+U approach: A simple hubbard correction for correlated ground states. In E. Pavarini, E. Koch, F. Anders, M. Jarrell. Correlated Electrons: From Models to Materials Modeling and Simulation **2**, *4*, 1 (2012).
[31] A. Jovanović, A. Dobrota, L. Rafailovic, S. Mentus, I. Pasti, B. Johansson, N. Skorodumova. Physical Chemistry / Chemical Physics **20**, **109**, 858 (2018).
[32] S. Grimme, S. Ehrlich, L. Goerigk. Journal of Computational Chemistry **32**, *7*, 1456 (2011).
[33] M. Giorgetti, S. Passerini, W.H. Smyrl, M. Berrettoni. Inorg. Chem. **39**, *7*, 1514 (2000).
[34] A.V. Il'inskij, E.B. Shadrin. FTT **64**, *6*, 702 (2022) (in Russian).
[35] A.V. Il'inskij, E.B. Shadrin. FTT **65**, *3*, 460 (2023) (in Russian).

Translated by A.Akhtyamov