

Relativistic component of chemical shift of Uranium X-ray emission lines

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Abstract

Twelve most intensive hard X-ray emission lines belonging to two multiplets (2p-3d and 2p-4d) and three doublets (2s-3p, 2s-4p, and 2p-3s) of the uranium L-series were studied by using a precise crystal-diffraction X-ray spectrometer. Chemical shift (CS) values were obtained for the first time for uranium (VI) oxide and uranium fluoride with respect to uranium (IV) oxide. The first attempt was made to separate CS of hard X-ray lines of an actinide atom into two components: the non-relativistic CS part characterizing the charge distribution of valence electrons between the atom and its partners in chemical bonding and the relativistic part reflecting the effects which are not related to electron removal from the atom. A method for calculating the relativistic CS component is proposed. It is concluded that it is the relativistic component that provides information about the changes in the valence state of the actinide atom in a compound. On the basis of model Dirac–Hartree–Fock calculations, it is shown that in the case of the uranium atom the relativistic component of CS is a direct consequence of intra-atomic electrons redistribution between $5f_{7/2}$ - and $5f_{5/2}$ -split levels of the uranium atom fine structure without changes in its charge state. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

The chemical behavior of actinide atoms (in particular, that of uranium) is determined by valence nl -electrons of three types: 7s, 6d, and 5f. Although the bond energies of these electrons are almost equal, their wave-functions differ greatly in distribution in the radial direction [1,2]. It can be said that the 5f-electrons have an only core arrangement in the atom. Therefore, when actinides chemical bonding is studied, several questions should be raised: (1) the possibility and form of 5f-electrons participation in chemical bonding; (2) the necessity for taking into account the splitting of valence levels of the atom into two sublevels nl_+ and nl_- with total angular momentum $j=1\pm 1/2$ because of the relativistic effect of spin-orbital splitting (SOS) [3–5]; (3) the energetic stabilization of the specific chemical state of the heavy atom due to fine effects of electron density redistribution on valence orbital; (4) the possibility of independent participation of split subshells in chemical bond formation. One of the methods of modern precise

spectroscopy capable of providing a correct description of chemical bonding process is the chemical shift (CS) method of X-ray emission lines, i.e. the change in their energy when the chemical state of the emitting atom is changed [6,7].

2. Experimental

Chemical shifts of X-ray emission lines of the L-series of uranium were measured with a 2-m crystal-diffraction spectrometer of Sumbaev's construction [8,9], focused by Couchois [10]. A detailed scheme of the instrument is shown in Fig. 1. 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 an optical angle meter by counting the required angle θ according to the Wulf–Braggs' equation:

$$n\lambda = 2d \sin\theta,$$

where n is the reflection order ($n=1$), d is the interplanar spacing of the reflecting surfaces of the

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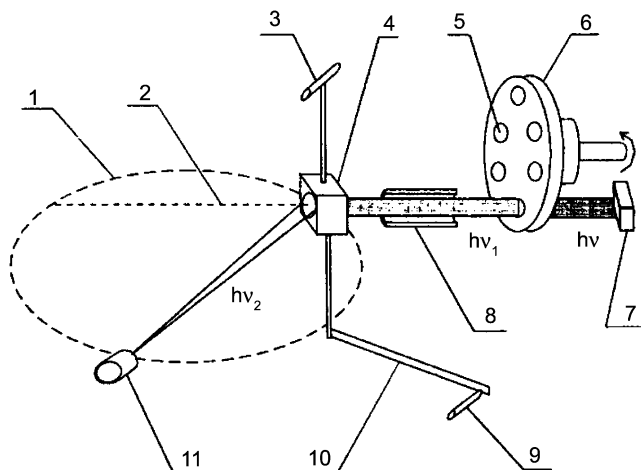


Fig. 1. X-ray spectrometer: (1) a focal point; (2) mirror-equivalence position; (3) optical angle meter; (4) quartz monochromator; (5) sample; (6) rotating cassette; (7) Roentgen tube; (8) collimator; (9) step-motor-driven micrometer; (10) the lever; and (11) scintillation detector.

monochromator ($d = 1.81674 \text{ \AA}$), and θ is the diffraction angle.

