Effect of the chemical state of uranium atom on the energy of spin-orbital splitting of its inner orbitals

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Summary. Chemical shifts (ChSh) of nine emission lines of the uranium L-series in uranium oxides UO_{2+x} $(x = 0\text{--}1)$ with respect to UO_2 were studied by using a precise crystal-diffraction X-ray spectrometer. ChSh of $L\alpha_1, \alpha_2$ uranium and thorium lines in solid solutions $yUO_2 \cdot (1-y)ThO_2$ $(y = 0 \div 1)$ were measured with respect to UO_2 and ThO_2, respectively. The changes in energy of spin-orbital splitting (SOS) – $\Delta\delta nl_\pm$ of inner nl-orbitals of the uranium atom were calculated from the data of ChSh of spin-doublet lines. For UO_{2+x} oxides, a linear decrease in $\Delta\delta nl_\pm$ values with increasing degree of uranium oxidation was found. Sign inversion of $\Delta\delta nl_\pm$ for uranium levels was found on passing to solid solutions. No change in the SOS energy of inner thorium levels was detected. The values of $\Delta\delta nl_\pm$ were found to correlate with the experimental values of the effective magnetic moment of uranium in oxides.

On the basis of the comparison of experimental $\Delta\delta nl_\pm$ values with Dirac–Hartree–Fock atomic calculations, it was concluded that the observed variations in $\Delta\delta nl_\pm$ values are due to the redistribution of electron and spin density between the $5f_{7/2}$- and $5f_{5/2}$-levels of the fine structure of the uranium atom without changes in atomic charge state. On the basis of the hypothesis of intraatomic relativistic $U\,5f_{7/2} \leftrightarrow U\,5f_{5/2}$ transition, a model of paramagnetic moment formation on the uranium atom in uranium dioxide was proposed.

1. Introduction

The chemistry of heavy element atoms was the subject of many theoretical and experimental studies in the past decades. In fundamental reviews by Pyykkö and Desclaux [1] and Pitzer [2], it is noted that the most outstanding chemical behavior anomalies of compounds of heavy atoms are due to relativistic effects (RE). The RE in chemical term is understood as all effects in the electron structure of an atom which appears passing to the finite value of the velocity of light $c = 137.0359895(61)$ a.u.[1] as compared to $c = \infty$ [3]. In chemistry, three main REs are usually considered:

1. Direct RE of contraction and energetic stabilization of $s_{1/2}$- and $p_{1/2}$-atomic orbitals (AOs).
2. Indirect RE of self-consistent expansion and energetic destabilization of d- and f-AOs.
3. Effect of spin-orbital splitting (SOS) of AOs having a non-zero orbital angular momentum l into two subshells nl_+ and nl_- with total angular momentum $j = l \pm 1/2$, respectively.

For the case of uranium valence orbitals, these effects are schematically shown in Fig. 1.

With increasing atomic number Z, the relativistic component of total energy increases proportionally to Z^n $(n > 1)$. The SOS energy of valence orbitals is proportional to Z^4 and in the case of light actinides according to the data of atomic calculations in the Dirac–Hartree–Fock (DHF) approximation, it is several electron-volts (eV, $1 \text{ eV} \approx 1.60 \times 10^{-19}$ J). In other words, it is comparable to chemical bond energy. Hence, there are prerequisites for the relatively independent participation in chemical bonding of wave functions corresponding to split $nl_\pm$ valence levels [4]. However, at present the question whether it is necessary to take into account RE (in particular the effect of SOS of valence orbitals) in modeling the chemical bonding of light actinide atoms is still unsolved [5–7]. This is mainly caused by the lack of experimental data on the basis of which qualitative and quantitative evaluation could be made about the participation of valence levels of the fine structure of the heavy atom in the process of chemical bonding.
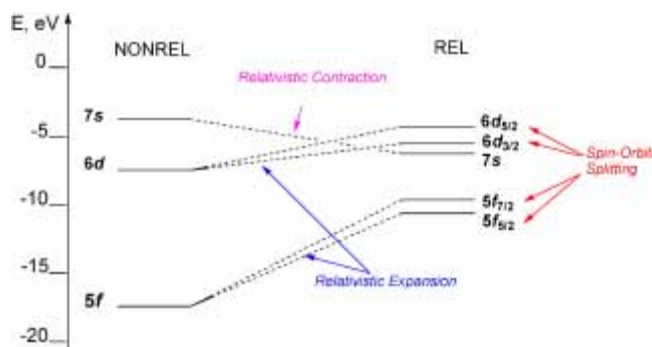

Fig. 1. Nonrelativistic (HF) an relativistic (DHF) valence levels (orbitals) of the uranium atom.

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[1] Atomic units, the system of units where $e \equiv m_e \equiv \hbar \equiv 1$.

In the case of the uranium atom, the problem of the degree of participation of $5f$-electrons in chemical bonding is also unsolved [7, 8]. In X-ray photoelectron spectra (XPS), a regularly decreasing intensity of the narrow line of $5f$-electrons (with an energy $E_b = 2.0 \pm 0.1$ eV) is observed in a series of UO_{2+x} oxides with increasing x [9–11]. The explanations of this phenomenon are very contradictory [9–13]. This is probably due to insufficient XPS sensitivity to fine energetic changes of the atomic electron structure (state). It is known that the error in the determination of the binding energy of electrons and of the line width in the XPS method is about 100 meV and that in the determination of relative line intensity is 10% [9].

A possibility to introduce clarity into these problems is to use the method of chemical shift (ChSh) of hard X-ray emission lines. ChSh is defined as a change in the energy of an X-ray emission line due to modification of bonds of the atom. This method gives information about the chemical state of the atom in the sample. The aim of our work is to search for an experimental parameter making it possible to characterize the chemical effects of SOS of valence orbitals in the uranium atoms.

2. Experimental

Twenty-one samples were measured, which were uranium oxides, uranium-thorium solid solutions, and uranyl compounds, as listed in Table 1. The structure of the samples was confirmed by our X-ray powder diagram investigations.

