STRUCTURE OF X-RAY PHOTOELECTRON SPECTRA OF LOW-ENERGY AND CORE ELECTRONS OF $Ln(C_6H_4OCH_3COO^-)_3$

by

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This paper deals with the results of an X-ray photoelectron spectroscopy of lanthanide ortho-metoxybenzoates $Ln(C_6H_4OCH_3COO^-)_3$, where Ln represents – lanthanides La through Lu except for Pm and $C_6H_4OCH_3COO^-$ – residuum of ortho-metoxybenzoic acid. The core and outer electron X-ray photoelectron spectroscopy spectra in the binding energy range of 0-1250 eV were shown to exhibit a complex, fine structure. The said structure was established due to the outer (0-15 eV binding energy) and inner (15-50 eV binding energy) valence molecular orbitals from the filled Ln5p and O2s atomic shells, multiplet splitting, many-body perturbation, dynamic effect, *etc*. The mechanisms of such a fine structure formation were shown to manifest different probabilities in the spectrum of a certain electronic shell. Therefore, the fine X-ray photoelectron spectroscopy spectral structure resulting from a certain mechanism can be interpreted and its quantitative parameters related to the physical and chemical properties of the studied compounds (degree of delocalization and participation of Ln4f electrons in the chemical bond, electronic configuration and oxidation states, density of uncoupled electrons on paramagnetic ions, degree of participation of the low binding energy filled electronic shells of lanthanide and ligands in formation of the outer and inner valence molecular orbitals, lanthanide close environment structure in amorphous materials, *etc*.).

Keywords: *X-ray photoelectron spectroscopy, outer and inner valence molecular orbitals, lanthanide*

INTRODUCTION

X-ray methods like X-ray photoelectron, emission and absorption spectroscopies have proven to be the most adequate methods for the study of physical and chemical states (oxidation state, elemental and ionic composition, radionuclide close environment structure, ligand nature, *etc*.) of radionuclides in the environment (see *e. g.* [1-3]). However, certain difficulties in the interpretation of the X-ray spectral fine structure arise while employing these methods. Therefore, great attention has been given to the interpretation of the fine spectral structure and determination of the correlation of its parameters with physical and chemical properties of the studied compounds [2-4]. For example, our work [2] suggests the technique of determining the cerium oxidation state in radioactive waste disposal matrixes on the basis of fine Ce3d, 4f X-ray photoelectron spectroscopy (XPS) structure parameters. The results of the electronic structure cluster calculations of compounds [3, 4] are widely used for the interpretation of fine XPS structures. Up to the present, such calculations in non-relativistic and relativistic approximations have been made for actinide compounds (see, for example, [3]). Unfortunately, as for lanthanide compounds, such calculations have been made only by non-relativistic approximation which allows only a qualitative XPS fine structure interpretation [4]. Since these calculations have been done for separate clusters, one can expect the results to be more correctly comparable with the XPS data for cluster samples (not condensed matter). In this case, the samples of lanthanide complexes with large organic ligands are more appropriate. They can be considered as

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quasiclusters in condensed matter. The present work is dedicated to the study of such compounds.

XPS spectra from lanthanides (Ln) in compounds are structured in the binding energy range of 0-1250 eV [4]. On one hand, this complicates the measurements of the traditional data (binding energies and peak intensities), on the other – it expands XPS abilities, since the structure reflects the properties of the studied compounds. For example, the data on: the degree of delocalization of the Ln4f electrons and their participation in the chemical bond, lanthanide electronic configuration and oxidation state, density of uncoupled electrons on paramagnetic ions, degree of participation of the low binding energy filled electronic shells of lanthanide and ligands in the formation of the outer (OVMO) and inner (IVMO) valence molecular orbitals, structure and nature of these orbitals, lanthanide close environment structure in amorphous materials, *etc*. can be obtained directly from the XPS fine structure parameters, something that cannot be achieved so directly on the basis of other methods [1-4]. Therefore, the establishment of a quantitative correlation of fine XPS structure parameters with physical and chemical properties of lanthanides in compounds is an important problem. The most reliable information on fine spectral structure formation can be drawn from the investigation of the row of isostructural vacuum and X-ray stable lanthanide compounds.