Each sample was powdered, mixed with polystyrene powder and pressed into a tablet, 20 mm in diameter. Fluorescent (secondary) X-ray emission of samples was excited by a combination of bremsstrahlung and characteristic (primary) radiations emitted by a vanadium anode of the Roentgen tube operating at 46 kV and 44 mA. The radiation was decomposed with a quartz monochromator, adjusted to the selected X-ray line, and was recorded with the aid of a scintillation detector on the basis of a NaI(Tl) crystal. 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. 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 structure of the monochromator [11,12].

An 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} .

3. Theoretical

It is known that X-ray emission spectra appearing during the transition between the deepest electron levels make it possible to obtain reliable information about the chemical (charge, valence, magnetic, etc.) state of the emitting atom in a molecule or a solid [6,7]. CS of hard X-ray emission lines can be applied to evaluate the effective atomic charge [13], as a sum of partial contributions of nl -valence electrons (Q_{nl}) participating in chemical bond formation. In other words, the perturbation of atomic system during chemical bonding is simulated by the distribution process of valence electron density between the atoms forming a molecular system (or a solid) [14]. In theory, the CS of the i -th X-ray line ($\delta^{(i)}$) is related to the population of nl -valence orbitals by the dependence of the general type:

$$\delta^{(i)} = f^{(i)}(Q_{nl}), \quad (1)$$

where Q_{nl} is the change in the population of nl -orbitals of the atom with respect to its reference state. For example, in the case of $(n-1)d$ -transition elements (neglecting the participation of virtual np -electrons in the chemical bond) the expected CS can be written as [14]:

$$\begin{aligned} \delta^{(i)} = & C_{ns}Q_{ns} + C_{(n-1)d}Q_{(n-1)d} + Q_{ns}(Q_{ns}-1)\Delta_{ns} \\ & + Q_{(n-1)d}(Q_{(n-1)d}-1)\Delta_{(n-1)d} \\ & + Q_{ns}Q_{(n-1)d}\Delta_{ns,(n-1)d} + \dots \end{aligned} \quad (1')$$

where C_{ns} and $C_{(n-1)d}$ are the shifts in the X-ray line energy when one ns -electron and one $(n-1)d$ -electron are removed, respectively, from the atom with the chosen reference configuration; Δ_{ns} , $\Delta_{(n-1)d}$, $(\Delta_{ns,(n-1)d})$ is the change in electrostatic interaction between equivalent (non-equivalent) electrons in the atom when an X-ray quantum is emitted. The C and Δ parameters can be easily calculated by quantum mechanics atomic methods [14,15] without the application of any quantum-chemical approximations (e.g. the MO theory). The combination of experimental values of CS of different X-ray lines forms a system of equations Eq. (1). This system makes it possible for most of the light elements (up to 5d) to find the values of Q_{nl} from the experimental values of $\delta^{(i)}$ in the 'free atom–free ion' model [15].

For heavy atoms in which prerequisites appear for relatively independent participation of split components of valence orbitals in chemical bonding, it is necessary

to take into account the SOS of valence orbitals:

$$\delta^{(i)} = f^{(i)}(Q_{nl\pm}). \quad (2)$$

Then for actinide atoms, the populations of five levels become the CS parameters:

$$\delta^{(i)} = f^{(i)}(Q_{5f+}, Q_{5f-}, Q_{6d+}, Q_{6d-}, Q_{7s}). \quad (2')$$

However, the system of equations (2') has no solutions or the solutions have no physical meaning [16,17]. We have suggested that this is due to the imperfection of the chemical bond model used. When the valence possibilities of an atom are manifested, in addition to the processes of valence electron density distribution between the chemical bond participants, finer *intra-atomic* processes of electron density redistribution probably also takes place between the split valence levels of the heavy atom. In this case, not only the charge non-relativistic component ($\delta_Q^{(i)}$) provides a contribution to the experimental value of CS but also the effects related to changes in the fine structure of valence levels of the atom when its chemical state changes. These may be the effects of redistribution of electron and spin density between the split (+) and (–) components of valence 5f- and(or) 6d-orbitals: $5f_+ \leftrightarrow 5f_-$ and(or) $6d_+ \leftrightarrow 6d_-$. It should be noted that these processes in valence orbitals do not change the charge state of the atom and, hence, cannot be taken into account in the system of equations (2'). However, they can lead to a considerable energetic stabilization of the atomic system. Therefore, their contribution to experimental values of CS for heavy atoms can be considerable. Then the experimentally measured CS can be represented by the sum:

$$\delta^{(i)} = \delta_Q^{(i)} + \delta_{\text{Rel}}^{(i)}. \quad (3)$$

The first item of this sum describes the fraction of electron density spent for chemical bond formation. This electron transition from split components of valence orbitals takes place strictly proportional to their statistical weights $2j+1$. This item has the following physical sense: the CS of the center of gravity of a multiplet (or a doublet), which includes the i -th X-ray line. The value of $\delta_Q^{(i)}$ can be found from the rule of sums [18,19], e.g. for 2p-3d multiplet of the L-series of uranium:

$$\delta_Q^{(i)} \equiv \delta(2p-3d) = \frac{9\delta(L\alpha_1) + 5\delta(L\beta_1) + \delta(L\alpha_2)}{15},$$

$$i = \{L\alpha_1, L\beta_1, L\beta_2\}. \quad (4)$$

The difference between CS of a single line and that of the center of gravity of the multiplet will determine the desired value of the relativistic component of CS.

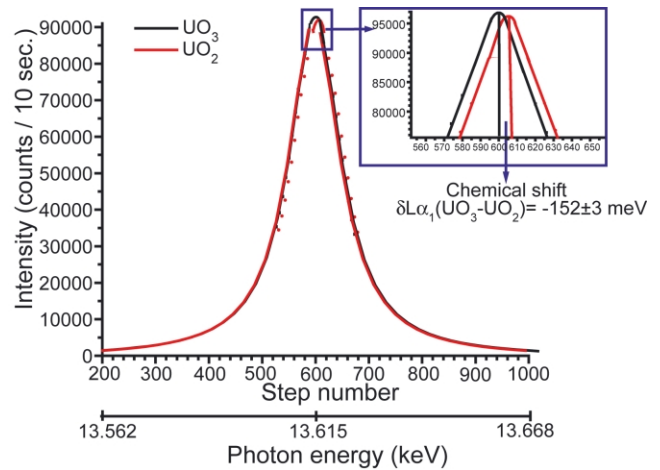


Fig. 2. Illustration to the calculation of $L\alpha_1$ -uranium line chemical shift in UO_3 with respect to UO_2 .

For example for $UL\alpha_1$ -line:

$$\begin{aligned} \delta_{\text{Rel}}(L\alpha_1) &= \delta(L\alpha_1) - \delta_Q(L\alpha_1) \\ &= \delta(L\alpha_1) - \delta(2p-3d). \end{aligned} \quad (5)$$

It should be noted that for most compounds with atoms of light elements (excepted some compounds of 3d-elements) the shifts of line contained in one multiplet are approximately equal [15,20–27] and, therefore, $\delta^{(i)} \approx \delta_Q^{(i)}$.

4. Results and discussion

The most complete information about the state of the atomic system can be obtained from the array of CS of a set of X-ray lines, which is a *pattern* of chemical states of the investigated atom in the multidimensional space of CS. The qualitative comparison of these patterns of atoms in different chemical states with the theoretically calculated patterns for models of chemical bonding process makes it possible to draw conclusions about changes taking place in the valence shell of the atom.

