Variation of Orbital Symmetry of the Localized 3d¹ Electron of the V⁴⁺ Ion upon the Metal-Insulator Transition in VO₂

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The electronic structure of the vanadium dioxide VO₂ in the tetragonal R and two monocinic \( M_1 \) and \( M_2 \) structural modifications was calculated in frames of the local-density functional (LDA) approach and the LSDA + U formalism of correction for correlation effects. Based on the results of calculation, we argue in favor of the Mott-Hubbard mechanism of the metal-insulator transition. It is shown that the transition is accompanied by the change of the orbital in which the 3d¹ electron of the V⁴⁺ ion is localized. The symmetry of the filled orbital is determined by the local oxygen environment of the vanadium atoms in each structural phase. Depending on the dispersion of the band that corresponds to the orbital occupied, the investigated compound can be either a metal or an insulator.

The metal-insulator transition in VO₂ is observed at a temperature of 340 K and is accompanied by a structural transition from the nonmagnetic high-temperature tetragonal rutile phase \( R \) to the nonmagnetic monoclinic \( M_1 \) phase. The rutile phase contains chains of equidistant vanadium atoms along the [001] direction. The unit cell of the \( M_1 \) phase doubles as compared to rutile, all vanadium atoms slightly deviate from the [001] \( R \) direction, forming zigzags and become nonequidistant, forming pairs.

A noncontradictory theoretical description of the metal-insulator transition in vanadium dioxide is still lacking. The origin of the nonmetallic state is explained now from two viewpoints.

If one starts from the results of band calculations in the local-density approximation (LDA), then the \( M_1 \) phase can be considered as a usual Peierls band insulator. From the other viewpoint, it is impossible to ignore electron correlations in the d shell of vanadium and they cannot be considered on the average, as is done in band calculations. A quarter of century ago, one more insulating phase (\( M_2 \)) with local magnetic moments at some vanadium atoms was discovered. The \( M_2 \) phase originates upon slight doping of VO₂ with chromium (≥ 0.1 at. %) or upon application of a small stress along the [110] \( R \) axis. In the \( M_2 \) phase, in one chain, vanadium atoms form pairs along the [110] \( R \) direction, as in the \( M_1 \) phase (but without deviation from the [110] \( R \) direction), while in the neighboring chain the atoms of vanadium again become equidistant, as in the \( R \) phase, but the zigzag configuration is preserved, as in the \( M_1 \) phase. Because of the existence of a chain of equidistant V⁴⁺ ions, the band-theoretical description of the insulating state of the \( M_2 \) phase becomes impossible: these chains are magnetic (Mott-Hubbard) insulators. Therefore, theoretical models were developed in which the \( M_1 \) and \( M_2 \) phases were considered as the Mott-Hubbard insulators, excluding the interatomic Hubbard correlations in the \( R \) phase. At the same time, arguments and experimental evidences indicating that all structural modifications of VO₂ must be considered as Mott-Hubbard rather than as band insulators appeared in the literature.

Discussion of the nature of the insulating state in VO₂ continues with allowance for new experimental and theoretical data on the electronic structure of the \( R \) and \( M_1 \) phases. From comparison of the results of spectroscopic measurements and band calculations, it was concluded that the electronic structure of VO₂ is well described within the local-density approximation without an account of any correlation effects. Experimental measurements of the temperature dependence of the velocity of surface acoustic waves in the VO₂ single crystal near the metal-insulator transition permitted Maurer et al. to conclude that it is unlikely that the driving force of the metal-insulator transition are electron correlations. Measurements of the delay time in the VO₂ metal/oxide/metal structures and the investigation of the influence of the injection of carriers on switching and metal-insulator transition in planar switching devices also confirm exclusively the Mott-Hubbard mechanism of transition in VO₂. It is known that the usual band calculations indicate only a tendency for the formation of an energy gap in the \( M_1 \) phase of VO₂ and give a resulting metallic spectrum in contrast to the experimental. An attempt to resolve this contradiction within the band approach was made. Thus, the introduction of the electron-phonon interaction into the combination of the three-dimensional periodic-shell model and the \( \alpha \) cluster method of discrete variation resulted in the appearance of a gap in the band spectrum. The introduction of the correction for self-energy within the model GW scheme also satisfactorily reproduces the properties of the nonmetallic \( M_1 \) phase of VO₂ observed experimentally. Note that no theoretical calculations of the electronic structure of the insulating \( M_2 \) phase are available at present.