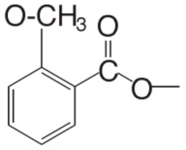
This work presents the results of an XPS study of a row of isostructural stable lanthanide ortho-metoxybenzoates $Ln(C_6H_4OCH_3COO^-)_3$, where Ln represents – lanthanides La through Lu except for Pm, with the aim of establishing general regularities and details of the fine XPS structure formation and correlation of its parameters with the properties and chemical bond nature in the studied compounds.

EXPERIMENT

XPS spectra of the solid samples of lanthanide ortho-metoxybenzoates were measured with an electrostatic spectrometer, HP 5950A Hewlett-Packard, using monochromatized $AlK_{\alpha1,2}$ ($h\nu$ = 1486.6 eV) radiation in a vacuum of $1.3\ 10^{7}$ Pa at room temperature. The device resolution measured as full width (Γ, eV) on the half-maximum (FWHM) of the $Au4f_{7/2}$ line on the standard rectangular gold plate of 0.8 eV. The binding energies E_b were measured relatively to the binding energy of C1s electrons from hydrocarbons absorbed on the sample surface, accepted to be equal to 285.0 eV. On the gold plate E_b(C1s) = 284.7 eV at $E_b(Au4f_{7/2})$ = 83.8 eV [2, 3]. The FWHM were measured relatively to the width of the C1s line of hydrocarbons, accepted to be equal to (C1s) = 1.3 eV. Errors in the determination of electron binding energies and line widths did not exceed 0.1 eV, while those concerning relative line intensities were less than 10%. For all samples, the quantitative elemental analysis was carried out using the following ratio: $n_i/n_j = (S_i/S_j)(k_j/k_i)$, where n_i/n_j is the relative concentration of considered atoms, S_i/S_j is the relative intensity of the core electron lines of these atoms, and k_j/k_i is an experimental sensitivity coefficient [1].

The samples of lanthanide orthometoxybenzoates for the XPS study, in the form of dense glass-like films on titanium substrates [5], were synthesized for the first time in the laboratory of Prof. Dr. Pirkes [6, 7] by precipitation from dimethyl-phormamide solution.

RESULTS AND DISCUSSION



Lanthanide ortho-metoxibenzoates LnL_3, where Ln – lanthanides La through Lu, except for Pm and L – residuum of ortho-metoxybenzoic acid, are a class of compounds with important properties [6, 7]. Thus, all lanthanides in these compounds are trivalent Ln^{3+}. These compounds are isostructural, non-hygroscopic, vacuum and X-ray stable.

One of the goals of this work was the study of fine XPS structure changes in the low binding energy range (0-50 eV) depending on the energetic position of the Ln5p shell relative the O2s one with the grow of lanthanide atomic number Z and filling of the Ln4f shell. The stability of these compounds enabled us to measure reliable XPS spectra of the valence and core electron shells, for example of cerium, which is important for the interpretation of fine structure formation and determination of lanthanide oxidation states in compounds [4].

Lanthanide ions in highly-molecular compounds with organic ligands can be considered, to a certain extent, as a "quasi-ionic gas", while their XPS spectra should not manifest the strong solid-state effects. The comparison of the XPS spectra of lanthanides in different compounds allows an evaluation of the influence of such effects on the spectral structure. For the XPS study of the samples in this case, the problem of correspondence of the sample surface to the bulk is not that critical. Therefore, the *X* theoretical calculations in the cluster approximation are more defensible in this case.

Low binding energy spectra. In general, the low binding energy XPS spectra from lanthanide ortho-metoxibenzoates (LnL_3) are complex because of the superposition of lanthanide and acid residuum spectral structures (fig. 1). However, due to the fact that the Ln5p, 4f photoionization cross-sec-

