X-RAY SPECTROSCOPY STUDY OF ThO₂ AND ThF₄

by
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The structure of the X-ray photoelectron, X-ray O(F)Kα-emission spectra from ThO₂ and ThF₄ as well as the Auger OKLL spectral structure from ThO₂ was studied. The spectral structure was analyzed by using fully relativistic cluster discrete variational calculations of the electronic structure of the ThO₂¹²⁻(D₄h) and ThF₄⁴⁻(C₂) clusters reflecting thorium close environment in solid ThO₂ and ThF₄. As a result it was theoretically found and experimentally confirmed that during the chemical bond formation the filled O(F)2p electronic states are distributed mainly in the binding energy range of the outer valence molecular orbitals from 0-13 eV, while the filled O(F)2s electronic states – in the binding energy range of the inner valence molecular orbitals from 13-35 eV. It was shown that the Auger OKLL spectral structure from ThO₂ characterizes not only the O2p electronic state density distribution, but also the O2s electronic state density distribution. It agrees with the suggestion that O2s electrons participate in formation of the inner valence molecular orbitals, in the binding energy range of 13-35 eV. The relative Auger OKL₂₋₃-L₂₋₃-peak intensity was shown to reflect quantitatively the O2p electronic state density of the oxygen ion in ThO₂.

Key words: X-ray photoelectron spectra, thorium oxide, thorium tetrafluoride, outer and inner valence molecular orbitals

INTRODUCTION

While studying the X-ray photoelectron spectra (XPS) from solid ThO₂ and ThF₄, the spectral structure in the binding energy range of 0-35 eV was found to form due to the electrons of the outer valence (OVMO, of 0-13 eV binding energy) and the inner valence (IVMO, of 13-35 eV binding energy) molecular orbitals with effective participation of the Th6p and O(2s)2s filled atomic shells [1]. Practically, these spectra reflect the valence band structure (0-35 eV), and they are observed as several eV wide bands. Furthermore, it was shown that under certain conditions the IVMO can form in compounds of any elements of the periodic table [2]. This fact stimulated intense theoretical and experimental studies of the chemical bond nature in actinides, in particular – thorium compounds [3].

This work analyses the fine XPS, high-resolution O(F)Kα X-ray emission (XES) of ThO₂ and ThF₄ and the Auger OKLL spectral structure of ThO₂, taking into account the fully relativistic cluster discrete variational (RDV) electronic structure calculations for the ThO₂¹²⁻(D₄h) and ThF₄⁴⁻(C₂) clusters reflecting thorium close environment in solid ThO₂ and ThF₄ in order to study the O(F)2s,2p electronic state density.

EXPERIMENTAL

XPS spectra of ThO₂ and ThF₄ were measured with an electrostatic spectrometer HP5950A using monochromatized AlKα₁,₂ (hv = 1486.6 eV) radiation under1.3×10⁻⁷ Pa at the room temperature [1]. The device resolution, measured as the full width at the half-maximum (FWHM), of the Au4f⁷/₂ peak on the standard rectangular gold plate was 0.8 eV. The binding energies E₉(eV) were measured relative to the binding energy of the C1s electrons from saturated hy-
Valence electrons XPS from ThO$_2$ and ThF$_4$ in the binding energy range 0-35 eV can be conditionally subdivided into two sub-ranges. The first one 0-13 eV exhibits the OVMO related structure formed from the incompletely filled valence Th6d,7s,5f,7p and O(F)2p AOs (fig. 1). The second one 13-35 eV shows the IVMO related structure formed due to the strong interaction of the completely filled inner Th6p and O(F)2s AOs. The valence XPS of the studied compounds exhibit a two-hump structure and reflect the electronic state density of the outer and inner orbitals taking into account the photoionization cross-sections (fig. 1).

The IVMO XPS from ThO$_2$ and ThF$_4$ are observed structured in the Th6p-O(F)2s binding energy range. This structure was studied in details for ThO$_2$ [7] and ThF$_4$ [8] taking into account the relativistic calculation results. The calculation results of the O(F)2p electronic state density in the binding energy ranges 0-13 eV and 13-35 eV (fig. 1). The relative O(F)2p and O(F)2s electronic state densities are normalized by 100% and are not correlated.

![Figure 1](image)

**Figure 1.** XPS from: (a) ThO$_2$, (b) ThF$_4$; the calculated O2p and O2s electronic state densities for the ThO$_2$$_{12}$ (D$_{ab}$) and ThF$_4$$_{8}$ (C$_2$) clusters normalized by 100% are shown under the spectra.