In this work, we tried to analyze in detail the electronic structure of the \( R \), \( M_1 \) and \( M_2 \) phases of VO₂ (for the first time in the case of the \( M_2 \) phase), in each case paying attention to the orbital that is filled by the sole electron of the V⁴⁺ ion. With this aim in mind, we used the first-
FIG. 1: The crystal structure of the $R$ phase of VO$_2$. Large spheres are the vanadium atoms, small spheres are the oxygen atoms. The axes of the crystallographic coordinate system are labeled by capital letters. The axes of the local systems of coordinates for the corner and body-center vanadium atoms are labeled by small letters.

principles linearized MT-orbital method of calculation in the tight-binding approximation (TB LMTO)\(^{17, 18}\). The nonmagnetic calculations were carried out within the conventional formalism of the local-density functional (LDA). In magnetic calculations, the electron correlations were taken into account within the LSDA+U approach\(^{19, 20}\). We used the experimentally determined values of the lattice parameters available in the literature (from\(^{21}\) for the $R$ phase, from\(^{22}\) for the $M_1$ phase, and from\(^{23}\) for the $M_2$ phase). In calculations, the radii of the atomic spheres of V and O were chosen to be equal with a 16% overlap; empty spheres were introduced to fill the volumes of the atomic spheres to the volume of the unit cell; the basic functions were 4s, 4p, and 3d for vanadium, 3s, 2p, and 3d for oxygen, and 1s, 2p, and 3d for the empty spheres. Within the LSDA formalism, we calculated the Coulomb $U$ and exchange $J$ interactions in the d shell of vanadium. The value of $U$ was calculated with allowance for screening of the $t_{2g}$ electrons by the $e_g$ electrons\(^ {22}\). The values $U = 3.8$ eV and $J = 1.0$ eV obtained were used unchanged in calculations of the electronic structure of all phases\(^ {24}\). Thus, our calculations do not contain adjustable parameters and, in this sense, are the first-principles.

The unit cell of the high-temperature $R$ phase of VO$_2$ (space group $P4_2/mnm$) contains two formula units. The vanadium atoms form a body-centered tetragonal lattice and are surrounded by slightly deformed oxygen octahedra. In such octahedra, the V–O distances in the direction normal to the tetragonal $c$ axis are slightly greater than the V–O distances in the plane parallel to the $c$ axis (Fig. 1 and table). In the same plane, the O-V-O angles are $84.2^\circ$ and $95.8^\circ$, while the other O-V-O angles are equal to $90^\circ$. The octahedra surrounding the vanadium atoms in the vertices and in the center of the unit cell are rotated by $90^\circ$ about the $c$ axis. In what follows, we will present the results for each vanadium atom in the local coordinate system, in which the $z$ axis is directed toward one of the most remote oxygen atoms (apical atom) in the octahedra. The direction of the chain of vanadium atoms along the $c$ axis is the bisector of the angle which is made by the $x$ and $y$ axes of the local coordinate system (see Fig. 1). The Euler angles used for passage from the crystallographic coordinate system to the local one for the vanadium atom at the position $(0; 0; 0)$ are the set $(\frac{\pi}{4}; \frac{\pi}{2}; -\frac{\pi}{4})$.

