RESEARCH OF ELECTRONIC STRUCTURE IN NdVO$_3$ AND HoVO$_3$ OXIDES: X-RAY ELECTRON SPECTRUM AND *AB INITIO* CALCULATION OF BAND STRUCTURE

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Complex researches of the electron structure and magnetic properties of NdVO$_3$ and HoVO$_3$ oxides have been carried out with the use of the X-ray electron spectroscopy and *ab initio* numerical calculations. Data have been obtained concerning the distributions of total and partial electron densities of states in the valence and conduction bands, the charge and spin states of atoms, the mechanism of chemical bond formation, and the band gap in the energy spectra of the oxides under consideration.

1. Introduction

Materials on the basis of complex oxides of elements with unfilled *d*- and *f*-electron shells find the wide application in various branches of science and technology, because they are characterized by a unique combination of electric, magnetic, optical, ferroelectric, and other useful properties. Their specificity depends to a large extent on the degree of filling of unoccupied electron shells, the corresponding orbital lengths, and the character of electron participation in interatomic chemical bonds. The variation of those parameters leads to a transformation of the conductivity type in oxides. As a result, this family of compounds includes such members, which can be characterized not only as insulators and semiconductors, but also as conducting materials. That is why vanadium oxides with a unique semiconductor–metal phase transition have acquired the great popularity. Very interesting among them are oxides with the common formula LnVO$_3$ (Ln = La ÷ Lu), as well as their derivatives which are lanthanum-substituted solid solutions.

The mentioned vanadites demonstrate a semiconductor-like dependence of their electric resistance with rather low activation energy in a wide temperature interval. As a rule, this conductivity has an impurity-induced character, which can be explained [1] by the formation of vacancies in the cation sublattice of LnVO$_3$ oxides. Among possible mechanisms governing the main properties of such vanadites, the intrinsic conductivity is mentioned [1], but no relevant accurate data – neither experimental, nor theoretical ones – for stoichiometric oxides have been presented. Note also that the electron structure, as a whole, of vanadites LnVO$_3$ (Ln = La ÷ Lu) has not been studied enough yet. In particular, there are still contradictions concerning a unique picture describing the distributions of total and partial electron states in the valence and conduction bands, the charge and spin states of atoms in rare-earth element (REE) compounds with 3d-metals, the mechanism of chemical bond formation, and the distribution of magnetic moments [2–6]. Therefore, researches of the electron structure in the mentioned vanadites could throw daylight upon the mechanisms of formation of many their properties.

In this work, the oxides LnVO$_3$ (Ln = Nd, Ho) are studied with the use of X-ray electron spectroscopy and quantum-mechanical calculations of their electron structure. The main attention is concentrated on the structure of subvalence, valence, and vacant states of vanadites, the character of their hybridization, the charge and spin characteristics of atoms, and the mechanisms of formation of chemical interatomic bonds.

2. Experimental Technique

Crystal lattices of vanadites LnVO$_3$ (Ln = Nd, Ho) are classified to the orthorhombic system and characterized by space group *Pnma* (No. 62). Their fragment is exhibited in Fig. 1.

To study the electron structure in the oxides concerned, we used a complex approach based on the analysis of X-ray electron spectra and the results of band calculations. The latter were carried out in the framework of the linearized augmented plane wave (LAPW) method [7] with the generalized gradient approximation (GGA) for the electron density of states [8] and taking advantage of the Wien2k computer code [9]. For the calculation of total and partial state densities and the dispersion dependences $E(k)$ of oxides, we used the spin-polarized
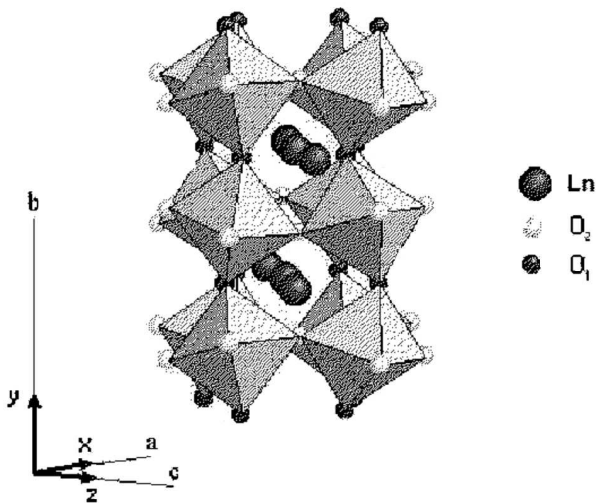
Fig. 1. Fragment of crystal lattices of the LnVO$_3$ (Ln = Nd, Ho) compound. Letters a, b, and c designate crystallographic axes, and vectors X, Y, and Z point to the orientation of the global (represented in the figure) and local (atomic) rectangular coordinate systems. Vanadium atoms are in oxygen octahedra

variant of the LAPW method [9], which makes allowance for spin-orbit interactions for all vanadite atoms and the correlation of $Ln4f$- and V3d-electrons in the framework of LDA+U formalism [10].

