

RESONANT EMISSION OF UO_2 , U_3O_8 , AND UO_{2+x} VALENCE ELECTRONS UNDER SR EXCITATION NEAR THE $\text{O}_{4,5}(\text{U})$ ABSORPTION EDGE

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The structure of the resonant electron emission (REE) spectra of UO_2 (REE appears under the excitation with synchrotron radiation near the $\text{O}_{4,5}(\text{U})$ absorption edge at ~ 100 eV and ~ 110 eV) is studied with regard to the X-ray $\text{O}_{4,5}(\text{U})$ absorption spectrum of UO_2 and a quantitative scheme of molecular orbitals based on the X-ray electron spectroscopy data and the results of a relativistic calculation of the electronic structure of UO_2 . The structure of the REE spectra of U_3O_8 and UO_{2+x} is studied for comparison, and the effect of the uranium chemical environment in oxides on it is found. The appearance of such a structure reflects the processes of excitation and decay involving the $\text{U}5d$ and electrons of the outer valence MOs (OVMOs, from 0 to ~ 13 eV) and inner valence MOs (IVMOs, from ~ 13 eV to ~ 35 eV) of the studied oxides. It is noted that REE spectra show the partial density of states of $\text{U}6p$ and $\text{U}5f$ electrons. Based on the structure of REE spectra, it is revealed that $\text{U}5f$ electrons directly participate (without losing the f nature) in the chemical bonding of uranium oxides and are delocalized within CMOs (in the middle of the band), which results in the enhancement of the intensity of the REE spectra of CMO electrons during resonances. The $\text{U}6d$ electrons are found to be localized near the bottom of the outer valence band and are observed in the REE spectra of the studied oxides as a characteristic maximum at 10.8 eV. It is confirmed that $\text{U}6p$ electrons are effectively involved in the formation of IVMOs, which leads to the appearance of the structure in the region of IVMO electron energies during resonances. This structure depends on the chemical environment of uranium in the considered oxides.

Keywords: resonance emission of valence electrons, synchrotron radiation, uranium oxides.

INTRODUCTION

Based on the results of the interpretation of the fine structure of X-ray photoelectron spectra (XPS) of the valence electrons of UO_2 and $\gamma\text{-UO}_3$ in the binding energy range from 0 to ~ 35 eV, it is found that this structure is mainly due to the formation of outer valence (OMOs, from 0 to ~ 13 eV) and inner valence (IVMOs, from ~ 13 eV to ~ 35 eV) molecular orbitals [1, 2]. It is shown that, apart from $\text{U}5f, 6d, 7s$ atomic orbitals (AOs), also $\text{U}6p, 7p$ AOs participate in the formation of OVMOs, while IVMOs are mostly formed of $\text{U}6p$ and $\text{O}2s$ AOs of the neighboring uranium and oxygen atoms. These spectra reflect the structure of valence bands from 0 до ~ 35 eV of the oxides being studied and are observed in the form of a band with

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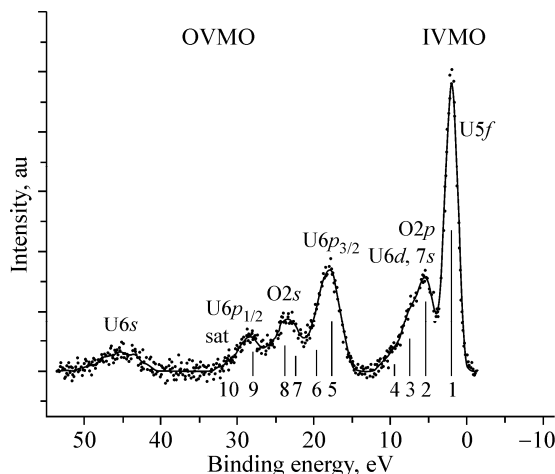


Fig. 1. X-ray electron spectrum of UO_2 valence electrons. Vertical lines show the correct XES spectrum of MO electrons marked by figures (MO scheme in Fig. 2).

a width of a few electron volts (Fig. 1). Some experimental [3] and theoretical results [1, 2, 4] indicate the presence of the occupied states of $\text{U}5f$ electrons in the valence band of UO_2 and $\gamma\text{-UO}_3$. The involvement of $\text{U}5f$ electrons in the chemical bonding of uranium oxides without losing the f nature must affect the structure of different X-ray (electron, resonant electron and emission, absorption, etc.) spectra if it is formed with their participation. Resonant emission of outer valence electrons with the binding energy from 0 to ~ 10 eV under synchrotron radiation (SR) excitation near the $\text{O}_{4,5}(\text{U})$ absorption edge has previously been studied for metallic uranium [5] and UO_2 [6, 7].