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*1 Å = 1 × 10^{-10} m*
As it was shown in [7, 8], since during the photoemission the molecule transits to an excited state with a hole on a certain level, for the more precise comparison of the experimental and the theoretical binding energies the calculated values for the transition state were used [9]. However, it is well known that the binding energies for the transition states differ from the corresponding ones for the basic state by a constant shift toward the higher energies. Therefore, for comparison of the theoretical and experimental results, in the present work the calculated binding energies were normalized relative to the ones corresponding to the more intense and sharp peaks (fig. 1).

The energy normalization was done so that the more intense peaks of 17γ/8, 13γ/7 IVMO for ThO2 and 11γ/4,12γ/4 IVMO for ThF4 formed mostly from the Th6p electrons were located at 16.5 eV and 18.4 eV, respectively (fig. 1, [7, 8]), while the O1s and F1s binding energies should be 530.2 eV and 685.5 eV for ThO2 and ThF4, respectively. In this case, the calculated O2p electronic state density range for ThO2 was shifted toward the higher binding energy by several eV, while the O2s-related calculated range approximately coincided with the experimental one – fig. 1(a). The observed discrepancy between the experimental and calculated O2p binding energies arose mostly from the calculation inaccuracy. For ThF4 one can see a qualitative agreement for the F2p, and to a lesser degree – for the F2s electrons – fig. 1(b). The calculated data show that the atomic O(F)2p orbitals participate mostly in the OVMO formation, while the O(F)2s ones – in the IVMO formation (see fig. 1, [7, 8]).

**O(F)Kα XES from ThO2 and ThF4** are associated with the O(F)2p→1s electronic transition in the energy range of 520 eV < \( h\nu < 535 \) eV for ThO2 and of 670 eV < \( h\nu < 690 \) eV for ThF4 (fig. 2). According to the dipole selection rules they reflect the partial density of the occupied O2p electronic states in the considered thorium compounds.

The OKα XES from ThO2 was observed as an asymmetric 3.1 eV wide peak with a maximum at 525.7 eV – fig. 2(a). The OVMO XPS from ThO2 is given above the XES. Its energy scale was determined as a binding energy difference O1s (530.2 eV) – OVMO. This scale corresponds to the photon energy in fig. 2(a). In the same energy scale the theoretical calculation results of the O2p electronic state density are given, see figs. 1(a) and 2(a). The energies of the calculated filled O2p electronic states lie in the range of 2.82 eV. Taking into account the experimental widening, one can see a satisfactory agreement of the value (\( \Gamma^* = 2.82 \) eV) with the width of the OKα XES peak (\( \Gamma = 3.1 \) eV) for ThO2 – fig. 2(a). Despite the incorrectness of the comparison of the energies calculated for the ground O1s and O2p electronic states with the XES OKα, one can conclude that the several eV energy shift of the calculated O2p band in ThO2 from the corresponding experimental data can be explained by the calculation inaccuracy.

**Comparison of the OVMO XPS and OKα XES from ThO2** shows that the filled O2p electronic states are mostly located at the roof of the outer valence band – fig. 2(a). At the bottom of this band thorium valence electronic states are mostly located. It agrees with the calculation results that show that the Th6d electrons are located at the bottom of the outer valence band, while the Th5f electronic states – in the middle [7]. The wide intensity shoulder from the higher energy side (530 eV to 535 eV) of the OKα XES, apparently, can be attributed to the electronic transitions from the excited states. Indeed, in this energy range empty electronic states are observed. These states can be filled during excitation [7].

The similar considerations can be applied to the FKα XES from ThF4 – fig. 2(b). This spectrum was observed as 3.2 eV wide line at 675.5 eV. A less intense maximum was observed at the higher energy side at 678.6 eV, as well as a low intensity shoulder in the photon energy range of 682-690 eV. The OVMO XPS from ThF4 is given above the XES. Its energy scale was determined as a binding energy difference F1s (685.5 eV) – OVMO. This scale corresponds to the photon energy in fig. 2(b). In the same energy scale the theoretical calculation results of the F2p electronic state density are

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**Figure 2.** XPS (dashed), O(F)Kα XES (solid) and the relative O(F)2p electronic state densities (vertical bars) for the ThO2(Ca) and ThF4(C4) cluster: (a) oxygen in ThO2; (b) fluorine in ThF4; spectral intensities are not normalized.
given, see figs. 1(b) and 2(b). These states are observed in the energy range of 2.3 eV and agree satisfactorily with the ThF₄ XPS.