As the initial structural data necessary for calculations, we used the constants of an orthorhombic cell and the coordinates of nonequivalent atoms in the sections of corresponding cell edges. Namely,

– for HoVO$_3$: a = 5.614 Å, b = 7.626 Å, c = 5.303 Å, Ho $(0.574, 0.25, 0.021)$, V $(0.0, 0.0, 0.0)$, O$_1$ $(-0.03, 0.25, -0.104)$, O$_2$ $(0.302, 0.051, 0.182)$ [11];

– for NdVO$_3$: a = 5.461 Å, b = 5.580 Å , c = 7.762 Å, Nd $(0.987, 0.052, 0.25)$, V $(0.5, 0.0, 0.0)$, O$_1$ $(0.085, 0.479, 0.25)$, O$_2$ $(0.702, 0.296, 0.048)$ [12].

The radii of non-overlapping muffin-tin (MT) spheres for each compound were selected, provided that the dimensions of the region beyond a sphere is minimal. In particular, the radius of MT spheres was 2.2 Å for Ln, 1.87 Å for V, and 1.75 Å for oxygen atoms O$_1$ and O$_2$. While calculating the density of states, 75 points in the irreducible part of the Brillouin zone of LnVO$_3$ compounds were used. We used the APW+lo basis sets to approximate the wave functions of $Ln4f$-, V3d-, and O$_{1,2}$2p-electrons, and the LAPW basis sets for the wave functions of other valence electrons. The product of the radius of minimal MT-spheres, R_{MT}, and the maximum value of the plane-wave wave vector, K_{max}, was selected to equal six. While calculating non-MT matrix elements,

we selected l = 10 and 4 as the maximal values of quantum numbers for partial waves in the middle of spheres. The best correspondence of the results of quantum-mechanical calculations to the experimental ones (see below) was achieved for the choice U_{eff} = 0.580 Ry for the holmium atom and U_{eff} = 0.2212 Ry for the vanadium one in the HoVO$_3$ oxide. Here, $U_{eff.}$ = $U - J$, and U and J are the Coulomb and exchange parameters, respectively. For the NdVO$_3$ compound, $U_{eff.}$ = 0.085 Ry for the neodymium atom and $U_{eff.}$ = 0.3075 Ry for the vanadium one.

The X-ray electron spectra of valence electrons in LnVO$_3$ vanadites (Ln = Nd, Ho) were obtained on a "Kratos" spectrometer with an aluminum anode. The reproducibility of measurement results for electron binding energies in atoms was about 0.2 eV.

3. Discussion of Results Obtained

In Fig. 2, the X-ray electron spectra of valence electrons in vanadites LnVO$_3$ (Ln = Nd, Ho) and the calculated curves for their densities of states are depicted. The coincidence of the latter with experimentally obtained spectra is observed with respect to components A and A' in the case of holmium oxide, and components p and p' for the compound with neodymium. The X-ray electron spectra turned out shifted by 2.90 and 3.38 eV toward lower electron binding energies for holmium and neodymium, respectively, oxides. The overestimated values of binding energies for valence electrons in comparison with calculated values are evidently associated with electron vacancies in final (excited) states of corresponding XES's.

In general, a strict correspondence between the main-peak positions in the spectra and the total electron densities of states is observed. The exceptions are some low intensive components in the XES's; the corresponding features are absent from the total electron density of states. Their origin may probably be connected with surface contaminations of researched oxides or stem from multielectron effects, which were not taken into account in full at calculations.

This circumstance, first, allows the major features in the X-ray electron spectra to be interpreted with a high reliability and, second, testifies to quite a good quality of our calculations.