Let us clarify the terms that will be used in the interpretation of the results. By occupancy of the $i$th orbital, we mean the integral $N_i = \int_{-\infty}^{\infty} n_i(\varepsilon) d\varepsilon$ where $n_i(\varepsilon)$ is the corresponding partial density of states, and $\varepsilon_F$ is the Fermi energy. By the center of gravity of the $i$th band, we mean the ratio $\varepsilon_i^{cg} = \int_{\varepsilon_1}^{\varepsilon_2} \varepsilon \cdot n_i(\varepsilon) d\varepsilon / \int_{\varepsilon_1}^{\varepsilon_2} n_i(\varepsilon) d\varepsilon$, where $\varepsilon_1$ and $\varepsilon_2$ are the boundaries of the energy interval under consideration. By the dispersion of the $i$th band, the expression $\sigma_i = \sqrt{\varepsilon_i^{cg} - \varepsilon_1^2 + \varepsilon_2^2}$ is meant. Because of the distortion of the oxygen octahedra, the $t_{2g}$ orbitals of the vanadium atom become nondegenerate. The $xy$, $yz$–$zx$, and $yz + zx$ wave functions, where $x$, $y$, and $z$ represent the basis of the local system of coordinates, will be the natural basis for the $t_{2g}$ orbitals.

The results of the nonmagnetic LDA calculation are shown in Fig. 2. Our LDA calculations show: (1) owing to the elongation of the oxygen octahedra along the local $z$ axis, the $yz – zx$ orbital is most populated; (2) the center of gravity of the $yz – zx$ band lies most deeply in the energy range from $–8$ to $+6$ eV; (3) in the energy interval from $–1.5$ to $+1.8$ eV, the dispersion of the $yz – zx$ band is approximately one and half times greater than that for the $xy$ and $yz + zx$ bands.

We also carried out LSDA+U calculations for the $R$ phase of VO$_2$ for the ferromagnetic and antiferromagnetic types of ordering of magnetic moments of vanadium ions in the chains located along the tetragonal $c$ axis. In the first case, the half-metallic ferromagnetic state is ob-

TABLE I: The V–O distances (Å) for the $R$ and $M_1$ phases and the average distances for the $M_2$ phase of VO$_2$. The "apical" and "in-plane" oxygen atoms are considered in the local coordinate systems: the $z$ axis passes through the apical oxygen and the $x$ and $y$ axes pass through the in-plane oxygen atoms.

| Oxygen atoms | $R$ | $M_1$ | $M_2$ |
|--------------|-----|-------|-------|
|               |     | in the | in the |
|               |     | dimerized | undimerized |
| Apical       | 1.93 | 1.91   | 1.87  | 1.93 |
| In-plane     | 1.92 | 1.94   | 1.97  | 1.95 |
For both solutions the sole solution was lower than the first one in the total energy. The fact that the LSDA+U calculations predict the antiferromagnetic state was found to be insulating with an energy gap of 0.38 eV and $\mu$=0.90 $\mu_B$. The second solution was lower than the first one in the total energy. For both solutions the sole $d$ electron of the $V^{4+}$ ion was localized in the $yz-zx$ orbital (Fig. 3). This naturally follows from the above results ((1) and (2)) of the LDA calculations: within the LSDA+U approach, the orbital that already was most populated and whose center of gravity was already the lowest among all the $t_{2g}$ orbitals is occupied. The third result (the maximum dispersion of the $yz-zx$ band) has preserved the ferromagnetic state as the metallic one even within the LSDA+U calculation and led to the appearance of the antiferromagnetic insulating state with a small energy gap [30].

The fact that the LSDA+U calculations predict the antiferromagnetic insulating state for the $R$ phase of VO$_2$ instead of the metallic one reflects the known tendency of the LSDA+U method to overestimate the electron localization as a result of consideration of the on-site spin-and orbit-dependent Coulomb repulsion in terms of the mean-field theory. At the same time, the LSDA+U approach gives an accurate description of the orbital nature of the localized electrons [31]. Our calculations of the electron structure of VO$_2$ in the $R$ phase predict localization of the $d$ electron of the $V^{4+}$ ion on the $yz-zx$ orbital. As will be seen below, this result is a key one for the description of the metal-insulator transition in VO$_2$.

