X-RAY SPECTROSCOPY STUDY OF ThO$_2$ AND ThF$_4$

by

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The structure of the X-ray photoelectron, X-ray O(F)K$_\alpha$-emission spectra from ThO$_2$ and ThF$_4$ as well as the Auger OKLL spectra from ThO$_2$ was studied. The spectral structure was analyzed by using fully relativistic cluster discrete variational calculations of the electronic structure of the ThO$_8^{12-}$(D$_{4h}$) and ThF$_8^{4-}$(C$_2$) clusters reflecting thorium close environment in solid ThO$_2$ and ThF$_4$. 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 ThO$_2$ 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 OKL$_{2-3}$L$_{2-3}$ peak intensity was shown to reflect quantitatively the O2p electronic state density of the oxygen ion in ThO$_2$.

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 ThO$_2$ and ThF$_4$, 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(F)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)K$_\alpha$ X-ray emission (XES) of ThO$_2$ and ThF$_4$ and the Auger OKLL spectral structure of ThO$_2$, taking into account the fully relativistic cluster discrete variational (RDV) electronic structure calculations for the ThO$_8^{12-}$ (D$_{4h}$) and ThF$_8^{4-}$ (C$_2$) clusters reflecting thorium close environment in solid ThO$_2$ and ThF$_4$ in order to study the O(F)2s,2p electronic state density.

EXPERIMENTAL

XPS spectra of ThO$_2$ and ThF$_4$ were measured with an electrostatic spectrometer HP5950A using monochromatized AlK$_{\alpha1,2}$ (hv = 1486.6 eV) radiation under 1.3 10^{-7} Pa at the room temperature [1]. The device resolution, measured as the full width at the half-maximum (FWHM), of the Au4f$_{7/2}$ peak on the standard rectangular gold plate was 0.8 eV. The binding energies E_b(eV) were measured relative to the binding energy of the C1s electrons from saturated hy-

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drocarbons absorbed on the sample surface, accepted to be equal to 285.0 eV. For the gold standard the calibration binding energies of $E_b(C1s) = 284.7$ eV and $E_b(Au4f_{7/2}) = 83.8$ eV were used. The C1s XPS peak from hydrocarbons on the sample surface was observed to be 1.3 eV wide. The error in the determination of the binding energy and the peak widths did not exceed 0.1 eV (10% of the relative peak intensity).

The ThO_2 and ThF_4 samples for the XPS study were prepared from the finely dispersed powder ground in an agate mortar as a dense, thick layer with a flat surface pressed in indium on a metal substrate. The elastic scattering related spectral background was subtracted by Shirley [4].

The $O(F)K_\alpha$ XES of ThO_2 and ThF_4 were measured by the primary procedure with the X-ray microanalyser JCXA-733 with the focusing by Johann ($R = 280$ mm) using the TAP ($2d = 25.76$ Å*) analyzer crystal with the energy resolution of 1.8 eV and 0.5 eV at $V = 5$ kV and $I = 100$ nA. The samples were ground in the agate mortar and as a powder pressed into a grooved silver plate attached to the X-ray anode. During the spectra registration the sample positioning was continuously scanned in order to avoid the sample decomposition under the beam.

The OKLL Auger and the O1s XPS spectra from ThO_2 were measured "simultaneously" under the same conditions with an electrostatic spectrometer MK II VG Scientific using AlK_α radiation under $1.3 \cdot 10^{-7}$ Pa at the room temperature. The device resolution measured as the FWHM, of the $Au4f_{7/2}$ line on the standard rectangular gold plate was 1.2 eV. The kinetic energies of the Auger electrons as well as the binding energies E_b(eV) were measured relatively to the binding energy of the C1s electrons from hydrocarbons absorbed on the sample surface, accepted to be equal to 285.0 eV. The error in the determination of the binding energy and the peak widths did not exceed 0.1 eV (10% of the relative peak intensity). The peak widths Γ(eV) are given relative to Γ(C1s) = 1.3 eV for comparison with other research data [5]. For the XPS and Auger study the ThO_2 sample was prepared as a surface oxide layer on the metallic thorium plate like that in [6].