One can see that the deepest components in the total density of states, with energies close to 38 eV, correspond to the states of vanadium atoms. Peaks that correspond to the states of neodymium atoms are also located here. In the X-ray electron spectrum of neodymium-including
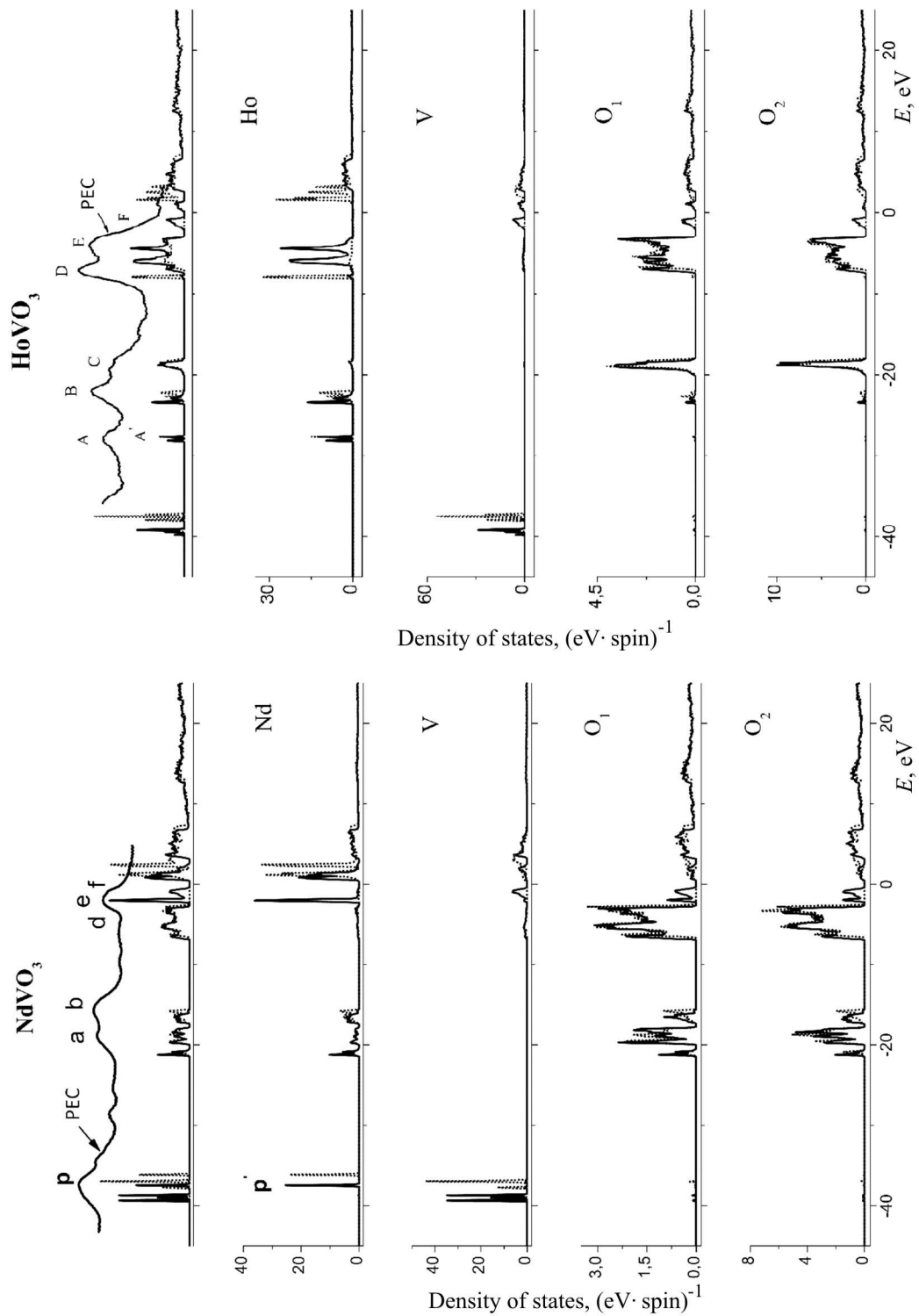
Fig. 2. X-ray electron spectrum (XES), the total electron densities of states (the upper panel), and the total atomic electron densities of states in holmium and neodymium vanadites. Solid (dotted) curve corresponds to the density of states for spin-up (spin-down) electrons. The zero at the energy scale corresponds to the calculated position of chemical potential

oxide, they form peak p. The features, which represent almost "pure" states of holmium atoms, correspond to components A (-28.06 eV) and B (-22.04 eV) in the X-ray electron spectrum of the HoVO$_3$ oxide. The same states give the main contribution to the formation of components with maximal intensity, D (-7.16 eV) and E (-4.06 eV). In its turn, feature C (-18.80 eV) in the experimental spectrum is substantially associated with the states of oxygen atoms. These states, but already hybridized with the states of vanadium atoms, manifest themselves in the spectrum concerned as peak F (-1.10 eV) with insignificant intensity. Changing over to the oxide with neodymium, the X-ray electron spectrum of valence electrons considerably changes: the three-peak structure (A, B, C) transforms into a two-peak one (a (-18.82 eV), b (-15.72 eV)). Figure 2 demonstrates that this transformation is associated with the hybridization of states of neodymium and oxygen atoms. The oxygen atom makes a considerable contribution to the formation of the intensities of component d (-6.22 eV) and strongly pronounced adjacent peak e (-2.02 eV), the latter being connected with the states of neodymium atoms. The origin of the low-energy shoulder f (-1.02 eV) in the NdVO$_3$ spectrum actually remains the same as in the holmium-including compound.

The results of our calculations showed that the compounds under consideration are characterized by insignificant hybridization between the valency states of REE atoms and the states of other atoms. This circumstance may testify to a weakening of the covalent interaction between REE and environmental atoms and, as a consequence, to a possibility of the vacancy formation in the cation holmium and neodymium sublattices in the examined vanadites [1]. An enhanced polarization of metal atom states is observed at that.

The results exhibited in Figs. 3 and 4 specify the interpretation of the data given above. One can see that the deepest components are nothing else but a manifestation of Vp-states genetically coupled with quasi-core V$3p_{1/2}$, V$3p_{3/2}$, and (in case of the compound with neodymium) Nd$5s$ atomic levels. Similarly, these two groups of peaks in the electron density of states, which are located in the localization range of components A and B, can be associated with quasi-core states Ho$5p_{1/2}$ and Ho$5p_{3/2}$ in the XES of HoVO$_3$, which are extremely weakly hybridized with O$2s$ states. The latters form a peak, which corresponds to component C in the X-ray electron spectrum. Concerning the oxide with neodymium, components a and b in the XES reflect hybridized Nd$5p_{1/2}$, Nd$5p_{3/2}$, and O$2s$ states. The growth of hybridization degree for the indicated states, when the holmium atom

is substituted by the neodymium one, is evidently connected with the energy convergence of quasi-core levels $Ln5p_{1/2}$, $Ln5p_{3/2}$, and O$2s$ [13]. In the range of X-ray electron spectra, where the major maxima D, E, and e are localized, the core states $4f_{5/2}$ and $4f_{7/2}$ of lanthanide atoms dominate. A considerable density and rather large ionization cross-sections [14] provide a high intensity of components in experimentally obtained spectra. As is seen from the figures discussed, a substantial contribution to this energy interval is also made by valence O$2p$ states, whereas the contribution by s and d states of metal atoms turns out insignificant in whole.

