ELECTRON STRUCTURE OF $La_{1+N}Ni_NO_{3N+1}$ (N=1,2,3..∞) COMPOUNDS: X-RAY SPECTRA AND BAND CALCULATIONS IN LAPW APPROXIMATION

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Introduction

Lanthanide-containing nickel oxides have a lot of physical properties, which are interesting either from scientific or practical points of view. At definite content, temperature, pressure rare-earth nickelites (REN) overcome metal-insulator transitions, change the type of magnetic ordering. Chemical and crystal structures allow to use these compounds also as the membranes for extracting of pure oxygen from different gaseous mixtures. Members of homological row of oxide compounds $La_{n+1}Ni_nO_{3n+1}$ (n=1, 2, 3… ∞) are interesting because in combination with solid oxide electrolyte they can work for a long time as cathodes in gaseous environments with high oxygen pressures at high tempetratures.

It is obvious that mentioned above properties are generally defined and controlled by electron structure of the given oxides. The aim of the present work was to investigate the electron structure of the compounds in the conducting state: to define the chemical bonds pattern, to find correlations between crystal and electron structures.

For solving these tasks complex approach based on the use of X-ray photoelectron and X-ray fluorescence spectra and also the results of band calculations in LAPW-approximation [1] with gradient approximation of the electron density in form [2] was applied.

Results and Discussion

On fig. 1-4 X-ray photoelectron, X-ray spectra and results of quantum-mechanical calculations superposed in unified energy scale are shown. The positions of Fermi level (E_F) for X-ray spectra of nickel and oxygen are defined from x-ray photoelectron spectra of Ni2$p_{3/2}$- and O1s- levels.

Evidently, that the results of calculation and experiment are in good agreement. As it can be seen from the figures, valence band of each compound consists of two energetically separated parts. The analysis of calculation data shows that band of deep states is situated in energy interval from -21 to -15 eV and generally is represented by hybridized La5p- and O2s-states. Prefermi band, predominantly formed by O2p- and Ni3d-orbitals, stretches onto 8 eV depth from Fermi level. 3d_{z^2}-electrons of nickel dominate on Fermi level. Band of conductivity is represented mostly by unoccupied La4f- and La5d-states.

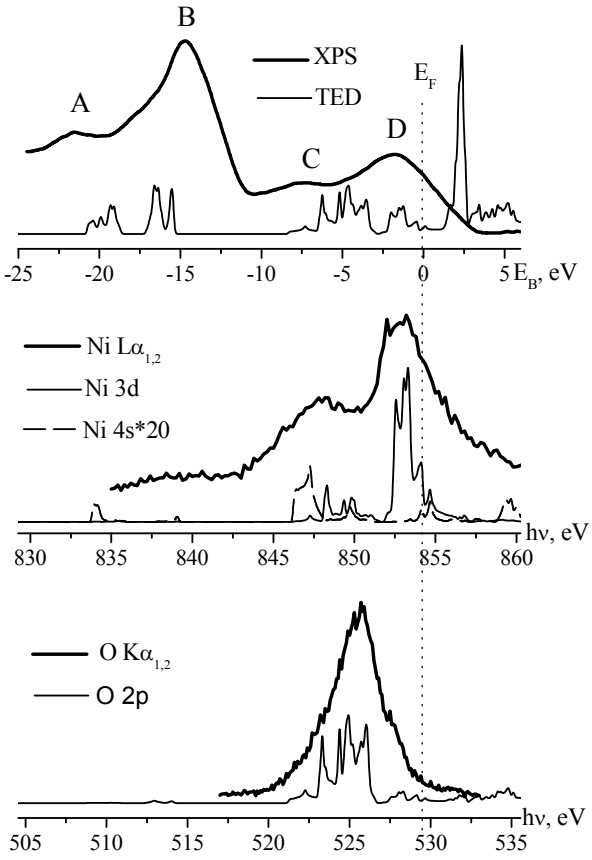

Fig.1. X-ray photoelectron (XPS- here and further on figures), X-ray NiL$\alpha_{1,2}$-, OK$\alpha_{1,2}$- spectra and the results of calculation of the La_2NiO_4 oxide electron structure: TED- total electron density; vertical lines (E_F) here and further correspond to Fermi level position; horizontal axes show binding energy (E_B) of the electrons and energies (hν) of the X-ray photons.