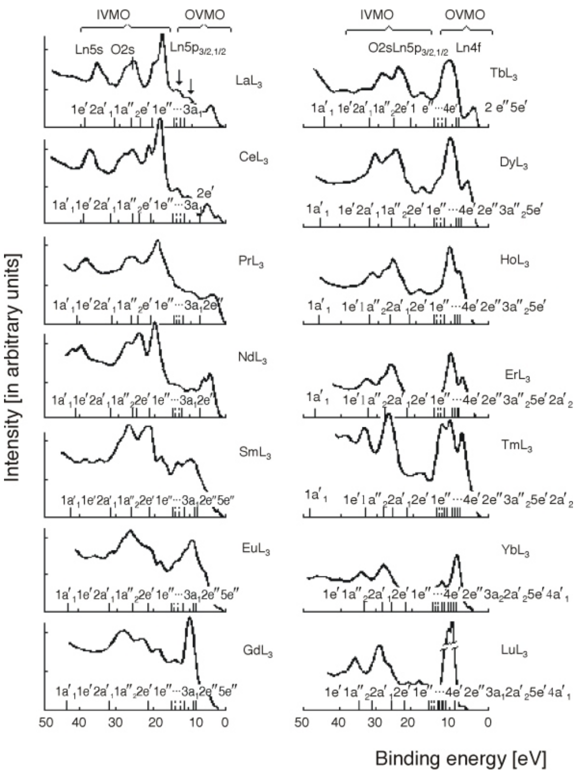


Figure 1. Low binding energy XPS spectra from lanthanide ortho-metoxibenzoates LnL_3 (L = $C_8H_7O_3^{1-}$). Results of the electronic structure calculations for the LnO_3^{3-} (D_{3h}) clusters [5] are given under the spectra. Ligand-related MOs are shown as arrows

tions are much higher than the O2s, O2p, and C2p ones, lanthanide spectral features prevail in this binding energy range [8]. In the binding energy range of 0-15.5 eV, XPS spectra from LnL_3 exhibit OVMO features due to the interaction of Ln5d, 6s, O2p and C2p atomic orbitals (AO). The Ln4f intensity grows with the lanthanide atomic number Z (fig. 1). In the ionic approximation, the Ln4f spectral structure, as it was shown for LnF_3 [4], comes mostly from the multiplet splitting of the energetic level in the final state after photoemission for the Ln^{3+} ion. This structure is, in general, similar to that of Ln4f XPS spectra from lanthanide oxides Ln_2O_3 and trifluorites LnF_3 [4] and agrees qualitatively with the calculation results for Ln^{3+} ion [9].

Dependence of the XPS Ln4f relative intensity ($I_{\exp}$) calculated as a ratio $[I(\mathrm{Ln4f^n}) + I(\Sigma\mathrm{OVMO})]/I(\Sigma\mathrm{IVMO})$, except for the Ln5s intensity, on the number n_{4f} of the Ln4f electrons in Ln^{3+} is given in fig. 2. Using the least square method, this dependence was described as (1):

$$I_{\exp} \quad 0.081n_{4f} \quad 0.29 \qquad (1)$$

and

$$I_{\mathrm{theor}} \quad 0.01n_{4f}^{2.24} \quad 0.18 \qquad (2)$$

Theoretical dependence I_{theor} (2) drawn in [1] for Ln_2O_3 is given for comparison in fig. 2. Just as for lanthanide trifluorites [4], experimental dependence $I_{\exp}$ (1) differs from the theoretical one (2) and is linear. The coefficient at n_{4f} and the free term in (1) depend on the ligand nature.

XPS spectra of the Ln5p – O2s region from LnL_3 are more complicated than it would be in the case of a superposition of the atomic spectra only (fig. 1). The multiplet splitting and secondary electronic processes with related extra structures in these spectra are finitely probable. However, there are some other reasons for the complication of the spectra in this range, such as: OVMO due to the O2s and C2s AOs from ligands and the interaction of the low binding energy filled shells of lanthanide and neighboring ligands.

During the XPS study of lanthanide compounds, the low binding energy (0-50 eV) peaks were noted to be several eV wide, which is wider than the corresponding core peaks [5]. For example, for LaL_3, the O1s peak was found to be 3.2 eV wide, while the corresponding O2s one (E_b~26.5 eV) – 4.3 eV wide and structured (fig. 1). According to the uncertainty ratio $\Delta E\Delta\tau \sim h/2\pi$, where h – Plank's constant, the natural width E of a level from which an electron was emitted is inversely proportional to the lifetime τ of the hole. Since τ decreases as the level energy grows, for the separate atoms, the peak