A detailed consideration of the state distributions for vanadium and oxygen atoms, which make the largest contributions to the states of valence band top, is of interest. In Fig. 5, the curves describing the electron density distributions for separate harmonics of V$3d$ and O$2p$ states are depicted. One can see that the spectrum of valence states includes two groups of components separated by an energy gap: one group is centered at about -5.0 eV, the other at about -1.0 eV. The latter is separated from the states in the conduction band by a forbidden gap. Attention is drawn by the energy separation of atomic state contributions between the mentioned subbands. The main contribution to the first subband is made by O$2p$ states, with the V$3d$ charge density amounting to only about 26.0% of this quantity. Approximately 55.0% of the total V$3d$-shell charge is located at chemical bonds described by the harmonics forming the second subband. Here, the relative contribution of O$2p$ electron density with respect to the total charge of O$2p$ shell is small (of about 2.8%), being equal, on the average, to 8.7% of the charge in V$3d$ shell.

Hence, the contribution of V$3d$ states dominates in the valence subband neighboring to the conduction one. If changing over to HoVO$_3$, the picture modifies insignificantly: the above-mentioned two-band structure is also present in the valence band, and the separation of atomic state contributions is preserved at a qualitative level.

Figure 6 specifies the picture of the distribution of oxygen and vanadium atomic states near the zero values of chemical potential μ. One can see that the valence states of vanadium atoms, as usual, and the valence states of oxygen atoms are strongly polarized and include the component of the electron density of states with the spin up.