Analysis of the partial densities of the $t_{2g}$ states of vanadium, obtained in the nonmagnetic LDA calculation for the $M_1$ phase and shown in Fig. 4, indicates a different sequence of filling orbitals, as compared to the $R$ phase. The $M_1$ phase (the space group $P2_1/c$) is characterized by a pairing of the vanadium atoms along the [0.842; 0; −0.539] vector in the crystallographic coordinate system: there are short and long vanadium-vanadium bonds. Moreover, each pair of vanadium atoms is inclined relative to this vector in the plane with the normal [0.381; 0.708; 0.595] for one chain of vanadium atoms and to the plane with the normal [0.381; −0.708; 0.595] for the neighboring chain. The difference in the oxygen surroundings of the vanadium atoms is not only in the variation of the O-V-O angles, but also in that the V-O distance to the apical oxygen atoms in the $M_1$ phase became smaller than to the in-plane oxygens (see table). We define the local system of coordinates for the $M_1$ phase in the following way: the $z$ axis is perpendicular to the plane of the vanadium atoms that belong to the same chain, and the $x$ and $y$ axes are deflected by an angle of 45° from the direction of the chain (Fig. 5). In other words, the local system of coordinates for the $M_1$ phase is chosen similar to that for the $R$ phase. Then, for the vanadium atom in the (0.259; −0.025; −0.136) position, the Euler angles for passing from the crystallographic system of coordinates to the local one will be (0.658$\pi$; −0.297$\pi$; −0.984$\pi$).

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vanadium for the R and M₁ phases (see Figs. 2 and 4), note a substantial difference in the density of states for the xy orbital. Owing to dimension of the vanadium atoms, the corresponding band for the M₁ phase is split into bonding and antibonding subbands and, which is more important, the filling of the xy orbital becomes maximum between the t₂g orbitals. The nonmagnetic LDA calculation does not reproduce the insulating nature of the energy spectrum for the M₁ phase of VO₂. Yet, it is clear that the allowance for correlations in calculations will not change this key result, i.e., the preferential filling of the orbitals of the xy symmetry.

The conclusion concerning filling of the 3d¹ xy states of the M₁ phase is supported by two factors. First, the distortions of the oxygen octahedra around the vanadium atom occur in such a way that the maximum V-O distances are observed in the xy plane in the local system of coordinates (see table), which, in turn, lowers the energy of the xy orbital. Second, we performed the LSDA+U calculations for the M₁ structure to determine which of the orbitals will be filled by the localized electron 32. Note that the LSDA+U calculation predicts for the M₁ phase the antiferromagnetic ground state with a gap equal to 0.55 eV and the spin magnetic moment of the d shell of vanadium μ=0.81 μB instead of the nonmagnetic insulating state with a gap of 0.2-0.7 eV observed experimentally [9, 27]. Quantum corrections, probably, could suppress the long-range magnetic order obtained in the LSDA+U calculation, and the calculated value of the gap is within the limits of the experimental one. Yet, turning to the discussion of the orbital nature of the localized d electron, one can see from Fig. 5 that the xy orbital became localized. Both factors permit us to conclude that upon transition of VO₂ from the R to the M₁ phase, along with a change in the ratio of the distances from the vanadium atom to the in-plane oxygen atom and to the apical oxygen atom, an important transformation of orbital symmetry of the localized 3d¹ electron of the V⁴⁺ ion occurs, namely, from the yz − zx to the xy.