In this work, we analyzed the fine structure of the resonant emission spectra of UO_2 , U_3O_8 , and UO_{2+x} valence electrons in the electron binding energy range from 0 to 40 eV, which appears under SR excitation near the $\text{O}_{4,5}(\text{U})$ absorption edge in the photon energy range $80 \text{ eV} < h\nu < 150 \text{ eV}$ [8] with regard to X-ray $\text{O}_{4,5}(\text{U})$ absorption spectra of these oxides, the structure of the XES spectra of UO_2 and $\gamma\text{-UO}_3$, and also the results of the relativistic calculations of their electronic structure.

EXPERIMENTAL

The spectra of the total quantum yield of uranium dioxide and resonant emission of UO_2 , U_3O_8 , and UO_{2+x} valence electrons with the binding energy from 0 to ~ 35 eV under excitation near the $\text{O}_{4,5}(\text{U})$ absorption edge were measured using SR (Russian-German soft X-ray beamline at BESSY II) and a CLAMA4 electron energy analyzer (0 to 2500 eV, resolution better than 0.009 eV) [8, 9].

Uranium dioxide was obtained on a mechanically cleaned surface of uranium metal foil ($10 \times 8 \times 0.2$ mm) by oxidation in air (see [10]). This foil was previously glued onto an aluminum plate ($13 \times 10 \times 1.5$ mm) using silver suspension (Leitsilber 204, Demetron). The U_3O_8 and $\gamma\text{-UO}_3$ samples, on whose surface UO_{2+x} oxide formed in vacuum of the spectrometer, were prepared in the form of dense powder layers pressed into indium with a thickness of 0.125 mm at the bottom of round 8 mm hollows in copper disks with a diameter of 13 mm and a thickness of 1 mm. All samples were stuck with vacuum glue (Bond Seal Repair, Huntington Mechanical Laboratories INC) onto a copper holder and the electric contact with them was made by means of silver suspension. The samples were heated at a temperature of 80°C for 13 h in a preparation chamber of the spectrometer to achieve an ultrahigh vacuum. The samples were not cleaned mechanically under vacuum in the spectrometer preparation chamber. The spectra were measured at a vacuum of 5×10^{-10} Torr with grid No. 2 (400 lin/mm) at $c_{\text{ff}} = 2.25$, $\text{RE} = 5$ eV, and a step of 0.2 eV after 50 scans. The spectral intensity was normalized to the SR

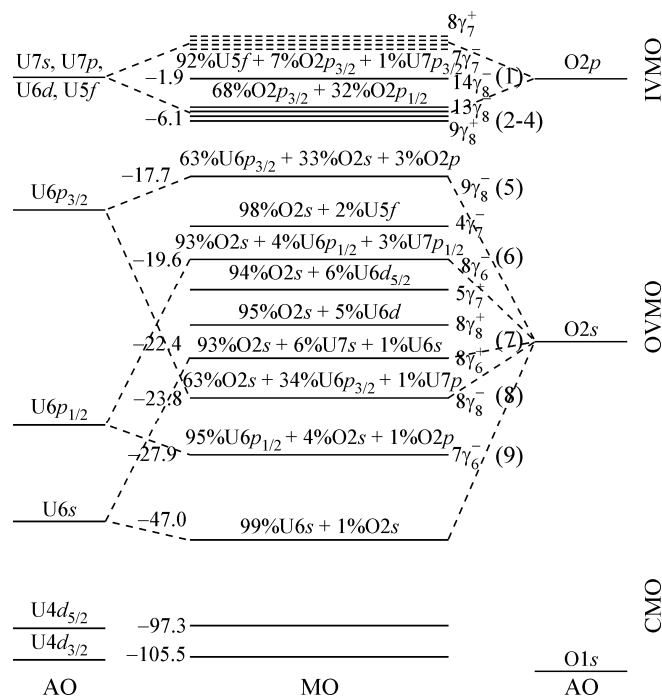


Fig. 2. Quantitative scheme of MOs, U5d and O1s levels for UO_2 . On the left the experimental binding energies are given (in eV) of MO and OMO electrons (Fig. 1 and [2]).

beam current. The C1s electron spectra of hydrocarbons on the sample surface were obtained at an SR excitation energy of 320.0 eV, whose value was taken to be 285.0 eV and used in the calibration of the emission spectra of valence electrons.