In order to reveal those processes in the atomic system which reflected the relativistic component of CS, spectra were measured and CS values were obtained for the first time for 12 most intensive hard X-ray emission lines of the uranium L-series for uranium (VI) oxide UO_3 and uranium fluoride UF_4 with respect to uranium (IV) oxide UO_2 (Fig. 2). Experimental results are given in Table 1. For the same compounds, CS of centers of gravity of two multiplets (2p-3d and 2p-4d) and three doublets (2s-3p, 2s-4p, and 2p-3s) were calculated from Eq. (4). After this, according to Eq. (3), relativistic components of CS of lines contained in these multiplets (doublets) were singled out. On the basis of the obtained

Table 1
Chemical shifts (δ , in meV) of 12 X-ray emission lines of the uranium L-series for UF₄ and UO₃ with respect to UO₂ and chemical shifts of the centers of gravity of multiplets (doublets) calculated on their basis

Multiplet line	2p-3d			2p-4d			2s-3p		2s-4p		2p-3s	
	L α_1	L α_2	L β_1^a	L β_2	L β_{15}	L γ_1	L β_4^b	L β_3^b	L γ_3^b	L γ_2^b	L b	L η^b
Transition	3d ₊ → 2p ₊	3d ₋ → 2p ₊	3d ₋ → 2p ₋	4d ₊ → 2p ₊	4d ₋ → 2p ₊	4d ₋ → 2p ₋	3p ₋ → 2s	3p ₊ → 2s	4p ₊ → 2s	4p ₋ → 2s	3s → 2p ₊	3s → 2p ₋
Error	±3	±3	±4	±3	±5	±4	±6	±6	±6	±4	±6	±7
UO ₂	0	0	0	0	0	0	0	0	0	0	0	0
UO ₃	-152	+88	+43	-85	+44	-1	+15	-169	-97	+5	-63	-102
	$\delta(2p-3d) = -71$			$\delta(2p-4d) = -48$			$\delta(2s-3p) = -108$		$\delta(2s-4p) = -63$		$\delta(2p-3s) = -76$	
UF ₄	-28	-38	-13	+6	-32	-7	-38	-85	-28	-14	-20	-40
	$\delta(2p-3d) = -24$			$\delta(2p-4d) = -1$			$\delta(2s-3p) = -69$		$\delta(2s-4p) = -23$		$\delta(2p-3s) = -27$	

^a To eliminate the effect of the L_{III}-absorption edge on the CS of $\delta L\beta_1$ -line [28], the following relation can be used: $\delta L\beta_1 = \delta L\gamma_1 - \delta L\beta_{15} + \delta L\alpha_2$.

^b Measurement of the CS was especially difficult because of low line intensity (50 times lower than the intensity of the most marked UL α_1 -line).

Table 2

Partial values of effective charges (in units of electron charge) of 5f- (Q_{5f}) and 6d- (Q_{6d}) orbitals on uranium atom in uranium (VI) oxide and uranium fluoride (with respect to uranium (IV) oxide)

Effective charge	Q_{5f}	Q_{6d}	$\Sigma Q = Q_{5f} + Q_{6d}$
Error	± 0.03	± 0.12	± 0.12
UO ₂	0	0	0
UO ₃	+0.25	+0.28	+0.53
UF ₄	+0.14	+0.45	+0.59

data by excluding the relativistic component of the CS, we calculated the *partial values of the effective charges* of 5f- (Q_{5f}) and 6d-orbitals (Q_{6d}) on the uranium atom (Table 2). It can be seen that quite expected data are obtained: the values of Q_{5f} and Q_{6d} are positive. The charges on the uranium atom (ΣQ) in UO₃ and UF₄ commensurable and are greater than in UO₂, which corresponds to general concepts about electronegativity of bond partners.

It is of interest to compare relativistic and non-relativistic components of two pairs of compounds: UF₄–UO₂ and UO₃–UO₂. It is evident that in the former case only the charge on the atom changes and in the latter case not only the charge but also *the valence state* of uranium atom changes from IV to VI. As can be seen in Fig. 3 in which relativistic patterns are shown, there is a drastic qualitative and quantitative difference in the behavior of $\delta_{\text{Rel}}^{(i)}$ for the pairs UF₄–UO₂ and UO₃–UO₂. The pattern of change in the uranium valence state (UO₃–UO₂) differs fundamentally from that only for charge change (UF₄–UO₂), although both these processes concern only valence orbitals of the atom. On passing to the non-relativistic (charge) case, the processes in split components of uranium valence orbitals (5f and/or 6d) are leveled out. As can be seen from Fig. 4, qualitative differences in two processes disappear. Now shifts reflect only the change of charge on the uranium atom and, as our Dirac–Hartree–Fock (DHF) calculation of C_{5f} - and C_{6d} -parameters shown, the non-relativistic patterns for the pairs UF₄–UO₂ and UO₃–UO₂ are qualitatively identical with the patterns of the removal of one electron from 5f- (C_{5f}) or 6d- (C_{6d}) uranium orbital to infinity.

