THE ELECTRONIC STRUCTURE OF THE $NDVO_3$ COMPOUND: X-RAY SPECTRA AND BAND CALCULATIONS IN LAPW-APPROXIMATION

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Introduction

Complex vanadium oxides containing rare-earth elements possess physical-chemical properties which are interesting from the scientific and practical points of view. The compounds with the common formula $LnVO_3$ (Ln=La…Lu, Y) have the perovskite-like structure (fig. 1). They demonstrate semiconductor-type dependency of the electrical resistance with comparably low magnitudes (of the order of several tens of electronvolts) of the conductivity activation energy, but also undergo the metal-semiconductor phase transition.

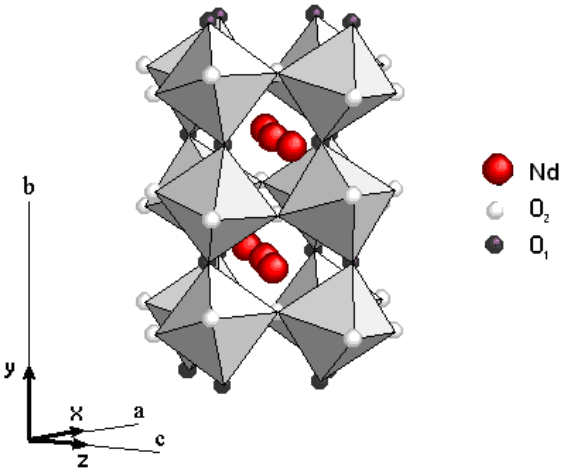

Fig. 1. NdVO3 structure fragment.

The electronic structure of these compounds is without a doubt the key for their physical-chemical properties explanation. The aim of the current work is the investigation of the electronic structure of the mentioned oxide series representative – the vanadite $NdVO_3$. For this purpose the complex approach based on X-ray photoelectron, X-ray fluorescent measurements and theoretical band calculation of the electronic structure in LAPW-approximation has been applied.

Results and Discussion

The crystal lattice of the $NdVO_3$ vanadite belongs to the orthorhombic syngony and is characterized by the Pnma (#62) space group. Its fragment is shown on the fig. 1. The orthorhombic lattice constants and the coordinates of the non-equivalent atoms given in fractions of the corresponding cell edges are: a= 5.58 Å, b= 7.762 Å, c= 5.461 Å; Nd (0.552, 0.25, 0.487), V (0.5, 0.0, 0.0), O_1 (0.979, 0.25,0,585), O_2(0.796, 0.048, 0.202) [1].

On fig. 2 X-ray photoelectron spectrum of the $NdVO_3$ vanadite valence electrons and calculated electron densities curves are given. The last are obtained as the result of the band calculation in LAPW-method [2] with the generalized gradient approximation (GGA) in the form [3]. For the calculation of total and partial densities of states of the $NdVO_3$ vanadite the spin-polarized version of LAPW-method has been used considering the spin-orbit interaction in all atoms and Nd4f- and V3d-electron correlations in LDA+U (AMF) [5] formalism.

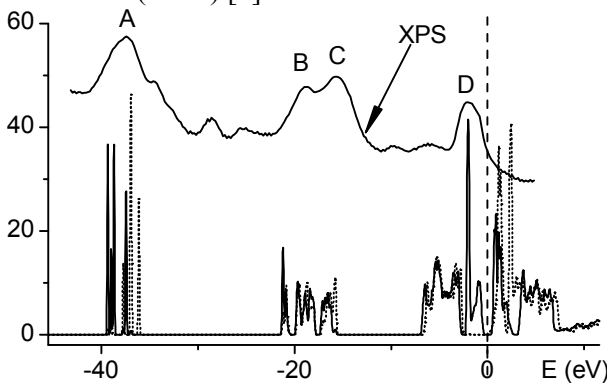

Fig. 2. X-ray photoelectron spectrum (XPS) and calculated density of electron states of $NdVO_3$ compound.