The XPS spectra of the UO_2 ($\text{UO}_{2.06}$) uranium oxide sample formed on the surface of uranium metal plate, which was mechanically cleaned as in the preparation of the UO_2 sample for the measurement of resonant spectra, were obtained on an MK II VG Scientific electrostatic spectrometer with the use of AlK_{α} -X-ray radiation in a vacuum of $1.3 \cdot 10^{-7}$ Pa at room temperature. Binding energies E_b (eV) are given with respect to the binding energy of the C1s electrons of hydrocarbons on the sample surface, which was taken to be 285.0 eV. An error in the determination of the electron binding energies and the line half-widths does not exceed 0.1 eV, and that of relative line intensities is below 10%. The characteristics of these XPS spectra did not differ within the measurement error from the corresponding values for the spectrum of a bulk powder-like sample of the dioxide [2], which confirmed the formation of this oxide on the surface of the uranium metal plate. The spectral background due to elastically scattered electrons was subtracted for the XPS spectra by the Shirley method [11].

RESULTS AND DISCUSSION

Before the measurement of the resonant emission spectra of the valence electrons of uranium dioxide formed on the surface of the metallic plate, the stoichiometric composition of this surface was analyzed using XPS. The XPS spectrum of the valence electrons of uranium dioxide formed on the surface of metallic uranium in the binding energy range from 0 to ~35 eV can be conventionally divided into two parts related to the electronic structure of OVMOs from 0 до ~13 eV and IVMOs from ~13 eV to ~35 eV (Fig. 1). The structure of this spectrum can be interpreted based on the quantitative scheme of MOs (Fig. 2, [2]). In the first part of the spectrum of UO_2 , a narrow peak is observed at $E_b = 1.9$ eV, which corresponds to U5f electrons not involved in chemical bonding, and the structure due to OVMO electrons, which is mainly formed by incompletely occupied U5f,6d,7s,7p and O2p AOs of the neighboring uranium and oxygen atoms. The IVMOs are mostly formed by U6p and O2s AOs (Fig. 2).

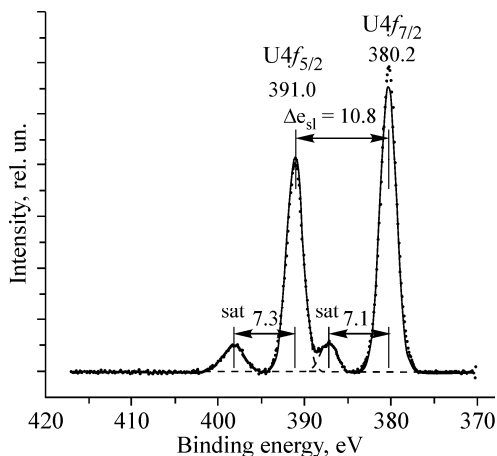


Fig. 3. X-ray electron spectrum of U4f electrons of UO₂.

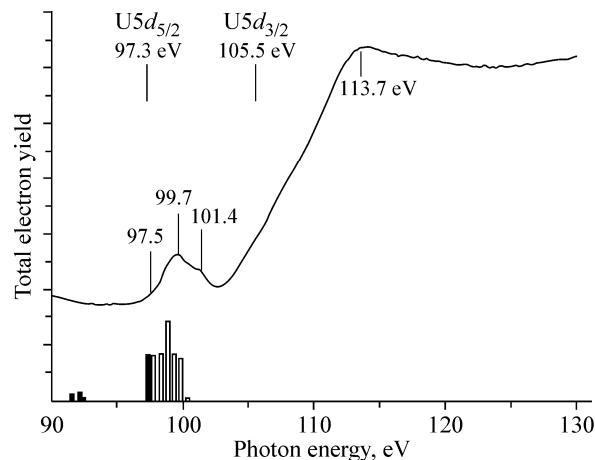


Fig. 4. Total quantum yield spectrum of electrons for UO₂. Above the spectrum the binding energies of U5d_{5/2,3/2} electrons in UO₂ are given. Under the spectrum in the form of dashed the density of occupied (black) and unoccupied (white) states of U5f electrons for the UO₂ ground state (see the MO scheme in Fig. 2) is given.

The XPS spectrum of the inner U4f electrons of uranium oxide consists of two components of the doublet with the spin-orbital splitting $\Delta E_{sl} = 10.8$ eV and shake-up satellites from the side of high binding energies at $\Delta E_{sat} \approx 7.1$ eV from the main peaks of the doublet (Fig. 3). The parameters of the considered spectra, as noted above, are characteristic of uranium dioxide. Based on the peak intensity ratio of U5f and U4f electrons (Figs. 1, 3), $I = 0.0298$, by the previously described procedure [12], the stoichiometric composition of this oxide (UO_{2.063}) and the composition of uranium ions (62% U⁴⁺, 31% U⁵⁺, 7% U⁶⁺) are found. These results are consistent with the data for U_{2.06} oxide studied by XPS in the powder form [13]. For reasons given, we may state that the oxide on the surface of the uranium metal plate is close in composition to UO_{2.06}.