The ThF₄ FKₓ XES’s shape corresponds to a lesser degree with the XPS and the calculation results unlike that of the ThO₂ OKₓ XES – fig. 2(b). The wide shoulder from a higher photon energy side in the range of 682-690 eV can be attributed to the electronic transitions from the excited states. Indeed, as it was noted for ThO₂, in this calculated energy range for ThF₄ the unoccupied electronic states were observed. These states can be filled during the excitation [8]. The total FWHM of the two lines at 675.5 eV and 678.6 eV exceeds the OVMO XPS one. The intensity ratio of these two lines does not agree with the calculated results which show that the Th6d electronic states should lie at the bottom of the outer valence band and determine to a certain degree the XPS intensity in this energy range. It allows a suggestion that despite all the measures taken for the sample stabilization, ThF₄ partially decomposed under the beam during the spectra registration. Apparently, this material must be studied at lower excitation energies or at synchrotron radiation sources. Despite this, we think the main task on the determination of the distribution range of the filled F2p electronic states in ThF₄ was accomplished. Indeed, the filled F2p electronic states in ThF₄ are observed only in the OVMO energy range and are not observed in the IVMO energy range. It agrees with the corresponding results for ThO₂.

The OKL₂,3 Au ger spectrum from ThO₂ consists of three structured lines reflecting the OKL₂,3 L₁,2,3 (O1s→O2p), OKL₁L₁,2,3 (O1s→O2s,2p), and OKL₁L₁ (O1s→O2s) electronic transitions (fig. 3). The OKL₂,3 L₁,2,3 width, in particular, reflects the width of the filled O2p electronic states related band (Γ = 3.1 eV) and that of the O1s (Γ = 1.4 eV) – figs. 1(a) and 2(a). The width of the more structured OKL₁L₁,2,3 line reflects the widths of the filled O2s, 2p bands, and the O1s peak, while the OKL₁L₁ width – the O2s and O1s peak widths. Therefore, the OKL₁L₁,2,3 and OKL₁L₁ lines were expected to be more complicated for the oxides where the IVMO form more effectively. For example, for ThO₂ the O2s energy range widens due to the IVMO formation from 1 eV to 9.1 eV – fig. 1(a). In this case the Auger peaks involving the O2s electrons widen significantly comparing to that for, for instance, Al₂O₃ where the participation of the O2s AOs in the IVMO formation is less expressed. Indeed, the OKL₁L₁ Auger spectrum from ThO₂ manifests a structure instead of a single line like that from Al₂O₃ (fig. 3). This is another evidence for the effective IVMO formation in ThO₂.

In previous studies a quantitative correlation between the relative OKL₂,3 L₁,2,3 and OKL₁L₁,2,3 Auger intensities calculated as (Auger OKLL)/(O1s XPS) areas ratios and the O1s binding energies for Bi₂O₃, Al₂O₃, SiO₂, and UO₂ was drawn [5]. This relative intensity characterizes quantitatively the partial density of the valence electronic states in oxygen ions, while the O1s intensity characterizes the total density of the core electronic states in oxygen ions. It has to be especially noted that these novel and important values allow a quantitative comparison of the oxygen partial electronic state densities for different oxides (tab. 1). Practically, the method of determination of the partial O2p electronic state density of oxygen ions in oxides was founded.

<table>
<thead>
<tr>
<th>Compound</th>
<th>E₀ (eV)</th>
<th>I₁ (rel. units)</th>
<th>I₃ (rel. units)</th>
</tr>
</thead>
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<tr>
<td>Bi₂O₃</td>
<td>529.4±0.2</td>
<td>1.27±0.07</td>
<td>0.38±0.05</td>
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<tr>
<td>Al₂O₃</td>
<td>531.4±0.3</td>
<td>0.99±0.08</td>
<td>0.29±0.02</td>
</tr>
<tr>
<td>SiO₂</td>
<td>532.4±0.1</td>
<td>0.68±0.08</td>
<td>0.23±0.03</td>
</tr>
<tr>
<td>ThO₂</td>
<td>530.2</td>
<td>0.85</td>
<td>0.24</td>
</tr>
<tr>
<td>UO₂</td>
<td>530.5</td>
<td>0.81</td>
<td>0.23</td>
</tr>
</tbody>
</table>

(a) Relative intensities are the ratio of the areas (Auger OKLL)/(O1s XPS) peaks measured simultaneously during the same experiment

It has to be noted that the considered results have underlay the novel perspective method of the quantitative determination of the relative valence state density on oxygen ions in metal oxides and other compounds on the basis of the X-ray spectral data.

CONCLUSIONS

On the basis of the X-ray spectral (XPS, XES, Auger) data and the RDV calculation results of the electronic structure of ThO₂ and ThF₄ it was established that the filled O(F)2p electronic states are distributed mainly in the binding energy range of the outer valence molecular orbitals (0-13 eV), while the filled O(F)2s electronic states – in the range of the inner valence molecular orbitals (13-35 eV).
Another experimental confirmation for the IVMO formation in ThO$_2$ on the basis of the Auger OKLL spectral structure was obtained. The relative O2p electronic state density in ThO$_2$ was determined and compared to the corresponding values for other metal oxides.

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REFERENCES


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