Physics of the Solid State, 2023, Vol. 65, No. 12

Phase transition of oxides of the Magneli series: VO, V_2O_3, VO_2, V_2O_5

© A.V. Ilinskiy, E.B. Shadrin¶

Ioffe Institute,
St. Petersburg, Russia

¶ E-mail: shadr.solid@mail.ioffe.ru

Received April 29, 2023
Revised June 21, 2023
Accepted October 30, 2023

It is shown that the crystals of vanadium oxides inherit the correlation properties of the oxidized chemical element — vanadium, namely: the energy position of the electronic zones of the crystals essentially depends on the degree of filling these zones with electrons. The complex Mott–Peierls character of the phase transitions in all the listed strongly correlated compounds has been established. As the oxidation state of vanadium in VO_x compounds increases (the x index increases from 1 to 2.5), the metallic properties of the oxides weaken, accompanied by an increase in the temperature of the semiconductor–metal phase transition and an increase in the band gap.

Keywords: Magneli series, Mott–Peierls transition.

DOI: 10.61011/PSS.2023.12.57643.4937k

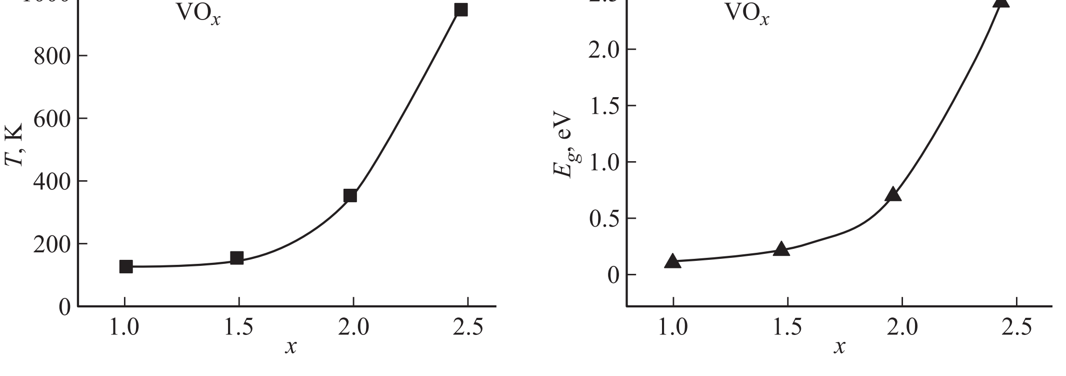
1. Introduction

Among metal oxides, vanadium oxides, forming the series VO_x $(0.2 < x < 2.5)$, occupy a special place, since in this series vanadium demonstrates its possession of variable valence [1]. In this article we discuss the physical properties of four vanadium oxides of the Magneli series: VO, V_2O_3 VO_2 and V_2O_5.

Unusual properties of oxides of the Magneli series are caused by the peculiarities of filling with electrons of levels of V atom [2]. Thus, in potassium (K, 19, $3d^04s^1$) instead of the „expected" filling of 3d level, the overlying level 4s is filled. After filling with two electrons of 4s level of calcium (Ca, 20, $3d^04s^2$) with one electron the 3d level of scandium is filled (Sc, 21, $3d^14s^2$), with two electrons — of titanium (Ti, 22, $3d^24s^2$) and with three electrons of vanadium (V, 23, $3d^34s^2$). However, for chromium (Cr 24, $3d^54s^1$) at the 3d level instead of the „expected" four electrons there are five electrons due to the transition of one electron from the 4s level to the 3d level due to the strong dependence of the level energy on the degree of their filling with electrons. Therefore, when describing the electronic spectra of these elements, a correction called correlation energy [3] should be introduced. The ability to lower the energy of atomic levels with their occupancy by electrons is transferred to compounds of strongly correlated element V — vanadium oxides [4]. This determines the complex Mott–Peierls nature of the phase transitions (PT) semiconductor–metal in the listed vanadium oxides. This article discusses PT mechanisms and the reasons for the weakening of the metallic properties of VO_x with an increase in the oxidation state of the atom V ($x = 1$, 1.5, 2, 2.5), accompanied by increase in PT temperature.