On the basis of the above facts and considerations, it can be concluded that the relativistic component of CS of hard X-ray emission lines provides an information about the change in the valence state of the atom in a compound. To elucidate the effects in the valence region of the uranium atom, which lead to the formation of the relativistic component of CS, we have carried out the theoretical DHF calculation of changes in energy of uranium L X-Ray lines during the following relativistic processes:

1. removal of one U 5f_{5/2}-electron (5f₋ → ∞);
2. removal of one U 5f_{7/2}-electron (5f₊ → ∞);

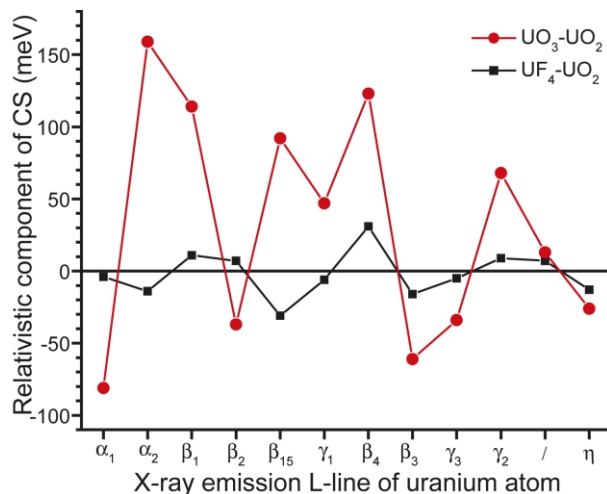


Fig. 3. Relativistic patterns of transitions with change in the valence state of the atom (UO₃ ← UO₂) and with a change only in the charge on the atom (UF₄ ← UO₂).

3. removal of one U 6d_{3/2}-electron (6d₋ → ∞);
4. removal of one U 6d_{5/2}-electron (6d₊ → ∞);
5. transition of one electron from U 5f_{5/2}- to U 5f_{7/2}-orbital (5f₋ → 5f₊); and
6. transition of one electron from U 6d_{3/2}- to U 6d_{5/2}-orbital (6d₋ → 6d₊).

The change in energy of the X-ray line $n'l' \rightarrow n''l''$ (i.e. theoretical CS) when the uranium atom passes from the initial configuration [Rn] 5f^{1.5}5f₊^{1.5}6d¹6d₊⁰7s² into

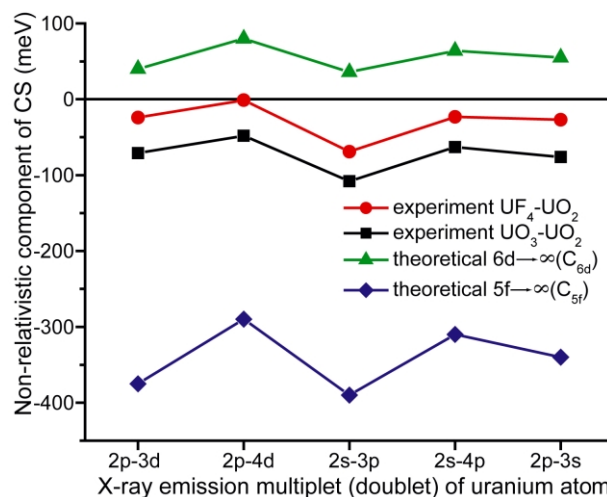


Fig. 4. Non-relativistic (charge) patterns of transitions with change in the valence state of the atom (UO₃ ← UO₂) and with a change only in the charge on the atom (UF₄ ← UO₂).