On heating of the sample holder during the achievement of ultrahigh vacuum in the spectrometer it was noticed that the color of the γ -UO₃ sample surface changed from orange-yellow to dark gray. This evidences the removal of oxygen from the sample surface and the formation of UO_{2+x} oxide on it. As a third sample we selected most stable U₃O₈ oxide. Since one of the goals of the work was to establish the dependence of the fine structure of REE spectra on the chemical environment and thus relate it to the formation of IVMOs in the studied oxides, then a change in the composition of the surface in the second sample (γ -UO₃) not principally important. Therefore for comparison with the REE spectra of uranium dioxide we also obtained these spectra for its two other oxides.

X-ray absorption near O_{4,5}(U) edge spectrum of uranium in UO₂ has the structure with two resonance absorption bands of different intensities and widths [14, 15]. It is found [14] that for uranium oxides the absorption spectra and the electron quantum yield spectra are similar in line shape, amount, energy position, and width; they are different only in the intensity ratio of these two peaks (Fig. 4). Since the absorption energy threshold of the low intensity peak is approximately 97.5 eV and is close in value to the binding energy of U5d_{5/2} electrons for UO₂ (97.3 eV), this peak is assigned to the U5d_{5/2} → U5f transition.

In [16], the U5f² (³H₄) → U5d⁹5f³ (³G₃, ³H₄, ³I₅) transition was considered in the ionic approximation for U(IV) and it was found that the low-energy peak mainly reflected U5d_{5/2} → U5f³ transitions, whereas a shoulder at 107 eV was due to U5d_{3/2} → U5f³ transitions. It was assumed here that the main intensity of the high-energy peak can be explained by U5d → U7p,8p and 6f transitions. For a qualitative comparison we give under the spectrum (Fig. 4) the results of the calculation of the density of occupied and unoccupied states of U5f electrons in the ground state of the UO₈¹²⁻ cluster (O_h),

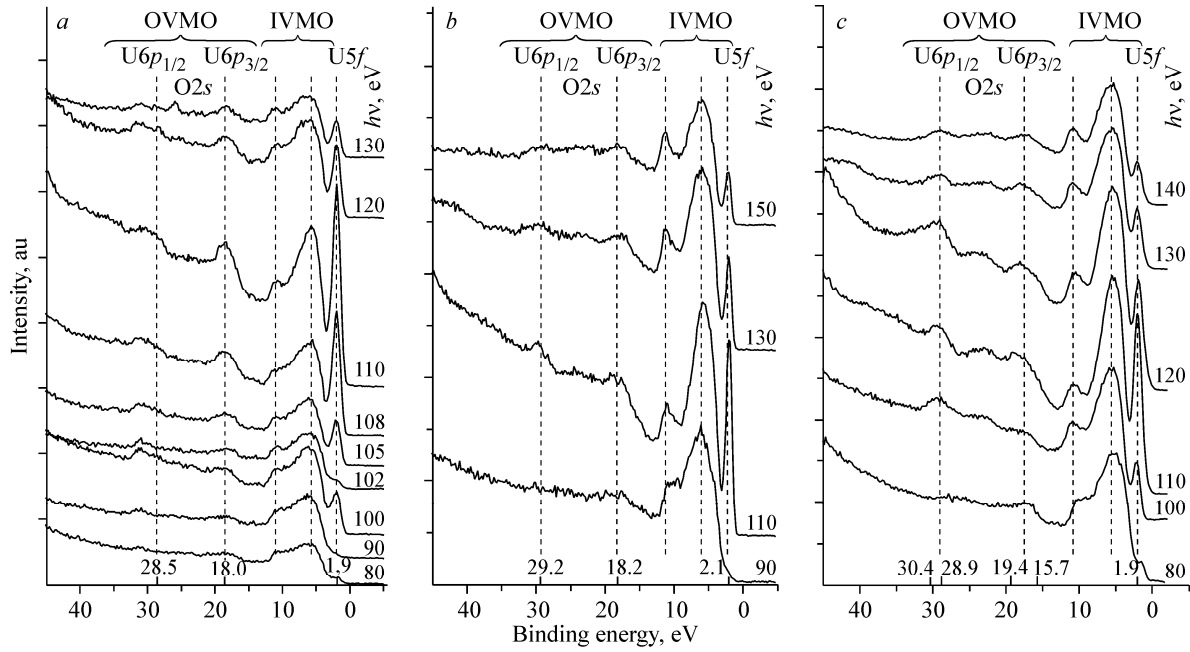


Fig. 5. Resonant electron emission spectra at different SR excitation energies $h\nu$ (eV) near the $O_{4,5}(U)$ absorption edge: (a) UO_2 ; (b) U_3O_8 ; (c) UO_{2+x} .