Chemical shifts were measured for:

a) Nine lines (composing two multiplets: $2p$-$3d$ and $2p$-$4d$, two doublets: $2s$-$3p$ and $2s$-$4p$) of the L-uranium series for uranium oxides UO_{2+x} ($x = 0$–1) with respect to UO_2 (Table 2).

b) $L\alpha_1, \alpha_2$-uranium and thorium lines for solid solutions $yUO_2 \cdot (1-y)ThO_2$ ($y = 0 \div 1$) with respect to UO_2 and ThO_2, respectively (Table 3).

c) $L\alpha_1, \alpha_2$- uranium lines for uranyl compounds: $UO_2(NO_3)_2 \cdot 2H_2O$, $UO_2(NO_3)_2 \cdot 6H_2O$, UO_2SO_4, $UO_2SO_4 \cdot 2.5H_2O$, UO_2SeO_4 and $UO_2SeO_4 \cdot 2.5H_2O$ with respect to UO_2 (Table 4).

Chemical shifts in X-ray emission lines of the L-series of uranium were measured with a 2-meter crystal-diffraction spectrometer of Sumbaev's construction [27, 28] with focus-

Table 1. The characterization of measured samples.

Compound	Crystal structure	Provided by	Synthesis references
$UO_{2.02}$	fluorite type, cubic UO_2	St. Petersburg University, Dept. of Radiochemistry	[14][a]
$ThO_{2.0}$	fluorite type, cubic ThO_2	Commercial	
U_4O_9 ($UO_{2.25}$)	fluorite type, cubic U_4O_9	V.G. Khlopin Radium Institute, St. Petersburg	[15, 16]
U_2O_5 ($UO_{2.50}$)	hexagonal U_2O_5	V.G. Khlopin Radium Institute, St. Petersburg	[17]
U_3O_8 ($UO_{2.67}$)	orthorhombic α-U_3O_8	St. Petersburg University, Dept. of Radiochemistry	[18]
$UO_{3.0}$	orthorhombic γ-UO_3	St. Petersburg University, Dept. of Radiochemistry	[19, 20]
$yUO_2 \cdot (1-y)ThO_2$	fluorite type, cubic[b]	St. Petersburg University, Dept. of Radiochemistry	[21, 22]
$UO_2(NO_3)_2 \cdot 6H_2O$	see ref.	St. Petersburg University, Dept. of Radiochemistry	[23]
$UO_2(NO_3)_2 \cdot 2H_2O$	see ref.	St. Petersburg University, Dept. of Radiochemistry	[24]
UO_2SO_4	see ref.	Samara State University, Inorganic Chem. Dept.	[25]
$UO_2SO_4 \cdot 2.5H_2O$	see ref.	Samara State University, Inorganic Chem. Dept.	[25]
UO_2SeO_4	see ref.	Samara State University, Inorganic Chem. Dept.	[25, 26]
$UO_2SeO_4 \cdot 2.5H_2O$	see ref.	Samara State University, Inorganic Chem. Dept.	[25, 26]

a: The reduction of commercial $UO_{2.14}$ with carbon monoxide at 400–500 °C.
b: The solid solutions of $UO_2 \cdot ThO_2$ obey Vegard's law.

Table 2. Chemical shifts (in meV) of the L-uranium series in oxides UO_{2+x}.

Multiplet/Doublet	$2p$-$3d^a$		$2p$-$4d$			$2s$-$3p$		$2s$-$4p$	
Line	$L\alpha_1$	$L\alpha_2$	$L\beta_2$	$L\beta_{15}$	$L\gamma_1$	$L\beta_4$	$L\beta_3$	$L\gamma_3$	$L\gamma_2$
Transition	$3d_+ \to 2p_+$	$3d_- \to 2p_+$	$4d_+ \to 2p_+$	$4d_- \to 2p_+$	$4d_- \to 2p_-$	$3p_- \to 2s$	$3p_+ \to 2s$	$4p_+ \to 2s$	$4p_- \to 2s$
Exp. error	±3	±4	±3	±6	±4	±6	±6	±6	±4
UO₂	0	0	0	0	0	0	0	0	0
U₄O₉	−51	3	−37	−8	−23	−7	−118	n/m	n/m
U₂O₅	−101	+19	−67	−10	−34	n/m^b	n/m	n/m	n/m
U₃O₈	−118	+46	−82	+9	−33	−31	−192	n/m	n/m
UO₃	−152	+88	−85	+44	−1	+15	−169	−97	+5

a: $2p$-$3d$ multiplet consists of three lines: $L\alpha_1$, $L\alpha_2$, and $L\beta_1$ ($3d_- \to 2p_-$ transition);
b: Not measured because of low line intensity (50 times lower than the intensity of the most marked U $L\alpha_1$-line).

Table 3. Chemical shifts (δ, in meV) of $L\alpha_1$- and $L\alpha_2$-lines of uranium and thorium and changes in SOS energy ($\Delta\delta 3d_\pm$, in meV) of $3d$-orbital of uranium and thorium in solid solutions yUO₂·$(1-y)$ThO₂.

Composition	δ U $L\alpha_1$	δ U $L\alpha_2$	$\Delta\delta$ U $3d_\pm$	δ Th $L\alpha_1$	δ Th $L\alpha_2$	$\Delta\delta$ Th $3d_\pm$
Exp. error	±3	±5	±6	±3	±5	±6
UO₂	0	0	0	–	–	–
0.9UO₂-0.1ThO₂	+2	+4	−2	−30	−33	+3
0.85UO₂-0.15ThO₂	−2	−3	+1	−29	−30	+1
0.8UO₂-0.2ThO₂	2	−9	+11	−23	−29	+5
0.7UO₂-0.3ThO₂	8	−5	+13	−13	−27	+14
0.5UO₂-0.5ThO₂	6	−12	+18	−5	−13	+8
0.3UO₂-0.7ThO₂	3	−27	+30	−3	−12	+9
0.2UO₂-0.8ThO₂	8	−24	+32	−5	−10	+5
0.15UO₂-0.85ThO₂	14	−28	+42	−3	−8	+5
0.1UO₂-0.9ThO₂	18	−39	+57	+1	−2	+3
ThO₂	–	–	–	0	0	0

Table 4. Chemical shifts (δ, in meV) of $L\alpha_1$- and $L\alpha_2$-uranium lines and changes in SOS energy ($\Delta\delta 3d_\pm$, in meV) of $3d$-uranium orbital in uranyl compounds.

