THE ELECTRONIC STRUCTURE OF SOME LANTHANUM NICKELITES

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Introduction

Nickelites $La_{n+1}Ni_nO_{3n+1-\delta}$ (n=1-3) were this work's study objects. They are the oxide materials of the La-Ni-O system. Here δ represents the change of the oxygen containing in the compound when part of trivalent nickel changes. The nickelite $LaNiO_3$ and oxides NiO and La_2O_3 were investigated for a comparison. Nickelites were obtained by solid phase synthesis from the oxides named above. $LaNiO_3$ was synthesised by coprecipitation of some hydroxides (CPH). The compounds have the following crystal structures: $La_2NiO_{4-\delta}$ has the distorted K_2NiF_4-type structure; $La_3Ni_2O_{7-\delta}$ and $La_4Ni_3O_{10-\delta}$ have the layered perovskite-like structures. All these structures are similar to the Ruddlesden-Popper phases structures [1]. The NaCl-type (LaO) layers along a crystallographic direction c alternate the n sequential perovskite layers ($LaNiO_3$). Therefore, these compounds formula composition can be noted as $(LaO)(LaNiO_3)$. $LaNiO_3$ has the rhombohedrical distorted perovskite structure. NiO and La_2O_3 have the NaCl-type and, respectively, La_2O_3-type structures. The common features of the nickel containing compounds structures are the oxygen octahedrons (correct or slightly distorted). The lanthanium atoms in nickelites place in the interoctahedrons gaps. The conductivity temperature dependence for La_2NiO_4, $La_3Ni_2O_7$ и $La_4Ni_3O_9$ in a temperature range below (200-300) ^oC has a semiconducting character. At the higher temperatures, it acquires a metal character. These compounds and materials based on its are capable to work for a long time at the increased temperatures with high partial pressure of oxigen. They are compatible with solid oxide electrolites. In particular, with those based at the cubic zirconia. All these properties provide the perspective for nickelites application as cathodes of the fuel elements and other current sources. As it known, the electrophysical and optical compounds properties are connected with their electronic structures (ES). Therefore clearing up of nickelites electronic structure character features and peculiarities is an actual problem. The study of these compounds zone structure by experimental methods and the analysis of a various symmetry electrons energy distribution (the electrons belong to the different sort atoms) was not fulfiled earlier. For $LaNiO_3$ the first ES research carried out by X-ray and X-ray photoelectron spectroscopy methods (and with the zone structure calculations) is published in [2]. At our work the nickel *Lα*-spectra of $LaNiO_3$ are obtained in the energy interval more wide than in [2]. This allowed to make clear a $LaNiO_3$ valence zone structure near it bottom more authentic.

The work's purpose

1. With X-ray and X-ray photoelectron spectroscopy methods use to define how the Ni/La ratio change influences at the nickelites valence zone structure.
2. To define whether the common regularities are in all considered Ni-containing complicated compounds ES.
3. To determine, whether subvalent La*5p*-electrons participate in the interatomic interaction.
4. To clarify the nickelites ES genesis.
5. To give the obtained results interpretation.
6. To construct the nickelites ES models.

The results and discussion

X-ray and X-ray photoelectron spectra are obtained, accordingly, by spectrometers SARF-1 and Kratos.

Ni*Lα*-spectra (bands) characterize the *Nids* (*3d4s*)-electrons distribution in the valence zone (VZ). By virtue of small *s*-states density it may be concluded that the spectra shape reflects the main features of the nickel valence *d*-electrons distribution.

O*Kα*-spectra characterize distribution of the valence *p(2p)*-oxygen electrons in the VZ. In the nickelites Ni*Lα*-bands there are a high-energy maximum and a low-energy shoulder. In these compounds the transition to smaller significances n (from n=3 at $La_4Ni_3O_{10-\delta}$ to n=2 at $La_3Ni_2O_{7-\delta}$) calls the increase of the shoulder intensity and the shoulder transformation to the second maximum in $La_2NiO_{4+\delta}$ (n=1). In nickelites of various composition the width of Ni*Lα*-bands main part

is 13 eV. The bands shape in nickelites is more complicated than in NiO, and its width is approximately twice more (in NiO it is 6-7 eV). The nickelites and NiO bands relative disposition allows to assert: the spectra placed in the energy interval about (848-854) eV characterise the distribution of nickel electrons taking part in the interoctahedrons Ni-O bands.

In all considered nickelites, the shape and the width are similar. The ratio Ni/La atoms change effects poorly at the bands main character. The nickelites and simple oxides O*Kα*-bands comparison shows: the O*2p*-states energy distribution shape in nickelites is more similar to that in NiO than in La_2O_3. It testifies that in nickelites more oxygen atoms take part in the O-Ni-bonds than in O-La bonds.

All data obtained about nickelites ES are analised with these compounds crystallochemical peculiarities taking into account.

The $La_4Ni_3O_{10-\delta}$, $La_3Ni_2O_{7-\delta}$ zone schemes and the $LaNiO_3$ scheme [2] allow to discribe the VZ of these and similar to its compounds (and $La_4Ni_3O_{10-\delta}$). Their VZ width is about 22-24 eV. VZ consists actually of two subzones: upper and lower. Their width is equal approximately 10-12 eV and 12 eV. There are nickel *d*-electrons in the whole VZ, and their distribution has the maximum in the upper subzone near the Fermi level. There is the bright feature such as a hump energetically below. There are also oxygen *p*-electrons hybridising with Ni*d*-electrons in the upper zone. The small Ni*d*-electrons density increase takes place near the VZ bottom in the O*2s*-electrons localization region. The O*2s*- and subvalent La*5p*-electrons hybridization is in the lower subzone, also. Our experience of *3d*-transition metals ES study [3, 4] allows to assert: the valent Ni*p*(*4p*)- and Ni*d(3d)*-electrons distribution will have the common features number. There will be a bright maximum of Ni*p*-electrons, hybridizing (as well as *d*-electrons) with O*2p*-electrons near the VZ top. The weaker Ni *p*-electrons (hibridizing both with O*2s*- and La*5p*-electrons) maximum will place at the VZ bottom.

Stated has allowed us to construct all considered nickelites ES models. Moreover, to predict also that ES for other compounds of La_2O_3 with the oxides of a number *3d*-metal (Mn, Fe, Co) will be largely similar to those for lanthanum nickelites.

Conclusions

1. It is shown: the ratio nickel to lanthanum atoms change noticeably influences at the Ni*d*-valent electrons energy distribution and much more poorly – at the valent O*p*- electrons disridution.
2. The nickelites electronic structure genesis is clarified. There are common features in all considered nickelites and NiO electronic structures. It is stipulated by availability of Ni-containing oxygen octahedrons in these compounds.
3. The subvalent La*5p*-electrons belonging to the filled shell participate in the interatomic interaction. This conclusion refutes the generally accepted idea about the impossibility of the filled shells electrons insertion in the interatomic interaction.
4. The nickelites electronic structure keeps the features of oxides used for nickelites synthesis.
5. The models of considered nickelites electron structure are constructed.
6. The prediction about the lanthanium contained manganites, ferrites and cobaltites electronic structure is made.

References

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