which reflects the close environment in UO_2 . For comparison the calculated spectrum of the occupied and unoccupied states of $U5f$ electrons is shifted to the right by 1.9 eV so that the binding energy of unbound $U5f$ electrons $E_b(U5f) = 1.9$ eV for UO_2 . Despite that such a comparison has an approximate character, it follows from its results that the low-energy peak seems to be indeed partially due to the unoccupied states of $U5f$ electrons. These data at least do not contradict to the assumption of the direct (without losing the f nature) participation of $U5f$ electrons in chemical bonding. Indeed, if we assume the structure of the X-ray absorption spectrum of UO_2 at ~ 100 eV (Fig. 4) to be associated with the formation of unoccupied antibonding MOs, including $U5f$ AOs, then the corresponding $U5f$ states of bonding OVMOs must be occupied.

Resonant electron emission for UO_2 formed on the surface of uranium metal foil was observed during SR excitation. The SR radiation energy $h\nu$ (eV) changed near the $O_{4,5}(U)$ absorption edge in the energy range $80 \text{ eV} \leq h\nu \leq 130 \text{ eV}$; its values are given on the right from the resonant electron emission (REE) spectra of the studied uranium oxides (Fig. 5). The intensity of the REE spectra was normalized to the SR beam current. In the ordinate scale, one mark is 5000 pulse/50 scan (43 min). These spectra are presented in the electron binding energy scale, in which $E_b(U5f) = 1.9$ eV for UO_2 and $E_b(C1s) = 285.0$ eV for saturated hydrocarbons on the sample surface [2]. In this case, the binding energies of $U5d_{5/2}$ and $U5d_{3/2}$ electrons are 97.3 eV and 105.5 eV respectively (Fig. 4). Under the spectra we give the electron binding energies of some UO_2 IVMOs (Figs. 2 and 5) and γ - UO_3 [1] (Fig. 5c).

At SR excitation energies $h\nu$ of 80 eV and 90 eV (to the resonance region) a hole cannot form on the $U5d$ levels (Fig. 2) and the structure characteristic of an ordinary photoelectron spectrum is observed (Fig. 5). The most intense structure is observed in the OVMO electron binding energy range, which is mostly due to $O2p$ oxygen electrons. Indeed, the photoionization cross-section σ for $O2p$ electrons at $h\nu = 80$ eV is 2.064 Mbarn and substantially exceeds the corresponding values for other valence electrons (Table 1, [17]). Note that there is no correlation between a change in the intensity of the structure of electron resonance emission peaks of the studied uranium oxides and the photoionization cross-sections of different shells with increasing SR excitation energy (Fig. 5 and Table 1).

In the electron binding energy range of $9\gamma_8^-$ (5) and $7\gamma_6^-$ (9) UO_2 IVMOs, a weak structure is observed at 17.7 eV and 27.9 eV, which is due to $U6p$ electrons (Figs. 2 and 5). Since the surface can be contaminated with hydrocarbon

TABLE 1. Energies I_i (eV) and Photoionization Cross-Sections σ (Mb = 10^6 Bar) of Atomic Shells (Anl) at Different Photon Excitation Energies $h\nu$ (eV) [17]

Anl	I_i	$h\nu$				
		40.8	80.0	132.3	151.4	1486.6
${}^6\text{C}1s$	290.9	—	—	—	—	0.13 E-1
$\text{C}2s$	17.5	1.170	0.5440	0.2252	0.1714	0.66 E-1
$\text{C}2p$	9.0	1.875	0.3262	0.78 E-1	0.47 E-1	0.10 E-4
${}^8\text{O}1s$	536.8	—	—	—	—	0.40 E-1
$\text{O}2s$	29.2	0.8342	0.6901	0.3677	0.2984	0.19 E-2
$\text{O}2p$	14.2	6.816	2.064	0.5772	0.4037	0.24 E-3
${}^{92}\text{U}5d$	114.8	—	—	3.267	1.755	0.83 E-1
$\text{U}6s$	40.3	—	0.2051	0.1289	0.1090	0.30 E-2
$\text{U}6p$	26.1	3.032	0.4699	0.2141	0.1817	0.82 E-2
$\text{U}7s$	4.8	0.68 E-1	0.30 E-1	0.16 E-1	0.13 E-1	0.35 E-3
$\text{U}6d$	6.1	0.6794	0.71 E-1	0.10 E-1	0.75 E-2	0.74 E-3
$\text{U}5f$	16.1	6.047	5.774	0.7824	0.3122	0.13 E-1

molecules that contain carbon and oxygen, this can substantially lower the intensity of the spectrum of $\text{U}6p$ electrons in this region.