Despite the mentioned weak hybridization of vanadium states and oxygen atoms, we can specify the type of chemical bonds between them. One can see (see the orientation of coordinate axes in Fig. 1) that the matter concerns the formation of weak co-
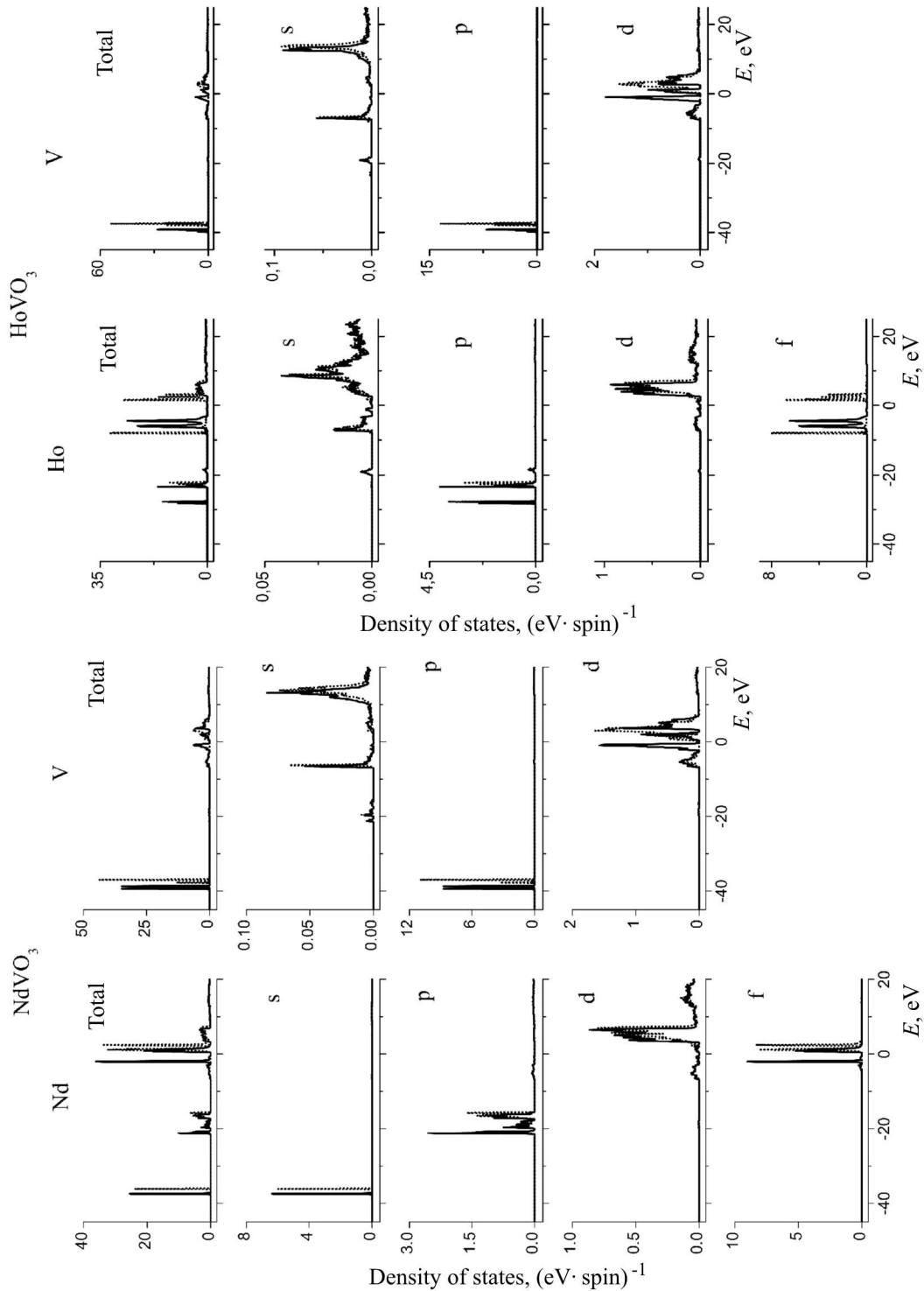
Fig. 3. Total and partial electron densities of states in holmium, neodymium, and vanadium atoms in the oxides. See notations in Fig. 2
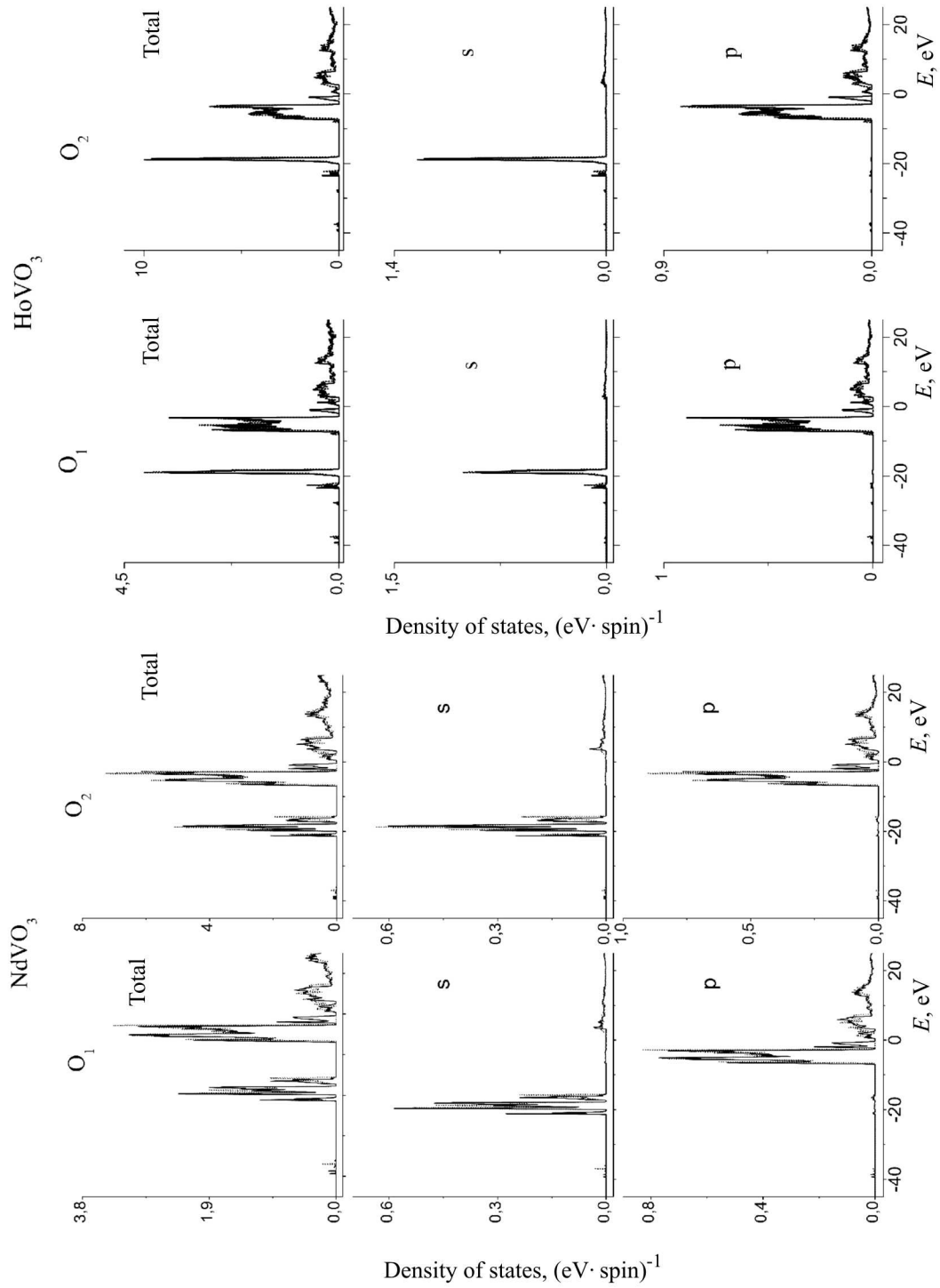