Compound	δ U $L\alpha_1$	δ U $L\alpha_2$	$\Delta\delta$ U $3d_\pm$
Exp. error	±3	±5	±6
UO₂	0	0	0
UO₂(NO₃)₂·6H₂O	−153	+116	−269
UO₂(NO₃)₂·2H₂O	−139	+101	−240
UO₂SO₄	−139	+125	−264
UO₂SO₄·2.5H₂O	−151	+108	−259
UO₂SeO₄	−131	+131	−262
UO₂SeO₄·2.5H₂O	−134	+119	−253
UO₃	−152	+88	−240

ing according Couchois' technique [29]. A detailed scheme of the instrument is shown in Fig. 2.

A 0.3 mm thick quartz crystal curved in the shape of a part of the cylinder with a 2000 mm radius was used as a monochromator. Adjustment to a certain line with a wavelength λ was done with the aid of a theodolit (3) by counting the required angle θ according to the Wulf–Braggs' equation:

$$n\lambda = 2d \sin\theta, \qquad (1)$$

where n is the reflection order ($n = 1$), d is the interplanar spacing of the reflecting surfaces of the monochromator ($d = 1.81674$ Å), and θ is the diffraction angle.
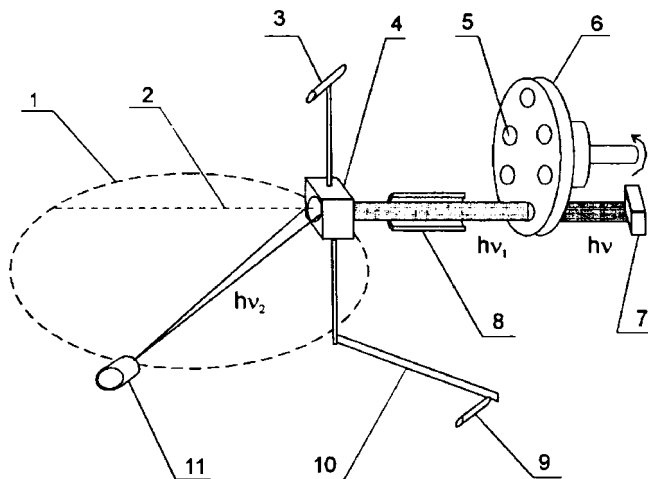
Fig. 2. Scheme of X-ray spectrometer: 1. a focal point; 2. mirror-equivalence position; 3. optical angle meter; 4. quartz monochromator; 5. sample; 6. rotating cassette; 7. Roentgen tube; 8. collimator; 9. step-motor-driven micrometer; 10. the lever; 11. scintillation detector.

Each sample was powdered, mixed with polystyrene powder and pressed into a tablet, 20 mm in diameter. The tablet was then placed in a metal holder and mounted in a special rotating cassette (6), which can carry six such samples (5). Fluorescent (secondary) X-ray emission $h\nu_1$ of samples was excited by a combination of bremsstrahlung and characteristic (primary) radiations $h\nu$ emitted by a vanadium anode of the Roentgen tube (7) operating at 46 kV

and 44 mA. After collimation (8), the radiation was decomposed with a quartz monochromator (4), adjusted to the selected X-ray line, and was recorded with the aid of a scintillation detector (11) on the basis of a NaI(Tl) crystal.

Preliminary adjustment to the appropriate X-ray emission line was carried out with the help of optical angle meter (3). Line scanning was carried out discretely (18–32 points per line) with different pitch for each line by a turning monochromator on 2–10 angle seconds with a step-motor-driven micrometer (9). Line intensity measurements at each point were carried out successively for all samples by their successive introduction into the primary beam. To compensate for optical aberration effects and the effects of external factors, the experiment was repeated many times. The obtained results were averaged.

The mathematical processing of the spectra (determination of the position of the line maximum and of its natural width) included the approximation of experimental data by the convolution of the Lorentzian function describing the true form of the X-ray line and the Gaussian function describing the widening of this line due to the mosaic (block) structure of the monochromator [30, 31].

The absolute error in the determination of the line shift attains 1 meV, and the relative precision in its determination is $\frac{\sigma E}{E} \approx 10^{-8}$ (where σE is the mean-square error in the determination of line energy E). The spectrometer resolution calculated by using the $K\alpha_1$-line of tin as the ratio of experimentally observed width of the emission line at half-height Γ to its energy is 10^{-5}. We emphasize this point because the photon energy region between 10 and 20 keV is rather unfavorable for crystal diffractometry measurements and the lack of accurate experimental data concerning L X-rays of heavy elements results.

3. Results and discussion

A physical value that should be chosen as the parameter making it possible to judge about the participation of split components of uranium valence orbitals in chemical bonding must provides information about changes in the SOS energy of the inner nl-orbital when the chemical state of the atom is varied [32]. It can be easily shown that this parameter is the difference ($\Delta\delta nl_\pm$) in the ChSh (δ) of spin-doublet lines having one common level. For instance, such a level for U $L\alpha_1$- and U $L\alpha_2$-lines is the $2p_+$-level. Then the difference in chemical shifts with respect to reference sample is

$$\delta L\alpha_1 - \delta L\alpha_2 =$$
$$\left\{ [E(2p_+) - E(3d_+)]^{\text{object}} - [E(2p_+) - E(3d_+)]^{\text{reference}} \right\}$$
$$- \left\{ [E(2p_+) - E(3d_-)]^{\text{object}} - [E(2p_+) - E(3d_-)]^{\text{reference}} \right\}$$
$$= [\varepsilon(3d_+) - \varepsilon(3d_-)]^{\text{object}} - [\varepsilon(3d_+) - \varepsilon(3d_-)]^{\text{reference}}$$
$$\equiv \Delta\delta 3d_\pm , \qquad (2)$$