The electronic structure calculations for the $ThO_8^{12-}(D_{4h})$ and $ThF_8^{4-}(C_2)$ clusters were done by the fully relativistic discrete variational cluster method (RDV) with local exchange-correlation potential. The RDV method is based on the solution of the Dirac-Slater equation for 4-component wave functions transforming according to irreducible representations of the double point groups. The extended bases of 4-component numerical atomic orbitals (AO) obtained as the solution of the Dirac-Slater equation for the isolated neutral atoms also included $Th5f,7p_{1/2}$ and $7p_{3/2}$ functions in addition to occupied AOs [7, 8].

* 1 Å = 1 $\cdot$ 10^{-10} m

RESULTS AND DISCUSSION

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.
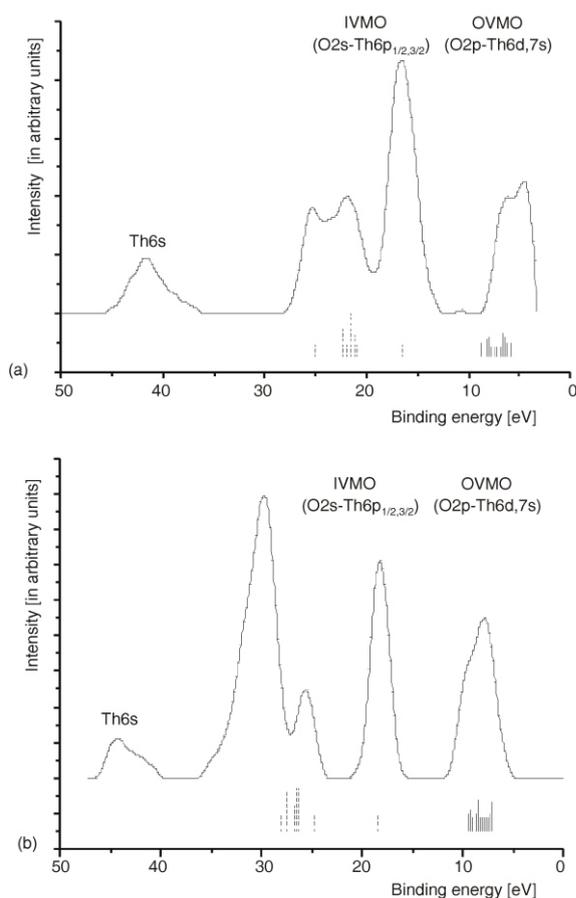
Figure 1. XPS from: (a) ThO_2, (b) ThF_4; the calculated O2p and O2s electronic state densities for the ThO_8^{12-} (D_{4h}) and ThF_8^{4-} (C_2) clusters normalized by 100% are shown under the spectra

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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 $17\gamma_6$, $13\gamma_7$ IVMO for ThO$_2$ and $11\gamma_{3,4}$, $12\gamma_{3,4}$ IVMO for ThF$_4$ formed mostly from the Th6p$_{3/2}$ 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 ThO$_2$ and ThF$_4$, respectively. In this case, the calculated O2p electronic state density range for ThO$_2$ 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 ThF$_4$ 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)K$_\alpha$ XES from ThO$_2$ and ThF$_4$ are associated with the O(F)2p – 1s electronic transition in the energy range of 520 eV < $h\nu$ < 535 eV for ThO$_2$ and of 670 eV < $h\nu$ < 690 eV for ThF$_4$ (fig. 2). According to the dipole selection rules they reflect the partial density of the occupied O(F)2p electronic states in the considered thorium compounds.