Since for uranium the relationship $E_b(\text{U}6s) \approx E_b(\text{U}6p_{1/2}) + E_b(\text{U}6p_{3/2})$ is approximately satisfied, then during the photoemission of the $\text{U}6s$ electron the appearance of an additional two-hole (two holes at the $\text{U}6p$ level) final state together with the final ground state is highly probable, which should result in a complex structure of the $\text{U}6s$ photoelectron spectrum [13]. This is related to giant Coster–Kronig transitions accompanying $\text{U}6s$ photoemission. Since the transition occurs mainly between the shells with an identical quantum number, then the intensity of this transition can be higher than the intensity of other transitions.

Since the transitions involve the electrons localized at uranium atoms, then instead of IVMOs the valence electron configuration of the ground state of uranium in UO_2 can be conventionally written in atomic designations (1)

$$\text{U}(\text{OVMO})^k (\text{IVMO})^m 5f^2 \approx \text{U}(6s^2 6p_{1/2}^2 6p_{3/2}^4) (\text{IVMO})^m 5f^2. \quad (1)$$

Under the radiation effect $h\nu$ several final states can form as a result of the photoemission of $\text{U}6s$ electrons: one-hole ground (2) and two-hole additional (3) states

$$\text{U}(6s^2 6p_{1/2}^2 6p_{3/2}^4) (\text{IVMO})^m 5f^2 + h\nu \rightarrow \text{U}(6s^1 6p_{1/2}^2 6p_{3/2}^4) (\text{IVMO})^m 5f^2 + e, \quad (2)$$

$$\rightarrow \text{U}(6s^2 6p_{1/2}^1 6p_{3/2}^3) (\text{IVMO})^m 5f^2 + e, \quad (3)$$

where $\text{U}5f^2$ are the states of weakly bound $\text{U}5f$ electrons; e is the ejected photoelectron.

The appearance of additional final state (3), as noted above, results in a complex structure of the XPS spectrum of $\text{U}6s$ electrons. This accounts for the appearance of the structure in the range of the binding energies of $\text{U}6s$ electrons, which leads to an increase in the intensity at 45 eV during resonance (Fig. 5). The resonance occurs when the SR energy $h\nu$ is equal to the binding energy of $\text{U}5d$ electrons (Fig. 2). In this case, holes in the $\text{U}5d$ shell effectively form and gigantic Coster–Kronig transitions, in which both $\text{U}5d$ and valence shells participate, occur with high probability, parallel to the electron photoemission process (Fig. 2). Consequently, an intense structure appears in the spectra (Fig. 5).

Thus, for uranium the equality $E_b(\text{U}5d_{5/2}) \approx 2E_b(\text{U}6s)$ is also approximately satisfied. During $\text{U}5d_{5/2}$ photoemission this gives rise to two-hole final state (5), additional to ground final state (4)

$$\text{U}5d_{5/2}^6 (6s^2 6p_{1/2}^2 6p_{3/2}^4) (\text{IVMO})^m 5f^2 + h\nu \rightarrow \text{U}5d_{5/2}^6 (6s^2 6p_{1/2}^2 6p_{3/2}^4) (\text{IVMO})^m 5f^2 + e, \quad (4)$$

$$\rightarrow \text{U}5d_{5/2}^6 (6s^0 6p_{1/2}^2 6p_{3/2}^4) (\text{IVMO})^m 5f^2 + e. \quad (5)$$

The appearance of such an additional state (5) during $U5d_{5/2}$ photoemission is due to Coster–Kronig transitions and results in a complex structure in the $U5d$ electron spectral region. During resonance the probability of state (5) can increase, while state (5) itself passes into (3) and leads to an increase in the intensity in the $U6s$ electron spectral region.