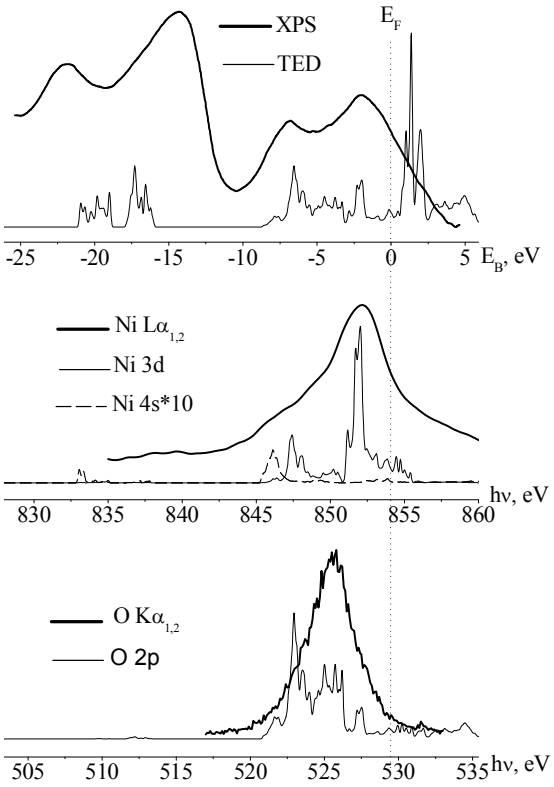

Fig.2. The results of $La_3Ni_2O_7$ oxide electron structure investigations.

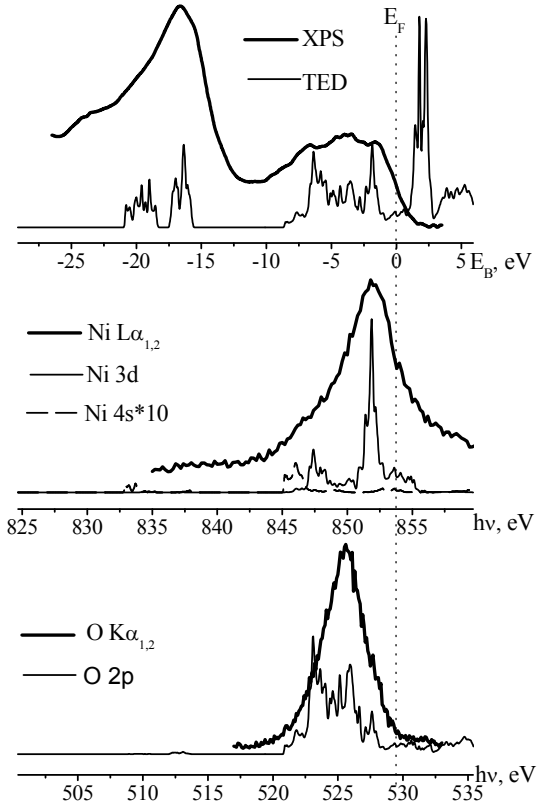

Fig.3. The results of $La_4Ni_3O_{10}$ oxide electron structure study.

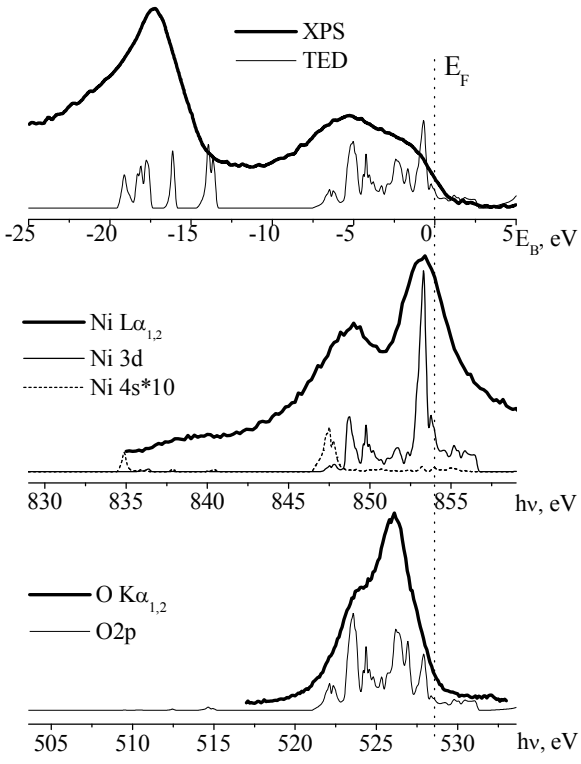

Fig.4. The results of $LaNiO_3$ oxide electron structure investigations.

Further analysis of the calculated data shows that with the increase of *n* takes place the transmitting of the electron density from Ni3d_{z^2}-states to Ni3$d_{x^2-y^2}$-ones. This leads to weakening of the covalent σ-bonds between La-O and Ni-O layers, and also causes essential decrease of Fermi level population. The conductivity of compounds from the row $La_{n+1}Ni_nO_{3n+1}$ (n=1,2,3) must decrease while *n* grows.

Conclusions

1. Ni3d_{z^2}-states prevail on Fermi level of compounds $La_{n+1}Ni_nO_{3n+1}$ (n=1, 2, 3).
2. With grows of *n* takes place the transmitting of the electron density from Ni3d_{z^2}- to Ni3$d_{x^2-y^2}$-orbitals. At the same time the population of Fermi level decreases, causing possible decrease of conductivity going from La_2NiO_4 to $La_4Ni_3O_{10}$.

References

1. Singh D. Plane waves, psedopotentials and LAPW method. Kluwer Academic, 1994.
2. Perdew J.P., Burke S., Ernzerhof M., Phys.Rev.Let. 1996; **77**: 3865.