STRUCTURE OF X-RAY PHOTOELECTRON SPECTRA OF LOW-ENERGY AND CORE ELECTRONS OF Ln(C₆H₄OCH₃COO⁻)₃

by

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This paper deals with the results of an X-ray photoelectron spectroscopy of lanthanide ortho-metoxybenzoates Ln(C₆H₄OCH₃COO⁻)₃, where Ln represents – lanthanides La through Lu except for Pm and C₆H₄OCH₃COO⁻ – 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...
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 isostuctural vacuum and X-ray stable lanthanide compounds.

This work presents the results of an XPS study of a row of isostuctural stable lanthanide orthometoxybenzoates Ln(C₈H₄OCH₂COO⁻)₃, where Ln represents – lanthanides La through Lu, except for Pm and L – residuum of ortho-metoxbenzoic acid, are a class of compounds with important properties [6, 7]. Thus, all lanthanides in these compounds are trivalent Ln³⁺. These compounds are isostuctural, 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 to the O2s one with the growth 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 “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 Xₗ theoretical calculations in the cluster approximation are more defensible in this case.

**RESULTS AND DISCUSSION**

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: \( n_j/n_i = (S_j/S_i) (k_i/k_j) \), where \( n_j/n_i \) is the relative concentration of considered atoms, \( S_j/S_i \) is the relative intensity of the core electron lines of these atoms, and \( k_i/k_j \) 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.

**EXPERIMENT**

XPS spectra of the solid samples of lanthanide ortho-metoxbenzoates were measured with an electrostatic spectrometer, HP 5950A Hewlett-Packard, using monochromatized AlK\(_{α1,2}\) (hv = 1486.6 eV) radiation in a vacuum of \( 1.3 \times 10^{-7} \) Pa at room temperature. The device resolution measured as full width (\( \Gamma \), eV) on the half-maximum (FWHM) of the Au4f/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 Cls electrons from hydrocarbons absorbed on the sample surface, accepted to be equal to 285.0 eV. On the gold plate \( E_b(Cls) = 284.7 \) eV at \( E_b(Au4f/2) = 83.8 \) eV [2, 3]. The FWHM were measured relatively to the width of the Cls line of hydrocarbons, accepted to be equal to \( \Gamma(Cls) = 1.3 \) eV.
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 LnL3 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 LnF3 [4], comes mostly from the multiplet splitting of the energetic level in the final state after photoemission for the Ln3+ ion. This structure is, in general, similar to that of Ln4f XPS spectra from lanthanide oxides Ln2O3 and trifluorites LnF3 [4] and agrees qualitatively with the calculation results for Ln3+ ion [9].

Dependence of the XPS Ln4f relative intensity \( I_{\text{exp}} \) calculated as a ratio \( [I/(\text{Ln4f}) + I(\Sigma\text{OVMO})]/I(\Sigma\text{IVMO}) \), except for the Ln5s intensity, on the number \( n_{4f} \) of the Ln4f electrons in Ln3+ is given in fig. 2. Using the least square method, this dependence was described as (1):

\[
I_{\text{exp}} = 0.081n_{4f} + 0.29 \tag{1}
\]

and

\[
I_{\text{theor}} = 0.01n_{4f}^{2.24} + 0.18 \tag{2}
\]

Theoretical dependence \( I_{\text{theor}} \) (2) drawn in [1] for Ln5O8 is given for comparison in fig. 2. Just as for lanthanide trifluorites [4], experimental dependence \( I_{\text{exp}} \) (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 LnL3 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 LaL3, the O1s peak was found to be 3.2 eV wide, while the corresponding O2s one (\( E_b \sim 26.5 \) 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 \( \Delta E \) of a level from which an electron was emitted is inversely proportional to the lifetime \( \Delta \tau \) of the hole. Since \( \Delta \tau \) decreases as the level energy grows, for the separate atoms, the peak

Figure 1. Low binding energy XPS spectra from lanthanide ortho-metoxibenzoates LnL3 (L = C8H7O3). Results of the electronic structure calculations for the LnO3– (D3h) clusters [5] are given under the spectra. Ligand-related MOs are shown as arrows.