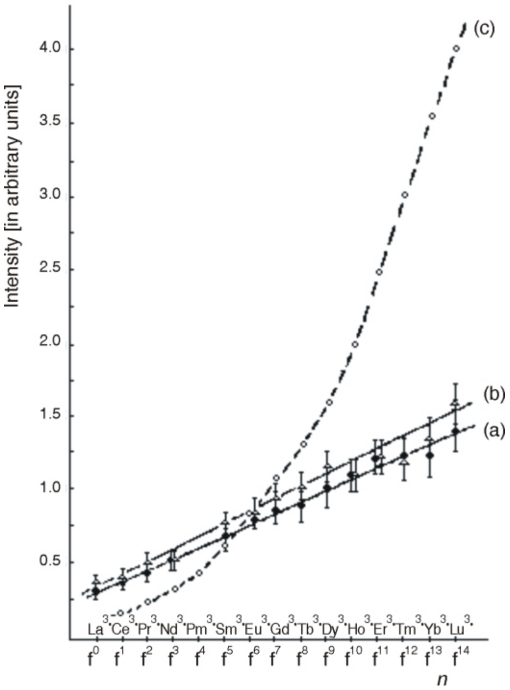


Figure 2. Dependence of the Ln4f XPS relative intensity on the number *n* of Ln4f electrons for lanthanide ortho-metoxibenzoates and diphenyl-acetates (LnL_3); (a) – experimental for LnL_3; (b) △ – experimental for LnL_3; (c) ○ – theory for Ln_2O_3 [4]

Table 1. MO energies *E* [eV], partial electronic contributions [%] in different regions of the $LaO_3^{3-}(D_{3h})$ cluster at $R_{La\text{-}O}$ = 0.174 nm and total partial charges Q_l^j (electronic charge units) calculated in the SCF X – SW approximation [4, 9]

Molecular orbital		–E	La				O		Region
			s	p	D	F	s	p	II, III
OVMO	2a2	6.25	–	–	–	88.0	–	6.3	5.7
	3a2	6.91	–	1.1	–	84.9	–	3.3	10.7
	5e	7.15	–	0.6	1.2	83.0	–	2.7	12.5
	$4a_1$	7.35	2.0	–	8.4	25.7	–	–	63.9
	2e″	7.38	–	–	2.2	77.9	–	–	19.9
	$3a_1$ [(a)]	12.29	1.3	–	5.0	15.7	0.3	53.1	24.6
	4e	12.60	–	7.4	5.3	4.0	–	52.2	41.1
	$2a_2$	13.51	–	6.2	–	4.2	–	57.0	32.6
	$1a_2$	14.66	–	–	–	6.8	–	57.6	35.6
	3e	14.96	–	2.3	3.0	–	1.5	55.8	37.4
	1e	15.11	–	–	2.8	1.8	–	53.7	41.7
IVMO	2e	20.67	–	40.0	0.7	0.1	20.4	10.2	28.6
	$1a_2$	24.03	–	59.6	–	–	–	3.0	37.4
	$2a_1$	26.50	13.1	–	0.9	1.1	61.8	0.3	22.8
	1_e	31.23	–	18.2	0.9	0.2	49.5	1.8	29.4
	$1a_1$	38.87	66.0	–	–	0.1	9.3	2.1	22.5
Q_l^j			1.6	4.0	0.6	0.8	4.3	10.4	10.3

(a) Upper filled orbital

width was expected to decrease with the decreasing of the binding energy of the electrons. One of the reasons for the widening of the peaks in the low binding energy range of 0-50 eV for lanthanide ortho-metoxibenzoates is the OVMO and IVMO formation [5]. These spectra practically reflect the structure of the valence electrons and appear as several eV wide bands. In particular, the IVMOs in these lanthanide compounds form due to the strong Ln5p – O2s interaction. Such a strong overlap of the Ln5p and O2s AOs from the neighboring lanthanide and ligands was for the first time experimentally established on the basis of the interpretation of the fine XPS structure, taking into account the binding energy differences between the core and outer electronic shells for lanthanide ortho-metoxibenzoates [5] and other lanthanide compounds [1, 2]. This agrees qualitatively with the non-relativistic (NR) self-consisting field (SCF) X_α discrete variation (DV) [10, 11] and scattered waves (SW) [5] theoretical calculation results.