At the photon energy $h\nu = 100$ eV near the first resonance (Figs. 4 and 5) a noticeable increase in the intensity is observed in the region of weakly bound $U5f$ electrons, OVMO electrons, and maxima at 18.0 eV and 28.5 eV in the electron binding energy range of $9\gamma_8^-$ (5) and $7\gamma_6^-$ (9) IVMOs (Fig. 5). As the excitation energy increases to $h\nu = 102$ eV, the intensity of the considered peaks drops and the structure is observed which is comparable with the structure of the spectra from the pre-resonance region of excitation ($h\nu = 80$ eV, 90 eV). As the excitation energy increases to $h\nu = 110$ eV, which is close to the second resonance energy (Fig. 4), in the REE spectrum of UO_2 an increase in the intensity of this structure is again observed, apart from the maximum at 10.8 eV. In this case, a significant increase in the spectral intensity is observed in the OVMO and IVMO binding energy range.

As already noted, the IVMO electron configuration of the uranium ground state with regard to the $U5d$ electron states in UO_2 can be written in atomic designations

$$U5d^{10}(OVMO)^k(IVMO)^m5f^2 \approx U5d^{10}(6s^26p_{1/2}^26p_{3/2}^4)(IVMO)^m5f^2. \quad (6)$$

It should be noted that near the unoccupied states of $U5f$ electrons there are the unoccupied states of $U7p$ electrons (Fig. 2 [2]) that with lower probability can participate in the considered transitions.

At resonance absorption a virtually excited state with a hole in the $U5d$ shell and three $U5f$ electrons appears

$$U5d^{10}(6s^26p_{1/2}^26p_{3/2}^4)(IVMO)^m5f^2 + h\nu \rightarrow U5d^9(6s^26p_{1/2}^26p_{3/2}^4)(IVMO)^m5f^3, \quad (7)$$

which because of the Coulomb interaction (e^2/r) of the hole with electrons can decay in different ways (8)-(11)

$$U5d^9(6s^26p_{1/2}^26p_{3/2}^4)(IVMO)^m5f^2 + (e^2/r) \rightarrow U5d^{10}(6s^26p_{1/2}^26p_{3/2}^4)(IVMO)^{m-1}5f^2 + e, \quad (8)$$

$$\rightarrow U5d^{10}(6s^26p_{1/2}^16p_{3/2}^4)(IVMO)^m5f^2 + e, \quad (9)$$

$$\rightarrow U5d^{10}(6s^26p_{1/2}^26p_{3/2}^3)(IVMO)^m5f^2 + e, \quad (10)$$

$$\rightarrow U5d^{10}(6s^16p_{1/2}^26p_{3/2}^4)(IVMO)^m5f^2 + e. \quad (11)$$

The appearance of state (8) gives rise to an increase in the intensity of the OVMO electron bands; of state (9) to an increase in the intensity of the $U6p_{1/2}$ electron peak that emerges as the excitation energy approaches the first resonance at $h\nu = 100$ eV; of state (10) to the appearance of the maximum of $U6p_{3/2}$ electrons; and of state (11) to an increase in the intensity of the $U6s$ electron spectrum at the resonant SR radiation absorption (Fig. 5).

Expressions (7)-(11) describe the resonant formation of a hole at the $U5d$ level (7) and then relaxation of the system through gigantic Coster–Kronig transitions (8)-(11). These processes can be considered as quasi-Auger transitions. Note that parallel to these transitions regular photoelectron emission occurs. Since the considered spectra are less determined by photoelectrons and more by quasi-Auger electrons during resonance, then these spectra should reflect the partial density of states of Unp and $U5f$ electrons. The observed smearing of the structure in the range from ~13 eV to ~35 eV seems to be due to the formation of IVMOs in these compounds.

Since during resonance the largest changes in the intensity of different parts of the spectrum should be expected for the lines corresponding to $U5f, 6p$ electrons, then four qualitative conclusions follow from the obtained data. The first is that the peak in the REE spectrum of UO_2 at 1.9 eV is due to weakly bound $U5f$ electrons. The second is that $U5f$ electrons directly participate (without losing the f nature) in chemical bonding and are delocalized within OVMOs (in the middle of the band), which results in an increase in the intensity of the OVMO electron spectra during resonance. The third is that $U6d$ electrons are localized near the bottom of the outer valence band and are observed in the REE spectra of UO_2 in the form of a characteristic maximum at 10.8 eV. The fourth is that $U6p$ electrons effectively participate in the formation of IVMOs, which

gives rise to an intense structure in the IVMO region during resonance, and reflects the partial density of states of $U6p$ electrons in this spectral range.