Figure 2. Dependence of the Ln4f XPS relative intensity on the number \( n \) of Ln4f electrons for lanthanide ortho-metoxibenzoates and diphenyl-acetates (LnL32): (a) * - experimental for LnL3; (b) Δ - experimental for LnL32; (c) o - theory for Ln2O3 [4].
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-metoxibenozoates 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-metoxibenozoates [5] and other lanthanide compounds [1, 2]. This agrees qualitatively with the non-relativistic (NR) self-consisting field (SCF) X\( _0 \) discrete variation (DV) [10, 11] and scattered waves (SW) [5] theoretical calculation results.

Indeed, to a certain extent, the 1\( a^\prime \)\( _1 \) IVMO can be viewed as a quasi-atomic MO consisting of La5p AO (tab. 1). IVMO couples 1\( e^\prime \) and 2\( e^\prime \) (1\( a^\prime \)\( _1 \) and 2\( a^\prime \)\( _1 \)) can be formally attributed to the bonding and antibonding MOs, respectively. The bonding 1\( a^\prime \)\( _1 \) IVMO contains 85% of La5s and 12% of O2s AOs, while the antibonding 2\( a^\prime \)\( _1 \) one contains 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 1\( e^\prime \) MO contains only 2.5% of the O2p AO, while the antibonding 2\( e^\prime \) 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 2\( e^\prime \) one. As a result, electrons of the IVMO couple, for instance 1\( e^\prime \) and 2\( e^\prime \), will strengthen the Ln-O chemical bond (tab. 1).

As lanthanide atomic number Z for LnO\( _2^\text{3-} \) 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 2\( a^\prime \)\( _1 \) 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 2\( e^\prime \)-2\( a^\prime \)\( _1 \) OVMOs and 1\( a^\prime \)\( _1 \) and 1\( a^\prime \)\( _1 \) IVMOs. The compositions of these MOs also change significantly. Thus, the OVMO couple 2\( e^\prime \)-2\( a^\prime \)\( _1 \), by the end of lanthanide row, can be attributed to a quasi-atomic 2\( e^\prime \)-2\( a^\prime \)\( _1 \) IVMO formation, the Ln5p – O2s AO mixing, for example in TbO\( _2^\text{3-} \), is significantly higher than that in LaO\( _2^\text{3-} \), and that, the lower 1\( a^\prime \)\( _1 \) IVMO becomes, it becomes more and more quasi-atomic.

### Core electron spectral structure.

The core electron XPS spectra from lanthanide ortho-metoxibenozoates exhibit a fine structure which has much in common with that of the spectra from Ln\( _2^\text{3-} \)O\( _3 \) and LnF\( _3 \). The Ln5s,4s spectra from Ln\( _2^\text{3-} \) 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\( _2^\text{3-} \)O\( _3 \). Despite some differences in the Ln4d spectra.

### Table 1. MO energies \( E \) [eV], partial electronic contributions [%] in different regions of the LaO\( _2^\text{3-} \)(D\( _{2h} \)) cluster at \( R_{\text{Ln-O}} = 0.174 \) nm and total partial charges \( Q/ \) (electronic charge units) calculated in the SCF \( X_0 \) – SW approximation [4, 9].