2. Increase in PT temperature and band gap of vanadium oxides VO_x with x increasing

A comparative analysis of the properties of vanadium oxides is based on their sequential arrangement in a row as the number of oxygen ions per vanadium ion increases. The following regularities are observed: PT critical temperatures, as well as the values of the band gaps monotonically increase with x increasing — Figure.



Temperatures of PT semiconductor–metal (a) and band gap E_g (b) for vanadium oxides VO_x ($x = 1$, 1.5, 2, 2.5).

Thus, vanadium monoxide VO at room temperature has metallic conductivity, passing into the semiconductor phase when the temperature decreases below $T_c = 126$ K — Figure, *a*. In vanadium sesquioxide V_2O_3 PT semiconductor–metal also occurs at a relatively low temperature $T_c = 140$ K, but more higher than in VO. In VO_2PT semiconductor–metal occurs at a much higher temperature $T_c = 340$ K. Vanadium pentoxide V_2O_5 remains semiconductor at all high temperatures, for which the integrity of the crystalline framework is maintained. The structural phase transition in vanadium pentoxide is, in contrast to the temperature-extended Mott transition, the melting of V_2O_5 crystal with rhombohedral symmetry of lattice (D_{2h}) into liquid phase of symmetry D_∞ ($T_{\text{melt}} = 680°\text{C}$).

The band gaps $E_g$have the following values (Figure, *b*): VO — $E_g = 0.1$ eV, V_2O_3 — $E_g = 0.2$ eV, VO_2 — $Eg = 0.7$ eV, V_2O_5 — $E_g = 2.4$ eV.

3. Analysis of structural and electronic PTs and the associated weakening of the metallic properties of VO_x with increase in the index x ($x = 1; 1.5; 2; 2.5$)

The possibility of formation in the semiconductor phase of $V{-}V$ — dimers during the synthesis of vanadium oxide crystals is a prerequisite for structural PT occurrence in them. In addition to the structural PT in vanadium oxides the electronic unhysteretic PT is possible, which preceding the structural one.

3.1. The range of low temperatures of the PT: $x = 1$, $x = 1.5$

In vanadium monoxide (VO_x, $x = 1$) in its metal phase, all V ions are located at the centers of the bases of the octahedra of the oxygen framework, and all O ions are located at the centers of the bases of the octahedra of the vanadium framework. VO has cubic face-centered crystal lattice. VO in the described configuration has metallic conductivity at room temperature, which is established experimentally.

When the temperature decreases to $T_c = 126$ K VO performs PT metal–semiconductor [5–7], and at the same time V–V-π-dimers are formed. Temperature $T_c = 126$ K — the lowest temperature of the thermal PT of transitions in all 4 vanadium oxides considered in this article. The conductivity during PT decreases abruptly by 7 orders of magnitude, which is significantly higher than similar jumps in conductivity during PT in other vanadium oxides that occur at higher temperatures. To perform a reverse thermal PT into the metal phase in VO, the energy $kT_c = 10$ meV of phonons at $T = 126$ K is not enough to overcome the gap $E_g = 0.1$ eV. Nevertheless, the transition occurs, and overcoming the difficulty of explaining this lies in the way of using Mott's idea [8], according to which consideration of the Coulomb (correlation) interaction between free electrons dictates the need to replace the Fermi distribution with the Migdal distribution, which ensures thermal overcoming E_g [3].

Thus, in vanadium monoxide, with T increasing, two PTs occur sequentially, at that the extended electronic transition (of the second kind) initiates an abrupt structural transition (of the first kind).

For vanadium sesquioxide (VO_x, $x = 1.5$) in its metal phase V ions are also located at the centers of oxygen octahedra. However, in the lattice V_2O_3 per every two octahedra containing V ions at the base, there is one octahedron not containing V. The lattice V_2O_3 at temperature $T > T_c$ has rhombohedral symmetry [9], and as the temperature decreases after PT, the symmetry decreases to monoclinic.