The matching of the density of states curve with the experimental spectrum has been performed by component A, which corresponds to the 5s-states of the neodymium. The X-ray photoelectron spectrum has appeared to be shifted by 3.38 eV to the low energies region.

The peak A (-37.4 eV) corresponds to the group of lines of the calculated densities of states located in the interval of energies from –38 to –36 eV. Among them there are 5s-states of neodymium and 3p-states of vanadium. Two maxima B (-18.8 eV) and C (-15.7 eV) are the results of the existence of hybridized Nd5p- and O2s-states. The component D (-2.0 eV) of the X-ray photoelectron spectra corresponds to the 4f-states of neodymium. These electrons are well-localized and have large ionization cross-section in contrast to the

2p-sublevels of the oxygen, which give the little contribution to the experimental curve in the energy interval considered.

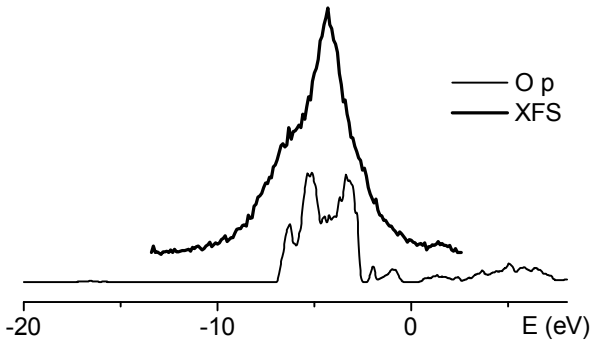

Fig. 3. X-ray fluorescence spectrum of the Kα-line of the oxygen (XFS) and the calculated density of p-states of the oxygen in the $NdVO_3$ compound.

On fig. 3 the experimental X-ray fluorescence Kα-spectrum of the oxygen of the compound being under investigation and the calculated electron density of the oxygen p-states are given. As one may see, the peculiarities of the experimental curve are well-adjusted with the maxima of the density of states, which is the evidence of the good quality of the carried out calculations.

According to the experimental results [6] the conductivity activation energy of the $NdVO_3$ vanadite is of magnitude of 0.25 eV, which corresponds to the band-gap width of 0.5 eV. Thus the almost full agreement of this value with the calculated forbidden zone width (0.5 eV) is observed. The calculations have resulted the minimal optical energy gap to be localized in the Γ-point and have the correlation V3d-dominating nature.

The calculations have shown, that the full magnetic moment of the conventional cell of the given compound containing 4 atoms of the neodymium and vanadium, 4 1^{st}-sort atoms of the oxyden and 8 2^{nd}-sort oxyden atoms has the magnitude of 19.92 Bohr magnetons (μ_B). The distribution of the magnetic moments in MT-spheres appeared to have the given values: Nd- 2.92 μ_B, V- 1.49 μ_B, O_1- 0.0548 μ_B, O_2- 0.0540 μ_B. The part of the magnetic moment is localized in the interstitial region and has the magnitude
of 1.63 μ_B. The overwhelming contribution in the formation of magnetic moment of the neodymium atoms is made by their 4f-electrons. The contribution of their 5d-electrons is quite little. The role of s- and p-electrons in magnetic moment formation is practically negligible. The magnetic moment of vanadium atoms is provided by their polarized d-electrons.

Conclusions

1. The valence electron states of metal atoms of the vanadite $NdVO_3$ are polarized. Near the valence band top V3d- and O2p-states are localized. They reflect mainly the weak covalent chemical π-bonds of the atoms of vanadium and oxygen placed near the planes, which are parallel to the (010) crystallographic plane.
2. The minimal optical band gap of the $NdVO_3$ oxide is localized at the Γ-point of the Brillouin zone and has the correlation V3d-dominating nature.
3. The magnetic moments in the MT-spheres of neodymium and vanadium atoms are mainly the results of their 4f- and 3d- electrons polarization correspondently.

References

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