We believe that the Peierls mechanism is not responsible for the formation of the insulating state of the M₁ phase. Even the LDA results show that the most filled orbitals in both cases are different: the xy orbital for the M₁ phase and the yz − zx orbital for the R phase. It is known (for example, from the theoretical investigations of CrO₂ 24 which also has a crystal structure of the rutile type) that the yz − zx band has substantial dispersion and is strongly hybridized with the O2p states, forming the π bond with them. Therefore, it is weakly localized even in the presence of strong correlations and the energy spectrum may remain metallic in the case of the preferential filling of this band. At the same time, the xy band is narrower than the yz − zx one and more sensitive to correlations. This results in localization of electrons on the xy orbital, its complete filling, and the appearance of a gap in the energy spectrum. It is what we obtained in our LSDA+U calculations. Thus, we can conclude that it is the Mott-Hubbard mechanism that is responsible for the formation of the energy gap in VO₂. The Peierls’ mechanism can be used only for explanation of the insulating state of the M₁ phase, but it is completely unacceptable for the M₂ phase, in which both dimerized and undimerized chains of vanadium atoms exist simultaneously. Taking into account which orbitals are filled by the d electron in each particular case and which are the properties of these orbitals, the Mott-Hubbard mechanism can be applied for the description of both metallic
and insulating states of all crystal phases of VO\(_2\).

The calculations of the electronic structure of the \(M_2\) phase (space group \(C2/m\)) fully confirm our assumption about the mechanism of formation of energy bands in VO\(_2\). Both dimerized chains of vanadium atoms (similar to the chains in the \(M_1\) phase) and the undimerized ones (as in the \(R\) phase) exist in the crystal structure of the \(M_2\) phase. As in the \(M_1\) phase, but contrary to the \(R\) phase, the V-O distances to the apical oxygen atoms in the oxygen octahedra which surround the vanadium atoms in both types of chains are smaller than to the inplane oxygens. The Euler angles for the passage to the local system of coordinates for the vanadium atoms in the dimerized and undimerized chains (Fig. 6) are given by the sets of \((-\pi/2; 0; \pi/2)\) and \((0; -\pi/2; 0)\).

The "nonmagnetic" calculations in the local-density approximation give the metallic ground state, which contradicts the experiment. Owing to a substantial distortion of the crystal structure and, correspondingly, complicated hybridization of the \(d\) states of vanadium with each other, it is impossible here to consistently separate the partial densities of the \(t_{2g}\) states in the cubic harmonics, which we had done, for example, for the \(R\) phase. The LSDA+U calculation is the sole possibility of determining which localized \(t_{2g}\) orbital will be filled.

The results of such a calculation are shown in Fig. 6. They demonstrate the occupied orbitals of vanadium that in the \(M_2\) phase are the \(xy\) orbitals both in the dimerized and undimerized chains. According to calculations, in the case of antiferromagnetic ordering the spin magnetic moment of the \(d\) shell of vanadium that belongs to the undimerized chain is equal to \(\mu = 0.89 \mu_B\) and the arising energy gap is 0.93 eV. We also calculated the exchange-correlation parameter \(J\) of the Heisenberg model for the vanadium atoms in the undimerized chain (the scheme of calculation within the LSDA+U method is described in [20]). Its value was found to be 205 K and the sign corresponds to the antiferromagnetic exchange. The value obtained is close to the result of [8] where, from an analysis of nuclear magnetic resonance experiments, it is shown that the \(V^{4+}\) ions in the undimerized chains behave as Heisenberg chains with spin \(S = 1/2\) and antiferromagnetic exchange \(J \approx 300\) K.

Thus, the principal difference between the rutile \(R\) phase and the monoclinic \(M_1\) and \(M_2\) phases is which of the localized \(t_{2g}\) orbitals is filled by the sole 3d electron of the \(V^{4+}\) ion: \(yz - zx\) or \(xy\). The choice of the filled orbital is determined by the local oxygen surroundings of the vanadium atoms. Since these bands have different properties relative to localization (or dispersion), the correlation effects variously influence the energy spectrum (metal or insulator) depending on which band is filled. It is correlations (the Mott-Hubbard mechanism) that are responsible for the insulating properties of the \(M_1\) and \(M_2\) phases of VO\(_2\). Correlations are also present in the metallic \(R\) phase. Owing to the localization of the \(d\) electron in the \(yz - zx\) orbital, they do not lead to the appearance of a gap in the band spectrum.

This work was supported by the Russian Foundation for Basic Research, project no. 01-02-17063, and by NWO (grant no. 047-008-012).