V_2O_3, being metal at room temperature, performs PT to the semiconductor phase at $T_c = 140$ K. At $T < T_c$ V–V-π-dimers appear. π-bonds of the metal phase form a zigzag chain along the crystal axis CR, along which one-dimensional metallic conductivity of the rhombohedral phase is formed. The period of the chain in the metal phase is equal to d, and in the semiconductor phase it becomes equal to $2d$ due to the pairwise approach of V–V-π-dimers when the temperature decreases, and PT occurs in the semiconductor phase. However, the band gap of the semiconductor phase is equal to $E_g = 0.2$ eV, in contrast to $E_g = 0.1$ eV for VO. Here, as in VO, the Mott transition turns out to be possible and initiates the completion of structural PT.

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

In vanadium dioxide (VO_x, $x = 2$), all V ions are located at the centers of the bases of oxygen octahedra. The lattice has tetragonal symmetry [10] at high temperature $T > T_c$, and monoclinic at low temperatures.

The electrical band gap VO_2 is equal to $E_g = 0.7$ eV. Metallic conductivity occurs at temperatures $T \geq 340$ K (67°C). At $T < T_c$, V–V-dimers are formed as a result of the formation of σ-bonds between $d_{x^2-y^2}$-orbitals of vanadium ions of neighboring octahedra. Here, as in the cases with VO_2 and V_2O_3, the phonon energy at $T_c = 340$ K is not enough to destroy dimers and to overcome the gap $E_g = 0.7$ eV. Therefore, here too, the electronic PT initiates the structural PT.

3.3. Range of high temperatures of the PT: $x = 2.5$

Vanadium pentoxide (VO_x, $x = 2.5$) has the most complex crystal lattice structure: it is characterized by 2 types of electronic configuration of vanadium ions and 3 types of configuration of oxygen ions. In the lattice V_2O_5 the six-coordinated ion V^{5+} is associated with the four-coordinated ion O^{2-}, which in turn forms bonds with three five-coordinated ions V^{5+}. V^{5+} ion is also surrounded by three O ions^{2-}, forming three σ-bonds with V^{5+} ions. At the same time, the six-coordinated ion V^{5+} is surrounded by two O ions^{2-} The structural PT for this oxide was not experimentally detected.

V_2O_5 is a semiconductor with „optical" bandgap $E_g = 2.4\,\text{eV}$. However, the experiment indicates the presence of high concentration of electrons in the conduction band at temperatures 300−450 K. This is due to the Migdal distribution instead of the Fermi distribution in the same way as in three oxides described above. In other words, in V_2O_5 with temperature increasing, the extended T purely electronic Mott PT occurs, i.e., vanadium pentoxide is a classical „Mott insulator".

4. Conclusion

With increase in index x $(1 \to x \to 2.5$ in $VO_x)$, the conductivity of the metal phase of the described oxides decreases, which is accompanied by increase in T_c of PT semiconductor-metal and an increase in E_g due to increase in the fraction of O^{2-} ions bound fracture of electron density of ions V^{4+}, providing the metallic conductivity of the crystal. Thus, at $T > T_c$ for VO electrical conductivity is possible in all directions, for V_2O_3 — along zigzag chain, for VO_2 only along a linear chain, for V_2O_5 it is impossible at all.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] A.V. Ilinskiy, E.B. Shadrin. FTT **62**, *8*, 1284 (2020). (in Russian).

[2] H. Kohn, J. Walter. Phys. Rev. **140**, A1133 (1965).

[3] M. Gatti, F. Bruneval, V. Olevano, L. Reining. Phys.Rev. Lett. **99**, 266402 (2007).

[4] A. Boum. Kvantovaya mekhanika: osnovy i prilozheniya. Mir, M. (1990), 720 s. (in Russian).

[5] I.C. Austin. Phil. Mag. **7**, 961 (1962).

[6] W.W. Warren, G.A. Miranda, W.G. Clark. Bull. Am. Phys. Soc. **12**, 1117 (1967).

[7] A.V. Ilinskiy, O.E. Kvashenkina, E.B. Shadrin. FTP **46**, *4*, 439 (2012). (in Russian).

[8] A.B. Migdal. UFN **147**, *10*, 210 (1985). (in Russian).

[9] W. Bruckner, H. Opperman, W. Reichelt, E.I. Terukov, F.A. Tschudnovskii. Vanadiumdioxide. Akademie-Verlag, Berlin (1983). 252 p.

[10] A.V. Ilinskiy, E.B. Shadrin. FTT **64**, *6*, 702 (2022). (in Russian).

Translated by I.Mazurov