Fig. 4. The same as in Fig. 3, but for O_1 and O_2 atoms
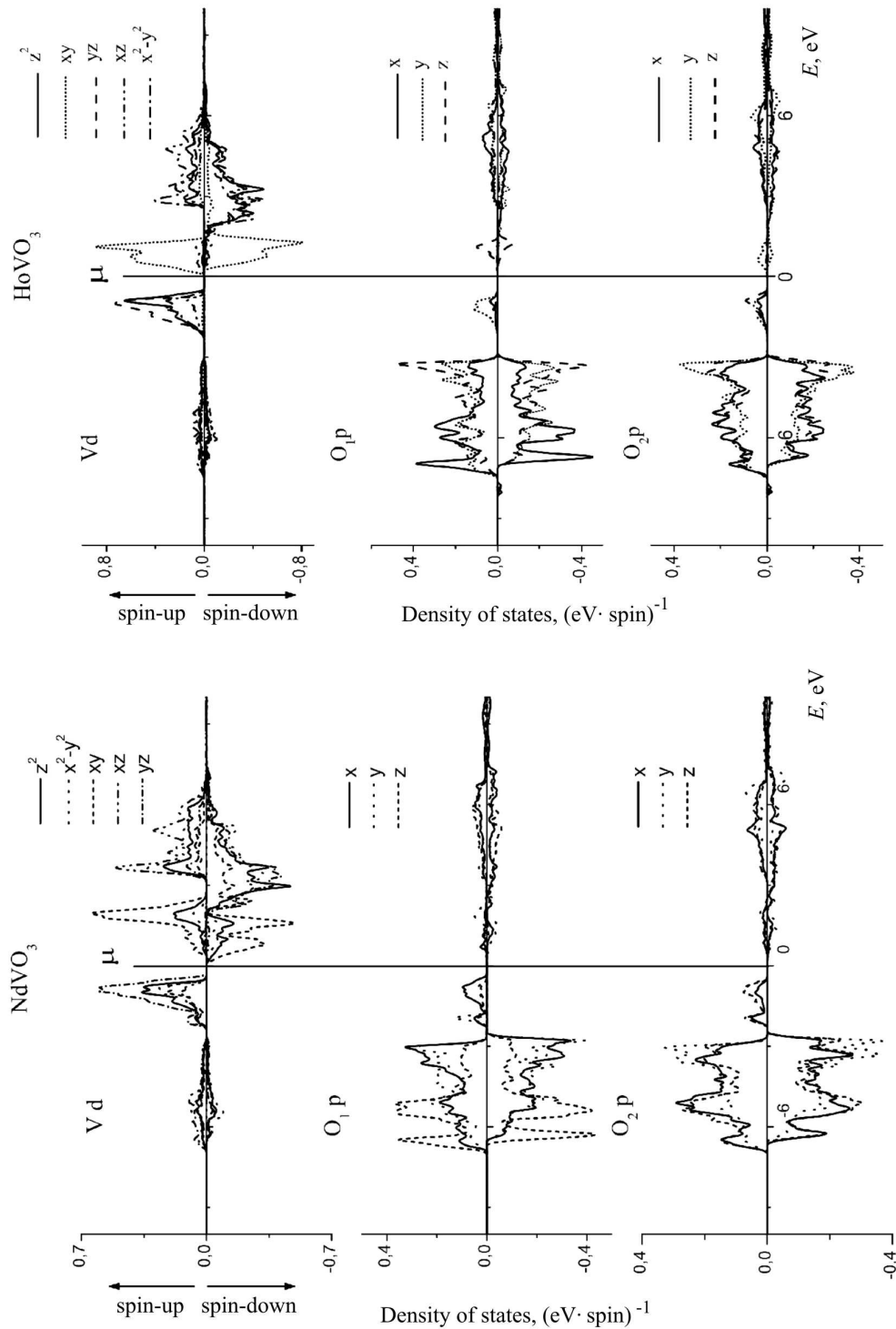
Fig. 5. Partial electron density of states in vanadium and oxygen atoms of NdVO$_3$ and HoVO$_3$ compounds decomposed into harmonics $d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{xz}, d_{yz}, p_x, p_y, and p_z (the Vs and Vp electron densities of states are not given owing to their low values). The vertical straight line marked by letter μ denotes the energy position of chemical potential