The OK$_\alpha$ XES from ThO$_2$ was observed as an asymmetric 3.1 eV wide peak with a maximum at 525.7 eV – fig. 2(a). The OVMO XPS from ThO$_2$ 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 (Γ = 2.82 eV) with the width of the OK$_\alpha$ XES peak (Γ = 3.1 eV) for ThO$_2$ – fig. 2(a). Despite the incorrectness of the comparison of the energies calculated for the ground O1s and O2p electronic states with the XES OK$_\alpha$, one can conclude that the several eV energy shift of the calculated O2p band in ThO$_2$ from the corresponding experimental data can be explained by the calculation inaccuracy.
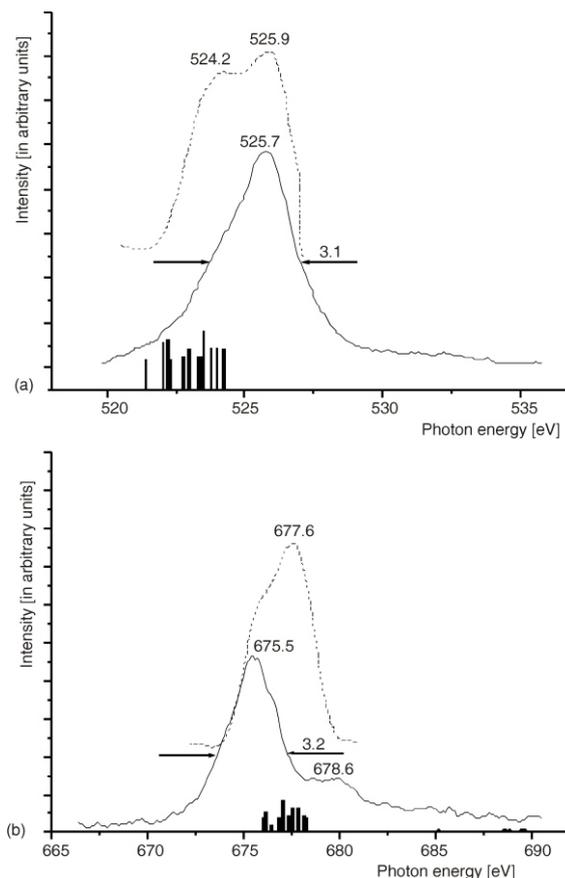
Figure 2. XPS (dashed), O(F)K$_\alpha$XES (solid) and the relative O(F)2p electronic state densities (vertical bars) for the ThO$_8^{12}$ (D$_{4h}$) and ThF$_8^4$ (C$_2$) cluster for: (a) oxygen in ThO$_2$; (b) fluorine in ThF$_4$; spectral intensities are not normalized

Comparison of the OVMO XPS and OK$_\alpha$ XES from ThO$_2$ 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 intense shoulder from the higher energy side (530 eV to 535 eV) of the OK 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 FK XES from ThF$_4$ – 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 intense shoulder in the photon energy range of 682-690 eV. The OVMO XPS from ThF$_4$ 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

given, see figs. 1(b) and 2(b). These states are observed in the energy range of 2.30 eV and agree satisfactorily with the ThF$_4$ XPS.

The ThF$_4$ FK$_\alpha$ XES's shape corresponds to a lesser degree with the XPS and the calculation results unlike that of the ThO$_2$ OK$_\alpha$ 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 ThO$_2$, in this calculated energy range for ThF$_4$ 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, ThF$_4$ 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 ThF$_4$ was accomplished. Indeed, the filled F2p electronic states in ThF$_4$ are observed only in the OVMO energy range and are not observed in the IVMO energy range. It agrees with the corresponding results for ThO$_2$.

The OKLL Auger spectrum from ThO$_2$ consists of three structured lines reflecting the OKL$_{2-3}$L$_{2-3}$ (O1s   O2p), OKL$_1$L$_{2-3}$ (O1s   O2s,2p), and OKL$_1$L$_1$ (O1s   O2s) electronic transitions (fig. 3). The OKL$_{2-3}$L$_{2-3}$ 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 OKL$_1$L$_{2-3}$ line reflects the widths of the filled O2s, O2p bands, and the O1s peak, while the OKL$_1$L$_1$ width – the O2s and O1s peak widths. Therefore, the OKL$_1$L$_{2-3}$ and OKL$_1$L$_1$ lines were expected to be more complicated for the oxides where the IVMO form more effectively. For example, for ThO$_2$ 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, Al$_2$O$_3$ where the participation of the O2s AOs in the IVMO formation is less expressed. Indeed, the OKL$_1$L$_1$ Auger spectrum from ThO$_2$ manifests a structure instead of a single line like that from Al$_2$O$_3$ (fig. 3). This is another evidence for the effective IVMO formation in ThO$_2$.