where $E(nlj)$ is the total energy of an atom with a vacancy on the inner nlj-shell, and $\varepsilon(nlj)$ is the bonding energy of the inner nlj-electron. Hence, if the ChSh of spin-doublet lines for various uranium compounds are known it is possible to calculate the change in the SOS energy ($\Delta\delta nl_\pm$) of inner nl-levels and to draw generalizing conclusions about RE of SOS.
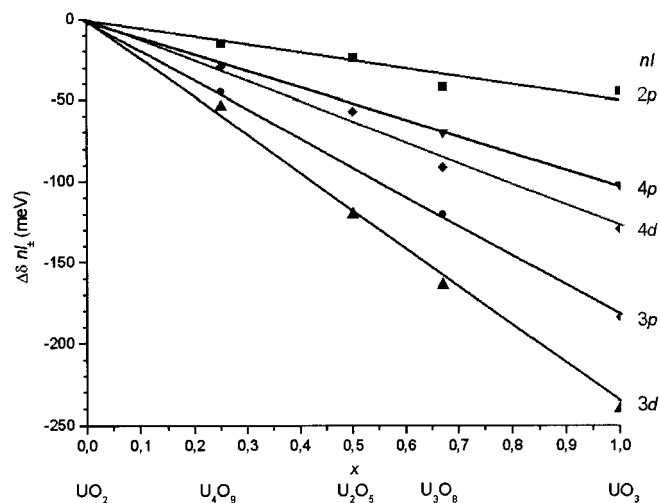

Fig. 3. Changes in SOS energy of inner uranium nl-orbitals $\Delta\delta nl_\pm$ (respect to UO$_2$) in oxides UO$_{2+x}$ *vs.* x.

It is necessary to study first the behavior of the parameter $\Delta\delta nl_\pm$ depending on the *redox state* of the atom. For this purpose, on the basis of the measured values of ChSh (with respect to UO$_2$) of spin-doublet lines (Table 2) the changes of the SOS energy of inner $2p$-, $3p$-, $3d$-, $4p$- and $4d$-orbitals of uranium were obtained (Table 5) in a series of oxides with the composition of UO$_{2+x}$ ($x = 0$–1). It is evident that with changing index at oxygen x a whole set of uranium atom characteristics also changes: partial charge on this atom as well as *magnetic state* and *valence state* from U(IV) in UO$_2$ to U(VI) in UO$_3$.

Fig. 3 shows the linear character of the dependence of the parameter $\Delta\delta nl_\pm$ on x for all inner uranium AOs. With increasing degree of uranium oxidation, a monotonic decrease in the SOS of all inner uranium orbitals is observed. Therefore, a conclusion can be drawn that the effect of processes in the valence shell at the atom on the change in the SOS energy of core AOs is of a monotonic character. The fact that the inner uranium levels respond linearly to changes in the chemical state of the atom (*i.e.* in the perturbation of the valence shell of the atom) is not trivial because the potential of inner electrons screening by valence ones is of a more complex character. Moreover, it should be noted that the greatest response (maximal changes in the SOS energy) are observed for the $3d$-uranium orbital. The SOS energy of the U $3d$-orbital in uranium trioxide is almost 250 meV lower than that in uranium dioxide. Therefore, it is the uranium $3d$-orbital that is convenient for studying the effect of the chemical state of the atom on RE of SOS.

To study the behavior of the parameter $\Delta\delta 3d_\pm$ in compounds of the same valency, the ChSh of U $L\alpha_1$-, and U $L\alpha_2$-lines were measured with respect to UO$_2$ for two groups of isovalent compounds:

1) solid solutions yUO$_2 \cdot (1-y)$ThO$_2$ ($y = 0$–1) (Table 3) in which uranium is in the tetravalent state;
2) uranyl compounds UO$_2$(NO$_3$)$_2 \cdot 2$H$_2$O, UO$_2$(NO$_3$)$_2 \cdot$ 6H$_2$O, UO$_2$SO$_4$, UO$_2$SO$_4 \cdot 2.5$H$_2$O, UO$_2$SeO$_4$ and UO$_2$SeO$_4 \cdot 2.5$H$_2$O of hexavalent uranium (Table 4). For solid solutions, ChSh of Th $L\alpha_1$-, and Th $L\alpha_2$-lines with respect to ThO$_2$ have been also obtained.

Table 5. Changes in SOS energy ($\Delta\delta nl_\pm$, in meV) of inner nl-uranium orbitals in oxides UO_{2+x}.

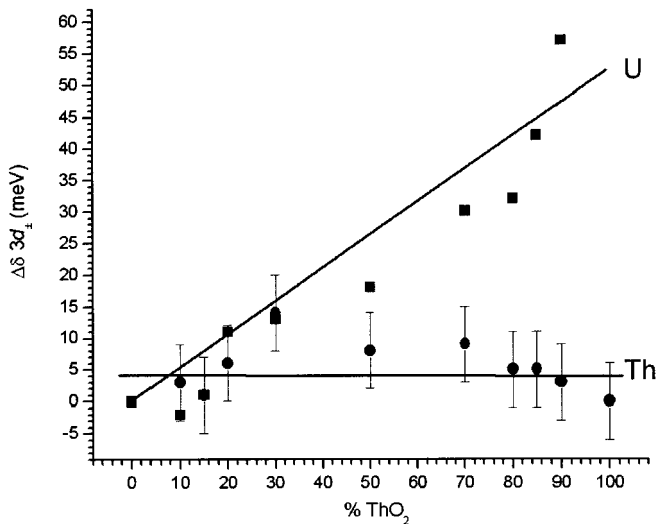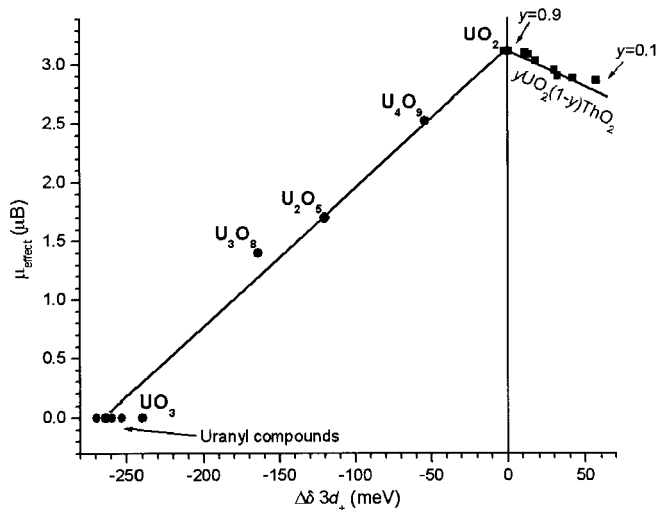| nl	Formula	$\Delta\delta nl_\pm$					
		UO_2	U_4O_9	U_2O_5	U_3O_8	UO_3	Error
$2p$	$\Delta\delta 2p_\pm = \delta L\beta_{15} - \delta L\gamma_1$	0	−15	−24	−42	−45	±5
$3p$	$\Delta\delta 3p_\pm = \delta L\beta_3 - \delta L\beta_4$	0	−45	n/m^a	−120	−184	±8
$3d$	$\Delta\delta 3d_\pm = \delta L\alpha_1 - \delta L\alpha_2$	0	−54	−120	−164	−240	±5
$4p$	$\Delta\delta 4p_\pm = \delta L\gamma_3 - \delta L\gamma_2$	0	n/m	n/m	−70	−102	±7
$4d$	$\Delta\delta 4d_\pm = \delta L\beta_2 - \delta L\beta_{15}$	0	−29	−57	−91	−129	±7