Indeed, to a certain extent, the $1a_2''$ IVMO can be viewed as a quasi-atomic MO consisting of La5p AO (tab. 1). IVMO couples 1e′ and 2e′ ($1a_1'$ and $2a_1'$) can be formally attributed to the bonding and antibonding MOs, respectively. The bonding $1a_1'$ IVMO contains 85% of La5s and 12% of O2s AOs, while the antibonding $2a_1'$ one – 17% of the La5s and 80% of the O2s AOs. Besides, a significant but different contribution of the valence MOs of lanthanide and oxygen in these IVMO couples takes place. For example, the bonding 1e′ MO contains only 2.5% of the O2p AO, while the antibonding 2e′ MO contains 14% of the O2p AO of oxygen. Such impurities of the outer valence AOs in IVMOs, as it was noted in [4] for molecules of light and heavy elements, weaken the antibonding nature of the upper MO, in particular, of the 2e′ one. As a result, electrons of the IVMO couple, for instance 1e′ and 2e′, will strengthen the Ln-O chemical bond (tab. 1).

As lanthanide atomic number Z for LnO_3^{3-} clusters grows, the MO energies and compositions change significantly. To build the dependence of MO energies for these clusters on Z, the energy of the quasi-atomic oxygen $2a_1$ MO was suggested to remain constant and equal to 26.5 eV (fig. 3). This energy was chosen as a standard for the comparison of the theoretical and experimental (fig. 1) results. As Z grows, the most noticeable energy change was observed for the upper 2e″-$2a_2'$ OVMOs and $1a_2''$ and $1a_1'$ IVMOs. The compositions of these MOs also change significantly. Thus, the OVMO couple 2e″-$2a_2'$, by the end of lanthanide row, can by its nature be attributed to a higher degree to the O2p AO, while the one 1e″-$3a_1'$ – to the Ln4f AO, respectively. The mixing of the Ln5p and O2s AOs grows with Z to the middle of the row. These data (fig. 3) show that during the 1e′ and 2e′ IVMO formation, the Ln5p – O2s AO mixing, for example in TbO_3^{3-}, is significantly higher than that in LaO_3^{3-}, and that, the lower $1a_1'$ IVMO becomes, it becomes more and more quasi-atomic.

Core electron spectral structure. The core electron XPS spectra from lanthanide ortho-metoxibenzoates exhibit a fine structure which has much in common with that of the spectra from Ln_2O_3 and LnF_3. The Ln5s,4s spectra from LnL_3 exhibit multiplet splitting, resulting in the two peaks that are best observed at the middle of the lanthanide row. The Ln4d multiplet splitting results in a structure similar to that of the spectra from Ln_2O_3 [4]. Despite some differences in the Ln4d spectra

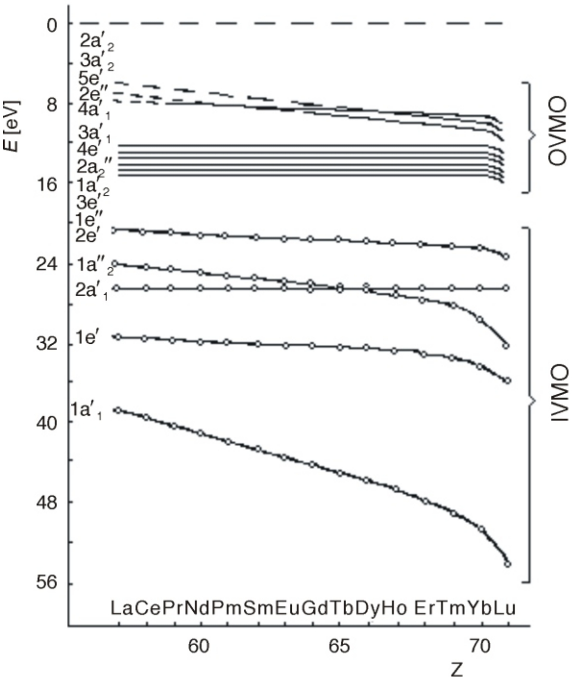


Figure 3. Dependence of MO energies in the LnO_3^{3-} (D_{3h}) cluster on lanthanide atomic number Z. Energies of $4a_1'$ and 5e′ OVMOs are not given. Vacant MOs are shown as dashed lines [4, 5]

structures from LnL_3 and LnF_3, the observed changes in the shape of the considered spectra from LnL_3 do not contradict the fact that their structures are due to multiplet splitting.