<table>
<thead>
<tr>
<th>Molecular orbital</th>
<th>–E</th>
<th>s</th>
<th>p</th>
<th>D</th>
<th>F</th>
<th>s</th>
<th>p</th>
<th>Region</th>
</tr>
</thead>
<tbody>
<tr>
<td>OVMO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2( a^\prime )</td>
<td>6.25</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>88.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3( a^\prime )</td>
<td>6.91</td>
<td>–</td>
<td>1.1</td>
<td>–</td>
<td>–</td>
<td>84.9</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>5( e^\prime )</td>
<td>7.15</td>
<td>–</td>
<td>0.6</td>
<td>1.2</td>
<td>83.0</td>
<td>–</td>
<td>2.7</td>
<td>–</td>
</tr>
<tr>
<td>4( a^\prime )</td>
<td>7.55</td>
<td>2.0</td>
<td>–</td>
<td>8.4</td>
<td>25.7</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2( e^\prime )</td>
<td>7.38</td>
<td>–</td>
<td>–</td>
<td>2.2</td>
<td>77.9</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3( a^\prime )(a)</td>
<td>12.29</td>
<td>1.3</td>
<td>–</td>
<td>5.0</td>
<td>18.7</td>
<td>0.3</td>
<td>53.1</td>
<td>–</td>
</tr>
<tr>
<td>4( e^\prime )</td>
<td>12.60</td>
<td>–</td>
<td>7.4</td>
<td>5.3</td>
<td>4.0</td>
<td>–</td>
<td>52.2</td>
<td>–</td>
</tr>
<tr>
<td>2( a^\prime )( _1 )</td>
<td>13.51</td>
<td>–</td>
<td>6.2</td>
<td>–</td>
<td>4.2</td>
<td>–</td>
<td>57.0</td>
<td>–</td>
</tr>
<tr>
<td>1( a^\prime )( _1 )</td>
<td>14.66</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>6.8</td>
<td>–</td>
<td>57.6</td>
<td>–</td>
</tr>
<tr>
<td>3( e^\prime )</td>
<td>14.96</td>
<td>–</td>
<td>2.3</td>
<td>3.0</td>
<td>–</td>
<td>1.5</td>
<td>55.8</td>
<td>–</td>
</tr>
<tr>
<td>1( e^\prime )( _1 )</td>
<td>15.11</td>
<td>–</td>
<td>–</td>
<td>2.8</td>
<td>1.8</td>
<td>–</td>
<td>53.7</td>
<td>–</td>
</tr>
<tr>
<td>2( e^\prime )( _1 )</td>
<td>20.67</td>
<td>–</td>
<td>40.0</td>
<td>0.7</td>
<td>0.1</td>
<td>20.4</td>
<td>10.2</td>
<td>–</td>
</tr>
<tr>
<td>1( a^\prime )( _2 )</td>
<td>24.03</td>
<td>–</td>
<td>59.6</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3.0</td>
<td>–</td>
</tr>
<tr>
<td>2( a^\prime )( _2 )</td>
<td>26.80</td>
<td>13.1</td>
<td>–</td>
<td>0.9</td>
<td>1.1</td>
<td>61.8</td>
<td>0.3</td>
<td>22.8</td>
</tr>
<tr>
<td>1( a^\prime )( _2 )</td>
<td>31.23</td>
<td>–</td>
<td>18.2</td>
<td>0.9</td>
<td>0.2</td>
<td>49.5</td>
<td>1.8</td>
<td>–</td>
</tr>
<tr>
<td>1( a^\prime )( _1 )</td>
<td>38.87</td>
<td>66.0</td>
<td>–</td>
<td>–</td>
<td>0.1</td>
<td>9.3</td>
<td>2.1</td>
<td>–</td>
</tr>
</tbody>
</table>

\( Q/ \) | 1.6 | 4.0 | 0.6 | 0.8 | 4.3 | 10.4 | 10.3 |

(a) Upper filled orbital.
structures from LnL₃ and LnF₃, the observed changes in the shape of the considered spectra from LnL₃ do not contradict the fact that their structures are due to multiplet splitting.

The configuration interaction is most pronounced in the Ln4p spectra from LnL₃. This spectral structure is similar to that from LnF₃ and Ln₂O₅. The Ln5d spectral structure for light lanthanides exhibits intense satellites and corresponds to the structure of the spectra from Ln₂O₃ [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 Eₖ) and inner (15-50 eV Eₖ) 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 ЛН(C₆H₄OCH₃COO)-3

У раду се разматрају резултати рендгеном индуковане фотоелектронске спектроскопије лантанид орто-метоксибензоата Ln(C₆H₄OCH₃COO)-3, где Ln представља лантанид од La до Lu, изузев Pm, док је C₆H₄OCH₃COO- остатак орто-метоксибензоатне киселине. Показало се да спектри средишњих и спољашњих електрона добијени рендгеном индукованом фотоелектронском спектроскопијом, у области енергије 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 цеања, вишечистиче петрутурације, динамичког ефекта, итд. Показано је да механизми настанка тако фине структуре испољавају различите вероватноће у спектру извесне електронске љуске. Отуда се фине рендгеном индуковане фотоелектронска спектрална структура, која настаје услед неког механизма, може протумачити а њени квантификативни параметри повезати са физичким и хемијским својствима прочуваних састава (степеном делокализације и партиципације Ln4f електрона у хемијској вези, електронском конфигурацијом и оксидацијним стањем, густином ненапуњених електрона парамагнетних јона, степеном учешћа попуњених електронских љуски лантанида са ниском енергијом везе и лиганида у формирању спољашњих и унутрашњих валентних молекулских орбитала, структуром непосредне околине лантанида у аморфним материјалима, итд).

Кључне речи: рендгеном индуковане фотоелектронске спектроскопије, спољашње и унутрашње валентне молекулске орбитаље, лантаниди