a: Not measured.

Fig. 4. Changes in SOS energy of $3d$-orbitals $\Delta\delta 3d_\pm$ of uranium (respect to UO_2) and thorium (respect to ThO_2) *vs.* composition of solid solution $yUO_2 \cdot (1-y)ThO_2$.

Fig. 5. Correlation of experimental values [21, 33] of effective magnetic moment on uranium atom (μ_{effect}) with the value of changes in SOS energy of uranium $3d$-orbitals ($\Delta\delta 3d_\pm$).

Fig. 4 shows the dependence of changes in the SOS energy of U $3d$- and Th $3d$-orbitals on the composition (y) of the solid solution $yUO_2 \cdot (1-y)ThO_2$. With increasing content of thorium dioxide in solid solution, the energy difference between the split components ($\pm$) of the uranium $3d$-orbital increases. This is probably due to the dilution of the paramagnetic matrix of uranium dioxide by diamagnetic thorium dioxide. The fact that such changes are not observed in the thorium system confirms the above suggestion about the effect of paramagnetic properties of UO_2.

Table 4 gives the ChSh of $L\alpha_1$-, and U $L\alpha_2$-lines with respect to UO_2, and $\Delta\delta 3d_\pm$ values calculated from their basis for diamagnetic uranyl compounds. It is quite clear that ChSh values for the compounds with uranyl group vary over a wide range. However, their differences ($\Delta\delta 3d_\pm$ values) are in a narrow range $(240-270) \pm 6$ meV. It can be suggested that this is caused by the uranyl structure of these compounds. Slight variation in the SOS energy is due to effect of ligands of the second coordination sphere. It should be noted that the observed effect, the constant value of $\Delta\delta 3d_\pm$ can serve as a distinguishing feature of uranyl compounds.

From the viewpoint of the role of the uranium atom *magnetic state* in chemical bonding effects it is of interest to examine the dependence of SOS energy of U $3d$-orbitals on the effective magnetic moment on the uranium atom (μ_{effect}). Fig. 5 shows the correlation of the $\Delta\delta 3d_\pm$ with experimental values of μ_{effect} taken from Refs. [21, 22, 33]. In a system of coordinates $\mu_{effect} - \Delta\delta 3d_\pm$, uranium oxides UO_{2+x} and solid

solutions $yUO_2 \cdot (1-y)ThO_2$ are located on straight lines corresponding to different linear functions. This indicates that the formation mechanisms of magnetic properties in these two systems differ greatly. Uranyl compounds are localized on the abscissa ($\mu_{effect} = 0$), as has been shown above, in a narrow range of $\Delta\delta 3d_\pm$ values. This correlation can be used for evaluating the uranium atom magnetic state in the investigated compound.

The above facts show that RE of SOS of inner atomic orbital levels directly depend on the uranium *magnetic state* which is determined by the state of valence shell of the atom.

This conclusion is confirmed by the data of isotopic effects [34, 35] in twosomes $^{233}U-^{238}U$ and $^{235}U-^{238}U$ for the compounds: U_3O_8, UO_2 and $Cs[UO_2(NO_3)_2]$. The value of $\Delta\delta nl_\pm$ ($nl = 2p$, $3p$, $3d$, and $4p$) for chemically identical compounds with different isotopic composition is lower by one order then in changing the chemical state of the atom (see Table 6). It should be noted that the $^{235}U-^{238}U$ isotopic shifts of $L\beta_3$-, $L\beta_4$-, $L\gamma_2$-, and $L\gamma_3$-lines attain the values of $+250 \pm 20$ meV [35]. Even if relative large errors in the results of measurements of isotopic effects of the parameter $\Delta\delta nl_\pm$ (Table 6) are taken into account, it can be suggested that the change in the SOS energy of inner orbitals of the atom is not greatly affected by changes in the isotopic state of its nucleus.

To determine the effects in the valence region of uranium atom that cause the above chemical response of core AOs, we have carried out theoretical calculations in which the process of chemical bonding was simulated in four ways:

Table 6. Isotopic effects (in meV, respect to ^{238}U) in SOS energy changes of inner nl-uranium orbitals for chemically identical compounds.

nl	$\Delta\delta nl_{\pm}$ (^{233}U$-^{238}$U)				$\Delta\delta nl_{\pm}$ (^{235}U$-^{238}$U)			
	$2p$	$3p$	$3d$	$4p$	$2p$	$3p$	$3d$	$4p$
U$_3$O$_8$	$+10\pm10$	$+34\pm12$	-18 ± 6	$+4\pm10$	-18 ± 8	-22 ± 10	$+2\pm6$	-13 ± 9
UO$_2$	-20 ± 6	$+24\pm12$	$+4\pm6$	$+11\pm9$	-22 ± 4	-12 ± 10	-16 ± 6	$+18\pm16$
Cs[UO$_2$(NO$_3$)$_2$]	$+6\pm21$	$+4\pm14$	-15 ± 8	-9 ± 18	$+15\pm15$	-10 ± 15	-10 ± 8	-39 ± 20