The configuration interaction is most pronounced in the Ln4p spectra from LnL_3. This spectral structure is similar to that from LnF_3 and Ln_2O_3. The Ln3d spectral structure for light lanthanides exhibits intense satellites and corresponds to the structure of the spectra from Ln_2O_3 [4]. The O1s spectra consist of the two components with the intensity ratio of 2/1. The most intense component attributed to the carboxyl group oxygen lies at the lower binding energies, while the less intense component was attributed to the metoxy-group. The C1s spectra exhibit the three components at 285.0, 286.7, and 288.9 eV, attributed to carbons of benzoic ring, metoxy-group and carbonyl-group, respectively.

In conclusion, we would like to note that the core and outer XPS spectra from lanthanide ortho-metoxybenzoates in the binding energy range of 0-1250 eV exhibit a complex structure. It was established that this structure can be attributed to the formation of the outer (0-15 eV E_b) and inner (15-50 eV E_b) valence MOs, in particular, from filled Ln5p and O2s AOs, multiplet splitting, many-body perturbation, dynamic effect, *etc*. The mechanisms of the fine XPS structure formation were found to manifest different probabilities in the spectra from different electronic shells. This enables us to interpret that structure due to a certain mechanism and to establish a quantitative correlation of its parameters with the properties of the studied compounds, such as: degree of delocalization and participation in the chemical bond of the Ln4f electrons, electronic configuration and oxidation state of the lanthanide ion, density of the uncoupled electrons on the paramagnetic ions, degree of participation of the low binding energy electrons from the neighboring lanthanide and ligand atomic orbitals in the OVMO and IVMO formation, lanthanide close environment structure in amorphous materials, *etc*. It also has to be noted that the fine spectral structure parameters, together with the traditional data like binding energies and peak intensities, expand significantly the abilities of the XPS method.

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СТРУКТУРА РЕНДГЕНОМ ИНДУКОВАНОГ ФОТОЕЛЕКТРОНСКОГ СПЕКТРА НИСКОЕНЕРГЕТСКИХ И СРЕДИШЊИХ ЕЛЕКТРОНА Ln$(C_6H_4OCH_3COO\ )_3$

У раду се разматрају резултати рендгеном индуковане фотоелектронске спектроскопије лантанид орто-метоксибензоата Ln$(C_6H_4OCH_3COO\ )_3$, где Ln представља лантаниде од La до Lu, изузев Pm, док је $C_6H_4OCH_3COO$ остатак орто-метоксибензоатне киселине. Показало се да спектри средишњих и спољашњих електрона добијени рендгеном индукованом фотоелектронском спектроскопијом, у области енергија везе од 0 eV до 1250 eV, испољавају сложену, фину структуру. Ова структура се успоставља услед спољашњих (0-15 eV енергија везе) и унутрашњих (15-50 eV енергија везе) валентних молекулских орбитала попуњених Ln5p и O2s атомских љуски, вишеструког цепања, вишечестичне пертурбације, динамичког ефекта, итд. Показано је да механизми настанка тако фине структуре испољавају различите вероватноће у спектру извесне електронске љуске. Отуда се фина рендгеном индукована фотоелектронска спектрална структура, која настаје услед неког механизма, може протумачити а њени квантитативни параметри повезати са физичким и хемијским својствима проучаваних састава (степеном делокализације и партиципације Ln4f електрона у хемијској вези, електронском конфигурацијом и оксидационим стањем, густином некуплованих електрона парамагнетних јона, степеном учешћа попуњених електронских љуски лантанида са ниском енергијом везе и лиганда у формирању спољашњих и унутрашњих валентних молекулских орбитала, структуром непосредне околине лантанида у аморфним материјалима, итд).

Кључне речи: рендгеном индукована фотоелектронска спектроскопија, спољашње и унутрашње валентне молекулске орбитале, лантаниди