References:

[1] J.B. Goodenough, The two components of the crystallographic transition in VO\(_2\),– J. Solid State Chem. 3, no. 4, pp. 490–500, 1971.
[2] R.M. Wentzcovitch, W.W. Schulz and P.B. Allen, VO\(_2\): Peierls or Mott-Hubbard? A view from band theory,– Phys. Rev. Lett. 72, no. 21, pp. 3389–3392, 1994.
[3] M. Marezio, D.B. McWhan, J.P. Remeika and P.D. Dernier, Structural aspects of the metal-insulator transitions in Cr-doped VO\(_2\),– Phys. Rev. B 5, no. 7, pp. 2541–2551, 1972.
[4] J.P. Pouget, H. Launois, J.P. D’Haenens, P. Merenda and T.M. Rice, Electron localization induced by uniaxial stress in pure VO\(_2\),– Phys. Rev. Lett. 35, no. 13, pp. 873–875, 1975.
[5] M. Imada, A. Fujimori and Y. Tokura, Metal-insulator transitions,– Rev. Mod. Phys. 70, no. 4, pp. 1039–1263, 1998.
[6] A. Zylbersztejn and N.F. Mott, Metal-insulator transition in vanadium dioxide,– Phys. Rev. B 11, no. 11, pp. 4383–4395, 1975.
[7] P. Lederer, H. Launois, J.P. Pouget, A. Casalot and G. Villeneuve, Contribution to the study of the metal-insulator transition in the \(V_{1-x}Nb_xO_2\) system – III Theoretical discussion,– J. Phys. Chem. Solids 33, no. 10, pp. 1969–1978, 1972.
[8] J.P. Pouget, H. Launois, T.M. Rice, P. Dernier, A. Gos-
sard, G. Villeneuve and P. Hagenmuller, *Dimerization of a linear Heisenberg chain in the insulating phases of V_{1-x}Cr_xO_2*.– Phys. Rev. B **10**, no. 5, pp. 1801–1815, 1974.

[9] S. Shin, M. Taniguchi, M. Fujisawa, H. Kanzaki, A. Fujimori, H. Daimon, Y. Ueda, K. Kosuge and S. Kachi, *Vacuum-ultraviolet reflectance and photoemission study of the metal-insulator phase transitions in VO_2, V_6O_{13} and V_2O_4*.– Phys. Rev. B **41**, no. 8, pp. 4993–5009, 1990.

[10] A.V. Nikolaev, Yu.N. Kostrubov and B.V. Andreev, *Electron Structure of the Metallic Phase and the Metallic-Insulator transition in VO_2*.– Fiz. Tverd. Tela **34**, no. 10, pp. 3011–3018, 1992.

[11] T.M. Rice, H. Lauzon and J.P. Pouget, *Comment on “VO_2: Peierls or Mott-Hubbard? A view from band theory”.*– Phys. Rev. Lett. **73**, no. 22, p. 3042, 1994.

[12] E.Z. Kurmaev, V.M. Cherkashenko, Yu.M. Yarmoshenko, St. Bartkowski, A.V. Postnikov, M. Neumann, L.-C. Duda, J.H. Guo, J. Nordgren, V.A. Perelyaev and W. Reichelt, *Electronic structure of VO_2 studied by x-ray photoelectron and x-ray emission spectroscopies*.– J. Phys.: Condens. Matter **10**, no. 18, pp. 4081–4091, 1998.

[13] D. Maurer, A. Leue, R. Heichele and V. Müller, *Elastic behavior near the metal-insulator transition of VO_2*.– Phys. Rev. B **60**, no. 19, pp. 13249–13252, 1999.

[14] G. Stefanovich, A. Pergament and D. Stefanovich, *Electrical switching and Mott transition in VO_2*.– J. Phys.: Condens. Matter **12**, no. 41, pp. 8837–8845, 2000.

[15] H. Nakatsujiwa and E. Iguchi, *Electronic structures in VO_2 using the periodic polarizable point-ion shell model and DV-Xa method*.– Phys. Rev. B **55**, no. 4, pp. 2157–2163, 1997.