Table 7. Theoretical (DHF) values of changes in SOS energy ($\Delta\delta nl_{\pm}$, in meV) of inner nl-uranium orbitals.

nl	U [Rn] $5f_-^{1.5}5f_+^{1.5}6d_-^{0.5}6d_+^{0.5}7s^2$				U [Rn] $5f_-^{1.5}5f_+^{1.5}6d_-^06d_+^07s^0$		
	NonRel $5f \to \infty$	Rel $5f_+ \to 5f_-$	Rel $5f_+ \to \infty$	Rel $5f_- \to \infty$	Rel[a] $5f_+ \to 5f_-$	Rel $5f_+ \to \infty$	Rel $5f_- \to \infty$
$2p$	$+91$	-5	$+87$	$+93$	-6	$+86$	$+92$
$3p$	$+23$	-156	-52	$+116$	-161	-58	$+115$
$3d$	$+17$	-300	-129	$+196$	-309	-133	$+201$
$4p$	-27	-64	-58	$+11$	-66	-66	$+5$
$4d$	$+20$	-108	-55	$+65$	-111	-58	$+62$

a: Equally to $C^{nl}5f_{\pm}$ coefficients (see text).

1) nonrelativistic removal of one U $5f$-electron (NonRel $5f \to 8$);
2) relativistic removal of one U $5f_{5/2}$-electron (Rel $5f_- \to 8$);
3) relativistic removal of one U $5f_{7/2}$-electron (Rel $5f_+ \to 8$);
4) relativistic transmission of one electron from U $5f_{7/2}$- to U $5f_{5/2}$-orbital (Rel $5f_+ \to 5f_-$).

Table 7 lists the results of our calculation by the Dirac–Hartree–Fock (DHF) method (the applicability of DHF-calculations for the purposes of X-ray emission spectroscopy, in particular, for the chemical shifts method has been shown in Ref. [36]) of changes in SOS energy on inner nl uranium AOs ($nl = 2p$, $3p$, $3d$, $4p$, and $4d$) for the four above transitions from two initial configurations of uranium: neutral atom U [Rn] $5f_-^{1.5}5f_+^{1.5}6d_-^{0.5}6d_+^{0.5}7s^2$ and trivalent ion U [Rn] $5f_-^{1.5}5f_+^{1.5}6d_-^06d_+^07s^0$ into the final configuration:

$$\Delta\delta nl_{\pm} \equiv [E(nl_-) - E(nl_+)]^{\text{final}} - [E(nl_-) - E(nl_+)]^{\text{initial}}, \tag{3}$$

where $E(nlj)$ is the total DHF-energy of an atom with a vacancy on the inner nlj-shell.

The data in this table show that the $\Delta\delta nl_{\pm}$ values almost do not depend on the number of electrons (occupancy) on uranium $6d$- and $7s$-levels. Hence, all energetics of RE of SOS is determined by $5f$-levels.

In Fig. 6 the theoretical $\Delta\delta nl_{\pm}$ values are compared with experimental values of the SOS energy of inner nl-uranium orbitals in UO$_3$ with respect to UO$_2$ (Table 5). For all four theoretical and experimental cases maximum values of $\Delta\delta nl_{\pm}$ are observed on the $3d$-orbital. Only the model of a relativistic electron transition from $5f_{7/2}$- to $5f_{5/2}$-orbital of uranium (Rel $5f_+ \to 5f_-$) describes the experiment satisfactorily. In other words, a conclusion can be drawn that an *intraatomic relativistic* U $5f_+ \to$ U $5f_-$ *transition* is possible. Its analogue is to some extent the nonrelativistic transition Th $6d \to$ Th $5f$ in thorium compounds from which the filling of $5f$-levels in the actinide series starts [37]. The change in the SOS energy of inner AOs is due to electron redistribution between $5f_+$- and $5f_-$-levels of the fine struc-
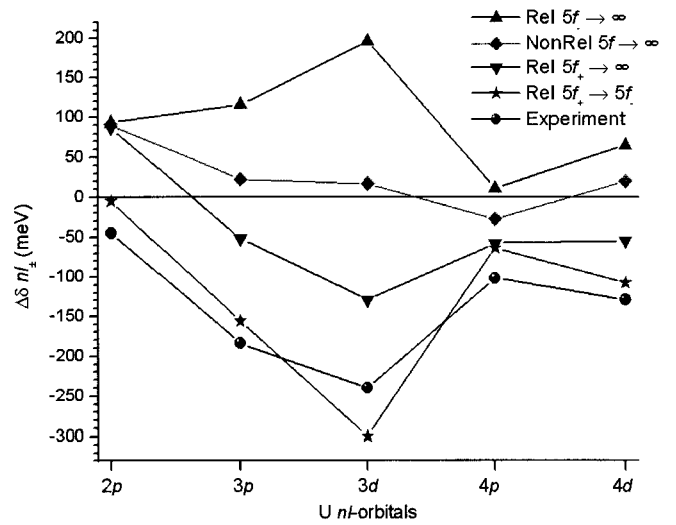
Fig. 6. Experimental and theoretical values of changes in SOS energy of inner uranium nl-orbitals ($\Delta\delta nl_{\pm}$).

ture of the uranium atom without a change in atomic charge state:

$$\Delta\delta nl_{\pm} = Q5f_{\pm} \cdot C^{nl}5f_{\pm}, \tag{4}$$

where $Q5f_{\pm}$ is the number of electrons redistributed between $5f_+$- and $5f_-$-levels of the uranium atom, $C^{nl}5f_{\pm}$ is the change in the SOS energy of the nl-level on transition of one electron $5f_+ \to 5f_-$. Then the appearance of paramagnetic moment on uranium in UO$_2$ from diamagnetic UO$_3$ (the unpaired electron density formation) can be illustrated by the following scheme:

UO$_3$ $5f_+ \to 5f_-$ **UO$_2$**

$5f_+$ ↑↓ $5f_+$ ↑

$5f_-$ ↑↓ $5f_-$ ↑↓ ↑
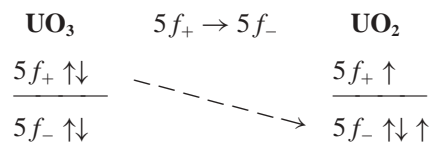
In this case the number of unpaired electrons is $N = 2 \cdot Q5f_{\pm}$. Then it can be written for the spin component of the
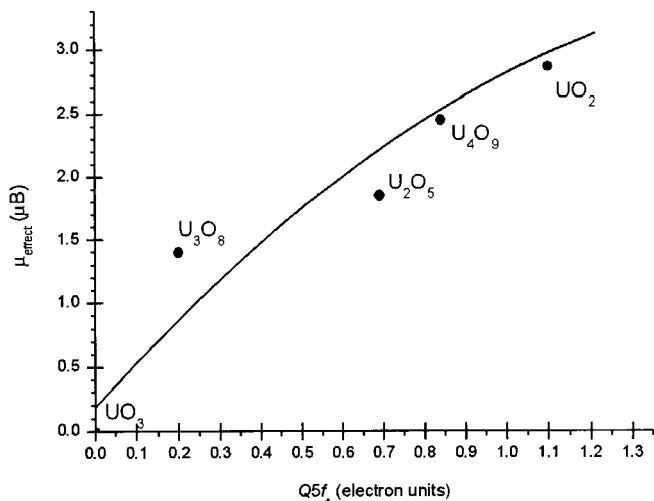
Fig. 7. Correlation of experimental values [21, 33] of effective magnetic moment on uranium atom (μ_{effect}) with the number of electrons ($Q5f_{\pm}$) participating in the redistribution between $5f_{+}$- and $5f_{-}$-uranium orbitals. Line – theoretical function (5), points – experiment.

effective magnetic moment:

$$\mu_{effect}^{s} = [N(N+2)]^{1/2} = 2[Q5f_{\pm}(Q5f_{\pm}+1)]^{1/2}. \quad (5)$$

On the basis of Eq. (4) from experimental values of $\Delta\delta nl_{\pm}$ (see Table 5) and calculated coefficients $C^{nl}5f_{\pm}$ (see Table 7) one can find the number of redistributed electrons $Q5f_{\pm}$ for uranium oxides UO_{2+x} (with respect to UO_{2}). In other words, one can ascribe to each compound in addition to the experimental value of effective magnetic moment on uranium atom μ_{effect} the number of electron $Q5f_{\pm}$ participating in the redistribution between $5f_{+}$- and $5f_{-}$-levels of uranium. In Fig. 7 the theoretical function (5) is compared with the dependence of experimental values [21, 33] of μ_{effect} on the number $Q5f_{\pm}$ for uranium oxides. The correlation between theoretical and experimental dependencies makes it possible to draw the conclusion that suggestion about the mechanism of the appearance of paramagnetic moment on uranium in UO_{2} because of redistribution of $5f$-electrons has a right to existence.

It may be suggested that the intraatomic relativistic $5f_{+} \rightarrow 5f_{-}$ transition is *a fine energetic tuning* to a specific chemical state. As a result of this transition unique chemical properties of uranium atom are probably formed in the uranium-oxygen system [38]: polyvalence of the oxide series, numerous structural modifications, and structural-chemical compromise which consists in the preservation of oxide structure with increasing oxygen content ($UO_{2.00} \rightarrow UO_{2.25}$).

It should be emphasized that these conclusions confirm the theoretical concept of core orbitals [39–41] developing recently. This concept is based on Clausius' virial theorem and reflects a very important role of inner atomic orbitals in chemical bonds formation.

4. Conclusion

On the basis of experiments and calculations, it is possible to draw the conclusion that the SOS effect of inner atomic orbitals strongly depends on the chemical state of the ura-

nium atom. This dependence is a direct consequence of the unique intra-atomic electron redistribution between $5f_{+}$- and $5f_{-}$-split levels of the uranium atom fine structure without changes in atomic charge state.

References

1. Pyykkö, P., Desclaux, J. P.: Relativity and the Periodic System of Elements. Acc. Chem. Res. **12**, 276 (1979).
2. Pitzer, K. S.: Relativistic effects on chemical properties. Acc. Chem. Res. **12**, 271 (1979).
3. Pyykkö, P.: Relativistic effects in structural chemistry. Chem. Rev. **88**, 563 (1988).
4. Schwarz, W. H. E., van Wezenbeek, E. M., Baerends, E. J., Snijders, J. C.: The origin of relativistic effects of atomic orbitals. J. Phys. B.: At. Mol. Opt. Phys. **22**, 1515 (1989).
5. Ionova, G.: Relativistic Effects in Properties of Heavy Elements: Theory and Experiment. In: 5th Intern. Conf. Nucl. Radiochem., Extended Abstracts, Vol. 1. Pontresina, Switzerland (2000) p. 213.
6. Balasubramanian, K.: Relativistic effects and electronic structure of lanthanide and actinide molecules. In: *Handbook of Physics and Chemistry of Rare Earth*. (Gschneidner, K. A., Eyring, L., Choppin, G. R., Lander, G. H., eds.) Elsevier, Amsterdam (1994) Vol. 18, Chapt. 119, p. 29.
7. Schwarz, W. H. E.: The Concept of the Chemical Bond. In: *Theoretical Models of Chemical Bonding*. (Maksic, Z. B., ed.) Springer, Berlin (1990) Vol. 2, p. 593.
8. Pepper, M., Bursten, B. E.: The electronic structure of actinide-containing molecules: a challenge to applied quantum chemistry. Chem. Rev. **91**, 719 (1991).
9. Teterin, Yu. A., Terechov, V. A., Ryzhkov, M. V., Utkin, I. O., Ivanov, K. E., Teterin, A. Yu., Nikitin, A. S.: The role of the U $6p$, $5f$ electrons in chemical bonding of uranil and uranium fluorides: X-ray photoelectron and X-ray emission studies. J. Electron Spectrosc. Relat. Phenom. **114**, 915 (2001).
10. Moser, H. R., Delley, B., Schneider, W. D., Baer, Y.: Characterization of f electrons in light lanthanide and actinide metals by electron-energy-loss and X-ray photoelectron spectroscopy. Phys. Rev. B **29**, 2947 (1984).
11. Veal, B. W., Lam, D. J.: X-ray photoelectron studies of thorium, uranium, and their dioxides. Phys. Rev. B **10**, 4902 (1974).
12. Batrakov, Yu. F., Makarov, L. L.: On the role of $5f$-electrons in the chemical bonding of the light actinides by their L X-ray emission spectra. Vestnik SPbGU. Ser. 4 **4**, 40 (1995).
13. Makarov, L. L.: X-ray emission effects as a tool to study light actinides. Czech. J. Phys. **49**, Suppl. S1, Part 2, 610 (1999).
14. Crosswhite, H. M.: *Gmelin Handbook of Inorganic Chemistry*. 8th edn., Springer, Berlin (1984), Uranium Suppl. Vol. C4 Uranium Dioxide, Sect. 1.2., p. 11.
15. Gronvold, F. J.: High-temperature X-ray study of uranium oxides in the UO_{2}-$U_{3}O_{8}$ region. Inorg. Nucl. Chem. **1**, 357 (1955).
16. Shaner, B. E.: Metallographic determination of the UO_{2}-$U_{4}O_{9}$ phase diagram. J. Nucl. Mater. **2**, 110 (1960).
17. Blinova, N. I., Kurbatov, V. V., Solncev, V. M.: X-ray investigation of the system $U_{3}O_{8}$-$U_{2}O_{5}$. Radiokhimija (Radiochemistry) **6**, 463 (1964).
18. Kovba, L. M.: The rectification of the homogenous regions for $U_{3}O_{8\pm x}$ and $U_{8}O_{21\pm x}$ oxides. Radiokhimija (Radiochemistry) **9**, 134 (1967).
19. Sheft, I., Fried, S., Davidson, N.: Preparation of uranium trioxide. J. Am. Chem. Soc. **72**, 2172 (1950).
20. Hoekstra, H. R., Siegel, S.: The uranium-oxygen system: $U_{3}O_{8}$-UO_{3}. Inorg. Nucl. Chem. **18**, 154 (1961).
21. Trizebiatowski, W., Selwood, P. W.: Magnetic susceptibilities of urania-thoria solid solutions. J. Am. Chem. Soc. **72**, 4504 (1950).