At excitation energies $h\nu$ (120 eV and 130 eV) from the after-resonance region the intensity of the REE structure appeared during resonance considerably decreases, but does not disappear. Here the photoionization cross-sections of the considered shells also substantially decrease (Table 1). Despite this the structure of the considered spectrum in general approaches the structure of the photoelectron spectrum obtained during excitation $h\nu = 80$ eV (Fig. 5). The difference is in that the spectrum obtained at $h\nu = 130$ eV contains the features of the spectral structure appeared during resonance. This is a fundamental experimental result, based on which it is possible to state that in the calculation of atomic shell photoionization cross-sections the effect of resonance on these values should be taken into account.

If the structure of the XRE spectra of UO_2 in the range from ~ 13 eV to ~ 35 eV is due to the formation of IVMOs, then it must depend on the chemical environment of uranium in oxides. This is explained by that U_3O_8 and UO_{2+x} oxides can be approximately considered as a mixture of UO_2 and UO_3 oxides, the structure of the XPS spectrum of OVMO and IVMO $\gamma-UO_3$ electrons substantially differs from the corresponding structure for UO_2 [13]. In the XPS spectrum of $\gamma-UO_3$ valence electrons, the $U5f$ electron peak is absent, and in the binding energy range of $U6p_{3/2}$ electrons, two characteristic components $17\gamma_6^-$ (4) and $11\gamma_7^-$ (5) IVMO for $\gamma-UO_3$ [13] are observed instead of one peak of $9\gamma_8^-$ (5) IVMO electrons for UO_2 .

Therefore, in the present work we attempted to obtain the REE spectrum of $\gamma-UO_3$ to reveal the effect of the chemical environment on the REE structure of the REE spectra of uranium oxides. However, under a high vacuum of the spectrometer ($5 \cdot 10^{-10}$ Torr) oxygen is removed from the sample surface and UO_{2+x} uranium oxide forms on it (Fig. 5c). The color of the sample surface changed from yellow-orange to gray-brown in the spectrometer chamber, which was visually observed. For comparison we studied a sample of a relatively stable phase of U_3O_8 uranium oxide (Fig. 5b). Speaking more strictly, UO_{2+x} and U_3O_8 oxides consist of several phases that can contain uranium of different oxidation states (U(IV), U(V), and U(VI)) on the surface [13]. This should lead to the complexation of the structure of REE spectra of IVMO electrons in these oxides. Indeed, the structure of the REE spectra of oxides depends on the chemical environment (Fig. 5). A decrease in the intensity of the $U5f$ electron peak and an increase in the intensity of the additional maximum at 23 eV in the $O2s$ electron binding energy range (Fig. 5b) are observed with increasing oxidation state of uranium. Similar changes occur also in the spectra of UO_{2+x} oxide (Fig. 5c). The structure at 23 eV in the REE spectrum of UO_{2+x} is observed to a larger extent than in the spectrum of U_3O_8 . This is likely to be due to that the surface of the UO_{2+x} sample contains a larger amount of the phase with U(VI) ions. Even the fact of the appearance of a maximum in the $O2s$ electron binding energy region, whose levels cannot participate in the formation of the structure of the REE spectrum, is consistent with that at this energy the occupied states of $U6p$ electrons are present (Fig. 2). Thus, we have qualitatively confirmed the dependence of the structure of the REE spectra of oxides on the chemical environment and the formation of IVMOs in uranium oxides.

CONCLUSIONS

1. Based on the X-ray $O_{4,5}(U)$ absorption spectrum and a quantitative scheme of UO_2 MOs in the relativistic approximation, we have studied the structure of the emission spectra of valence electrons in the electron binding energy range from 0 to ~ 35 eV for UO_2 , U_3O_8 , and UO_{2+x} oxides, which appears under SR excitation near the $O_{4,5}(U)$ resonant absorption edge at 100 eV and 110 eV.

2. As could be expected, the peak at 1.9 eV in the REE spectra of UO_2 is shown to be due to weakly bound $U5f$ electrons.

3. It is confirmed that $U5f$ electrons directly participate (without losing the *f nature*) in the chemical bonding of uranium oxides and are delocalized within OVMOs (in the middle of the band), which causes an increase in the intensity of the REE spectrum of OVMO electrons during resonances.

4. The U6*d* electrons are found to be localized at the bottom of the outer valence band and are observed in the REE spectra of UO₂ in the form of a characteristic maximum at 10.8 eV.

5. It is confirmed that U6*p* electrons effectively participate in the formation of IVMOs and, probably, OVMOs, which gives rise to a low-intensity structure in the IVMO region, which reflects the partial density of states of U6*p* electrons in this spectral region, during resonances.

6. It is confirmed experimentally that in the calculation of the photoionization cross-sections of atomic shells the resonance effect on these values should be taken into account.

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