Fig. 6. Structures of valence and conduction bands in the vicinity of forbidden gap in LnVO$_3$ oxides

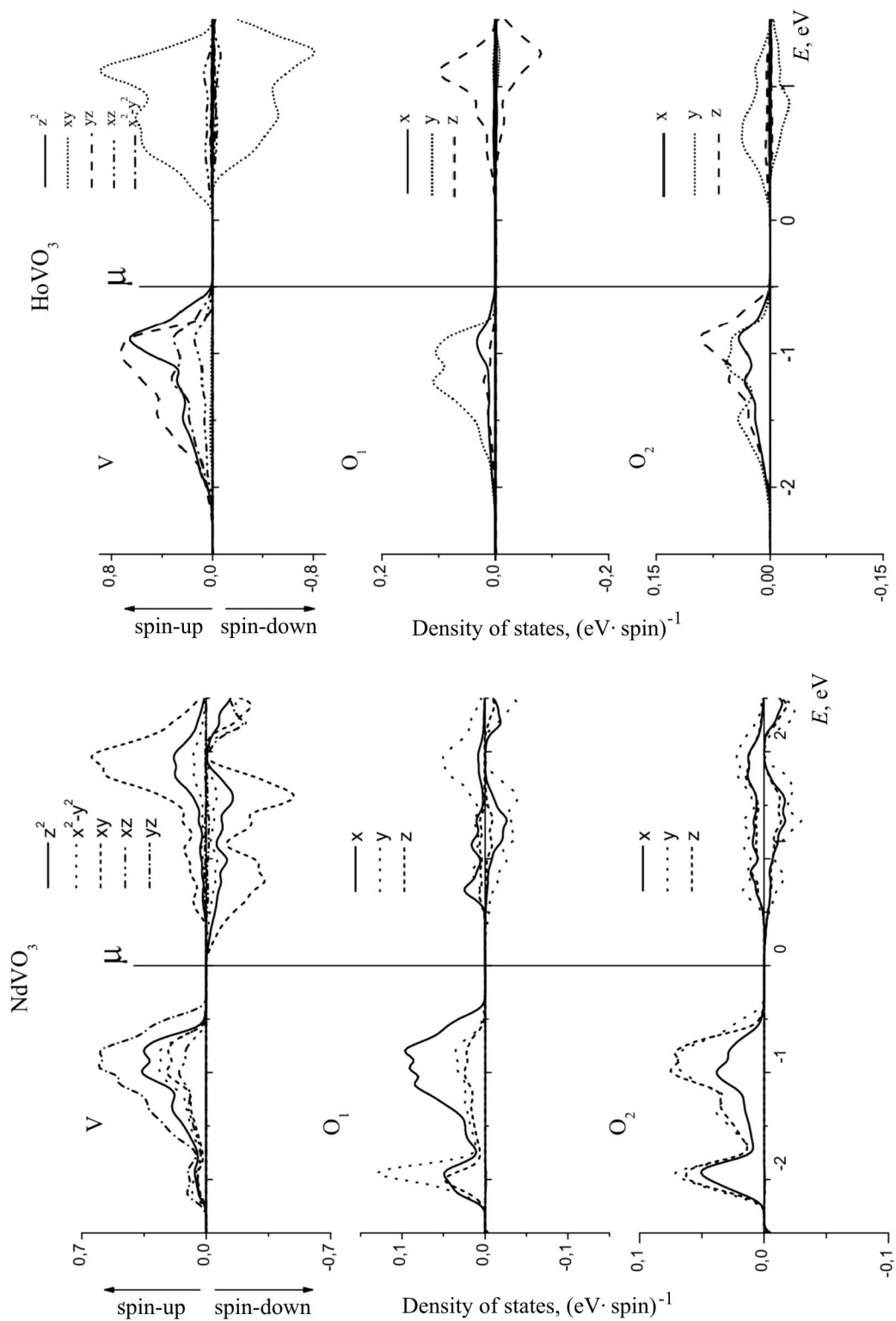**T a b l e 1.** Total charge of valence electrons, Q, and their partial charges (in terms of e^--units) at atomic orbitals in HoVO$_3$ oxide for spin-up (↑) and spin-down (↓) electron states

Atom	Spin	Q	s	p	d	f	px	py	pz	pz^2	px^2-y^2	dxy	dxz	dyz
Ho	↑	10.87	1.00	2.77	0.21	6.89	0.81	0.80	0.80	0.04	0.04	0.04	0.04	0.05
	↓	6.92	1.00	2.75	0.17	3.00	0.78	0.77	0.78	0.03	0.04	0.03	0.03	0.04
V	↑	5.89	1.03	2.95	1.91	0.01	0.03	0.03	0.02	0.51	0.45	0.09	0.21	0.65
	↓	4.38	1.02	2.94	0.41	0.01	0.03	0.03	0.02	0.06	0.12	0.07	0.11	0.05
O$_1$	↑	2.83	0.84	1.98	0.01	0.00	0.68	0.65	0.65	0.00	0.00	0.00	0.00	0.00
	↓	2.80	0.84	1.95	0.01	0.00	0.65	0.65	0.65	0.00	0.00	0.00	0.00	0.00
O$_2$	↑	2.84	0.84	1.98	0.01	0.00	0.66	0.66	0.67	0.00	0.00	0.00	0.00	0.00
	↓	2.80	0.84	1.95	0.01	0.00	0.65	0.65	0.65	0.00	0.00	0.00	0.00	0.00

T a b l e 2. Total charge of valence electrons, Q, and their partial charges (in terms of e^--units) at atomic orbitals in NdVO$_3$ oxide for spin-up (↑) and spin-down (↓) electron states

Atom	Spin	Q	s	p	d	f	px	py	pz	pz^2	px^2-y^2	dxy	dxz	dyz
Nd	↑	6.60	0.95	2.53	0.17	2.95	0.50	0.50	0.50	0.03	0.04	0.03	0.03	0.04
	↓	3.68	0.94	2.51	0.14	0.09	0.43	0.43	0.43	0.02	0.03	0.03	0.03	0.03
V	↑	5.88	1.03	2.94	1.90	0.01	0.03	0.03	0.03	0.37	0.37	0.24	0.26	0.67
	↓	4.39	1.02	2.94	0.42	0.01	0.03	0.03	0.02	0.07	0.11	0.06	0.12	0.05
O$_1$	↑	2.84	0.84	1.99	0.01	0.00	0.68	0.65	0.66	0.00	0.00	0.00	0.00	0.00
	↓	2.79	0.84	1.94	0.01	0.00	0.65	0.64	0.65	0.00	0.00	0.00	0.00	0.00
O$_2$	↑	2.84	0.84	1.98	0.01	0.00	0.66	0.66	0.66	0.00	0.00	0.00	0.00	0.00
	↓	2.78	0.84	1.93	0.01	0.00	0.65	0.64	0.64	0.00	0.00	0.00	0.00	0.00

valent bonds of the σ-type between oxygen atoms of the first type and vanadium atoms through the combination of O$_1$2p_y and V3$d_{x^2-y^2}$ orbitals. Concerning oxygen atoms of the second type, they mainly form π-bonds with vanadium atoms. These bonds are organized by engaging the following orbital pairs: O$_2$2p_y and V3$d_{x^2-y^2}$, O$_2$2p_y and V3d_{yz}, O$_2$2p_x and V3d_{xz}, O$_2$2p_z and V3d_{z^2}. As the figure demonstrates, the spectrum of states in the conduction band includes the components with both spin directions.