In previous studies a quantitative correlation between the relative OKL$_{2-3}$L$_{2-3}$ and OKL$_1$L$_{2-3}$ Auger intensities calculated as (Auger OKLL)/(O1s XPS) areas ratios and the O1s binding energies for Bi$_2$O$_3$, Al$_2$O$_3$, SiO$_2$, and UO$_2$ was drawn [5]. This relative intensity characterizes quantitatively the partial density
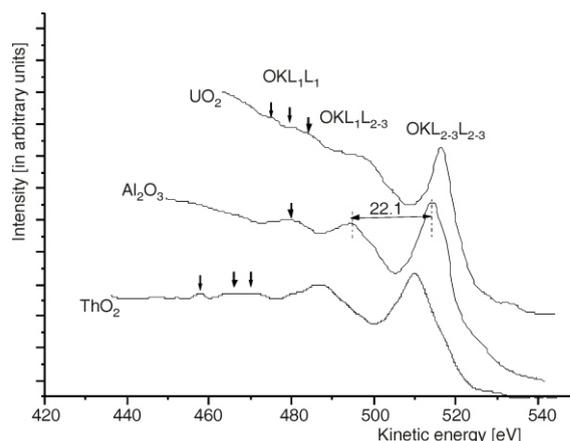
Figure 3. OKLL Auger spectra from UO$_2$, Al$_2$O$_3$ [5], and ThO$_2$, the peak structures are shown by arrows

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 1. Binding energies E_b(eV) of the O1s electrons and relative intensities I$^{(a)}$ (rel. units) of the OKL$_{2-3}$L$_{2-3}$ and OKL$_1$L$_{2-3}$ Auger peaks in: Bi$_2$O$_3$, Al$_2$O$_3$, SiO$_2$, UO$_2$ [5] and ThO$_2$

Compound	E_b (eV)	I$_1$ (rel. units)	I$_2$ (rel. units)
Bi$_2$O$_3$	529.4 0.2	1.27	0.38 0.05
Al$_2$O$_3$	531.4		0.29
SiO$_2$			
ThO$_2$			
UO$_2$			

(a) Relative intensities are the ration 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 ThO$_2$ and ThF$_4$ 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).

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Another experimental confirmation for the IVMO formation in ThO₂ on the basis of the Auger OKLL spectral structure was obtained. The relative O2p electronic state density in ThO₂ was determined and compared to the corresponding values for other metal oxides.

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ПРОУЧАВАЊЕ ТОРИЈУМДИОКСИДА И ТОРИЈУМТЕТРАФЛУОРИДА РЕНДГЕН-ИНДУКОВАНОМ СПЕКТРОСКОПИЈОМ

Проучавана је структура рендген-индукованих фотоелектронских и рендген-индукованих O(F)Kₐ – емисионих спектара ThO₂ и ThF₄, као и Аугер OKLL спектара ThO₂. Спектрална структура је анализирана помоћу потпуно релативистички кластер дискретних варијационих прорачуна електронске структуре ThO₈¹²⁻ (D₄ₕ) и ThF₈⁴⁻(C₂) кластера која одржава блиску околину торијума у чврстом ThO₂ и ThF₄. Као резултат, теоријски је пронађено и експериментално потврђено да су, у току формирања хемијских веза, попуњена O(F)2p електронска стања распоређена углавном у области енергије везе спољних валентних молекулских орбитала од 0 до 13 eV, док су попуњена O(F)2s електронска стања – у области енергије везе унутрашњих валентних молекулских орбитала од 13 eV до 35 eV. Показано је да структура Аугер OKLL спектара ThO₂ карактерише не само расподелу густине O2p електронских стања, већ такође и расподелу густине O2s електронских стања. Ово се слаже са претпоставком да O2s електрони учествују у формирању унутрашњих валентних молекулских орбитала у области енергије везе од 13 eV до 35 eV. Показано је да релативни интензитет Аугер OKL₂₋₃L₂₋₃ пика квантитативно одражава густину O2p електронских стања кисеониковог јона у ThO₂.

Кључне речи: рендген-индуковани фотоелектронски спектар, торијумоксид, торијум-тетрафлуорид, спољашње и унутрашње валентне молекулске орбитале