22. Hinatsu, Y., Fujino, T.: Magnetic susceptibilities of UO_2-ThO_2 solid solutions. J. Solid State Chem. **60**, 195 (1985).

23. Vdovenko, V. M., Stroganov, E. V., Sokolov, A. P., Zandin, V. N.: The structure of the uranyl nitrate hexahydrate. Radiokhimija (Radiochemistry) **2**, 24 (1960).

24. Vdovenko, V. M., Stroganov, E. V., Sokolov, A. P.: The structure investigating of the crystals of uranyl nitrate trihydrate and uranyl nitrate dihydrate. Radiokhimija (Radiochemistry) **3**, 19 (1961).

25. Brandenburg, N. P., Loopstra, B. O.: β-uranyl sulphate and uranyl selenate. Acta Cryst. B **34**, 3734 (1978).

26. Serezhkin, V. N., Tabachenko, V. V., Serezhkina, L. B.: Synthesis and investigating of the uranyl selenate. Radiokhimija (Radiochemistry) **20**, 214 (1978).

27. Sumbaev, O. I.: The effect of the chemical shift of the X-ray K lines in heavy atoms. Phys. Lett. A **30**, 129 (1969).

28. Sumbaev, O. I.: *Crystal-diffraction gamma-spectrometers*. Gos AtomIzdat, Moscow (1963) pp. 110–111.

29. Cauchois, Y.: Spectrographie des rayons x par transmission d'un faisceau noncanalise' a travers un cristal courbe' (I). J. Phys. Rad. **3**, 320 (1932).

30. Lee, P. L., Boehm, F., Vogel, P.: Gen. Phys. **9**, 616 (1974).

31. Tupitsyn, I. I., Makarov, L. L., Batrakov, J. F.: Sign of the spin-polarized effects in the chemical shifts of the X-ray Cu $K_{\alpha_{1,2}}$ emission transitions. J. Phys. Chem. Solids **59**, 809 (1998).

32. Batrakov, Yu. F., Krivitsky, A. G., Puchkova, E. V.: Relativistic Effects on Light Actinides Chemical Properties. In: 2nd Russian Youth Science Conference on the Fundamental Problems of Radiochemistry and Atomic Energy. Abstract, N. Novgorod (2002) p. 26.

33. Selwod, P. W.: Bull. Soc. Chim. **D**, 122 (1949).

34. Makarov, L. L., Suglobov, D. N., Batrakov, Yu. F.: The isotope shifts in U L X-ray emission lines. Radiokhimija (Radiochemistry) **38**, 206 (1996).

35. Makarov, L. L., Batrakov, Ju. F., Solomennikov, A. A.: U L X-ray emission isotope effects: 238–235–233. In: 5th Intern. Conf. Nucl. Radiochem., Extended Abstracts, Vol. 1. Pontresina, Switzerland (2000) p. 346.

36. Bratcev, V. F., Deyneka, G. B., Tupitsyn, I. I.: Application of Hartree–Fock method to calculation of relativistic wave functions. Izvestija AN SSSR. Ser. Fizicheskaja **41**, 2656 (1977).

37. Makarov, L. L., Karazija, R. I., Batrakov, Yu. F., Chibisov, N. P., Mosevich, A. N., Zaytsev, Yu. M., Udris, A. I., Shishkunova, L. V.: Chemical effects in the Th L-spectra. Radiokhimija (Radiochemistry) **20**, 116 (1978).

38. Katz, J. J., Seaborg, G. T., Morss, L. R.: *The chemistry of the actinide elements*. 2nd edn., Chapman and Hall, New York (1986) pp. 1131–1165.

39. Korolkov, D. V.: *Theory of valency in Progress*. (Kuznetsov, V. I., ed.) Mir, Moscow (1980) p. 210.

40. Korolkov, D. V.: Core and Valence Atomic Orbitals in Chemical Bond Formation. In: *Series Sov. Sci. Rev*. B. Chem. Harwood Academic Publishers GmbH, UK (1992) Vol. 17, p. 103.

41. Korolkov, D. V.: *Electronic Structure and Properties of Non-Transition Element Compounds*. NOVA Science Publishers Inc., New York (1996) p. 431.