It is easy to see that the forbidden gap, which separates the electron states in the valence and conduction bands, has predominately the V3d_{z^2}-V3d_{xy} character in case of holmium vanadite and the V3d_{yz}-V3d_{xy} one for the compound with neodymium. The detailed analysis of the results of our calculations shows that the forbidden gap emerges only if additional correlations of electrons in Ho4f and V3d shells are taken into account in the LDA+U approximation. The minimal optical gap is located in this case at point Γ of Brillouin zone for examined vanadites and amounts to 0.67 eV for HoVO$_3$ and 0.50 eV for NdVO$_3$. According to experimental data [1], the gap width is 0.66 eV for HoVO$_3$ and 0.5 eV for NdVO$_3$. Hence, we practically have a coincidence between the experimental and calculated values of the forbidden gaps.

Let us discuss an issue concerning the formation of magnetic moments and charge states of atoms in the oxides under investigation. The calculations showed that the total magnetic moment of the elementary cell in the studied oxides, which includes 4 holmium atoms, 4 vanadium atoms, 4 oxygen atoms of the first type, and 8 oxygen atoms of the second type, is 24.0μ_B for HoVO$_3$ and 19.2μ_B for NdVO$_3$; μ_B being the Bohr magneton. The distribution of magnetic moments in the atomic MT-spheres turned out as follows: (i) Ho – 3.98μ_B, V – 1.53μ_B, O$_1$ – 0.002μ_B, O$_2$ – 0.02μ_B for the holmium-including oxide and (ii) Nd – 2.92μ_B, V – 1.49μ_B, O$_1$ – 0.05μ_B, O$_2$ – 0.05μ_B for the neodimium-including oxide. Some part of the magnetic moment is localized beyond the spheres. The corresponding values are 1.80μ_B and 1.63μ_B for Ho and Nd, respectively.

The origin of moments in MT-spheres and the charge densities at atoms can be understood by analyzing the data quoted in Table 1. They testify that the prevailing contribution to the formation of magnetic moment in HoVO$_3$ at holmium atoms is expectedly made by holmium 4f electrons. The role of Ho d-electrons is very weak at that, and it is completely neglected for its electrons with s- and p-symmetry. The magnetic moment at vanadium atoms is provided by their polarized d-electrons. The roles of electrons at various orbitals turn out nonequivalent in this case: the magnetic moment of

vanadium atoms is mainly provided by the strong polarization of $3d_{yz}$ and $3d_{z^2}$ states, to a less degree by the polarization of $3d_{x^2-y^2}$ and $3d_{xz}$ orbitals, whereas V$3d_{xy}$ electrons remain almost inert with respect to the process of magnetic moment formation. For oxygen atoms, the occupation degrees for the electron states with differently oriented spins are approximately equal, which results in an almost zero magnetic moments for them.

As to NdVO$_3$, the picture of the magnetic moment distribution over individual atoms remains qualitatively the same as that for HoVO$_3$, but a number of quantitative differences (see Table 2). In particular, the tables demonstrate that the charge states of vanadium and oxygen atoms are practically the same in holmium and neodymium vanadites. Some differences are observed between the occupation numbers of certain d-harmonics in vanadium atoms.

4. Conclusions

In vanadites LnVO$_3$ (Ln = Nd, Ho), the valence electron states of metal atoms are polarized and weakly hybridized, both with one another and with the states of oxygen atoms. The top of the valence band is the region, where strongly polarized V$3d$ and O$2p$ states are localized. These states mainly correspond to weak covalent chemical π-bonds between the vanadium and oxygen atoms located near the planes parallel to the crystallographic plane (a, c). The minimal optical gap in the studied oxides is located at point Γ of the Brillouin zone. It has a correlation nature and a dominating V$3d$ character. The magnetic moments in MT-spheres of lanthanide (Nd and Ho) and vanadium atoms are associated with the polarization of electrons in their $4f$ and $3d$ shells, respectively.

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ДОСЛІДЖЕННЯ ЕЛЕКТРОННОЇ БУДОВИ ОКСИДІВ NdVO$_3$ І HoVO$_3$: РЕНТГЕНОЕЛЕКТРОННІ СПЕКТРИ І ЗОННИЙ РОЗРАХУНОК

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Р е з ю м е

За допомогою методів рентгеноелектронної спектроскопії та з використанням квантово-механічних розрахунків електронної структури проведено комплексне дослідження електронної структури та магнітних властивостей оксидів NdVO$_3$ та HoVO$_3$. Отримано дані про розподіл повних та парціальних електронних станів у валентній зоні та смузі провідності, зарядових та спінових станів атомів, механізм формування хімічних зв'язків та забороненої щілини в енергетичному спектрі оксидів LnVO$_3$ (Ln = Nd, Ho).