[16] A. Continenza, S. Massidda and M. Posternak, *Self-energy corrections in VO_2 within a model GW scheme*.– Phys. Rev. B **60**, no. 23, pp. 15699–15704, 1999.

[17] O.K. Andersen and O. Jepsen, *Explicit, first-principles tight-binding theory*.– Phys. Rev. Lett. **53**, no. 27, pp. 2571–2574, 1984.

[18] O.K. Andersen and Z. Pawlowska and O. Jepsen, *Illustration of the linear-muffin-tin-orbital tight-binding representation: compact orbitals and charge density in Si*.– Phys. Rev. B **34**, no. 8, pp. 5253–5269, 1986.

[19] V.I. Anisimov, J. Zaanen and O.K. Andersen, *Band theory and Mott insulators: Hubbard U instead of Stoner I*.– Phys. Rev. B **44**, no. 3, pp. 943–954, 1991.

[20] A.I. Liechtenstein, V.I. Anisimov and J. Zaanen, *Density-functional theory and strong interactions: orbital ordering in Mott-Hubbard insulators*.– Phys. Rev. B **52**, no. 8, pp. R5467–R5470, 1995.

[21] D.B. McWhan, M. Mareazio, J.P. Remeika and P.D. Dernier, *X-ray diffraction study of metallic VO_2*.– Phys. Rev. B **10**, no. 2, pp. 490–495, 1974.

[22] G. Andersson, *The crystal structure of vanadium dioxide*.– Acta Chem. Scand. **10**, pp. 623–628, 1956.

[23] W.E. Pickett, S.C. Erwin and E.C. Ethridge, *Reformulation of the LDA + U method for a local-orbital basis*.– Phys. Rev. B **58**, no. 3, pp. 1201–1209, 1998.

[24] M.A. Korotin, V.I. Anisimov, D.I. Khomskii and G.A. Sawatzky, *CrO_2: a self-doped double exchange ferromagnet*.– Phys. Rev. Lett. **80**, no. 19, pp. 4305–4308, 1998.

[25] V.I. Anisimov, I.S. Elfilm, M.A. Korotin and K. Terakura, *Orbital and charge ordering in Pr_{1-x}Ca_xMnO_3 (x=0 and 0.5) from the ab initio calculations*.– Phys. Rev. B **55**, no. 23, pp. 15494–15499, 1997.

[26] M.A. Korotin, I.S. Elfimov, V.I. Anisimov, M. Troyer and D.I. Khomskii, *Exchange interactions and magnetic properties of the layered vanadates CaV_2O_5, MgV_2O_5, CaV_2O_7 and CaV_4O_9*.– Phys. Rev. Lett. **83**, no. 7, pp. 1387–1390, 1999.

[27] G.A. Sawatzky and D. Post, *X-ray photoelectron and Auger spectroscopy study of some vanadium oxides*.– Phys. Rev. B **20**, no. 4, pp. 1546–1555, 1979.

[28] The diagram of mutual arrangement of V atoms in the three VO_2 phases can be found, for example, in [2], Fig. 215. The phase diagram is shown in [2], Fig. 217. The triclinic T phase of VO_2 will not be considered in this work.

[29] The existing experimental estimates of the Coulomb interaction U in VO_2 give 2.1 eV for the insulating phase and 1.3 eV for the metallic phase. These values are slightly below that used in calculations U ≈ 3.8 eV.

[30] For U ≤ 3.0 eV, the antiferromagnetic state of the R phase in the LSDA+U calculation is metallic. See also [29].

[31] This is shown in the series of our works devoted to the investigation of orbital filling in CrO_2 KCuF_3 perovskites PrMnO_3, layered vanadates of the CaV_nO_{2n+1}-type, etc.

[32] In calculating the M1 and M2 phases of VO_2, it is incorrect to substantiate conclusions by comparing the centers of gravity of orbitals and the dispersions of the corresponding bands obtained in nonmagnetic LDA calculations in view of the lower symmetry of these phases and substantial hybridization of the states under investigation.