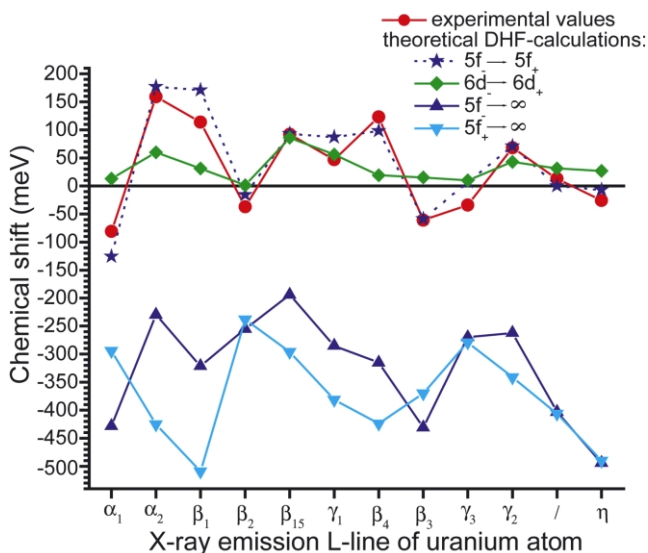


Fig. 5. Comparison of experimental relativistic pattern for the $\text{UO}_3 \leftarrow \text{UO}_2$ transition with theoretical patterns for: (1) removal of one $\text{U}5f_{5/2}$ -electron ($5f_- \rightarrow \infty$); (2) removal of one $\text{U}5f_{7/2}$ -electron ($5f_+ \rightarrow \infty$); (3) transition of one electron from $\text{U}5f_{5/2}$ - to $\text{U}5f_{7/2}$ -orbital ($5f_- \rightarrow 5f_+$); (4) transition of one electron from $\text{U}6d_{3/2}$ - to $\text{U}6d_{5/2}$ -orbital ($6d_- \rightarrow 6d_+$).

the final configuration was calculated from the equation:

$$\Delta E_{n'l' \rightarrow n''l''} = [E(\overline{n'l'}) - E(\overline{n''l''})]_{\text{final}} - [E(\overline{n'l'}) - E(\overline{n''l''})]_{\text{initial}} \quad (6)$$

where $E(\overline{nl})$ is the total DHF-energy of an atom with a vacancy on the inner nl -shell.

In Fig. 5, the results of CS calculations of a series of uranium L X-Ray lines for the processes in the valence region of the atom (in other words, the pattern of theoretical models of chemical bonding in actinides) are compared with the values of $\delta_{\text{Rel}}^{(i)}$ ($i = \{\text{UL}\alpha_1, \text{UL}\alpha_2, \text{UL}\beta_1, \text{UL}\beta_2, \text{UL}\beta_3, \text{UL}\beta_4, \text{UL}\beta_{15}, \text{UL}\gamma_1, \text{UL}\gamma_2, \text{UL}\gamma_3, \text{UL}l, \text{UL}\eta\}$) for UO_3 with respect to UO_2 from experimental data. The removal of one electron from the $5f_+$ - or $5f_-$ -orbital leads to a great negative shift of all investigated lines ($-500 \text{ meV} < \delta^{(i)} < -150 \text{ meV}$). The removal of one electron from the $6d_+$ - or $6d_-$ -orbital leads to a slight positive shifts of all investigated lines ($+50 \text{ meV} < \delta^{(i)} < +80 \text{ meV}$). Moreover, CS of different lines does not differ greatly. The relativistic transition of one electron from $\text{U}6d_-$ - to $\text{U}6d_+$ -subshell is represented by a more complex pattern. However, energy shifts of all lines are positive (from +1 meV for the $\text{UL}\beta_1$ -line to +86 meV for the $\text{UL}\beta_{15}$ -line). Fig. 5 shows that only the relativistic electron transition from $\text{U}5f_-$ - to $\text{U}5f_+$ -subshell ($5f_- \rightarrow 5f_+$) is in good agreement with experiment. Complex variations of CS of different lines are observed: from -127 meV for the $\text{UL}\alpha_1$ -line to +177 meV for the $\text{UL}\alpha_2$ -line.

This behavior is demonstrated by the relativistic components of experimental CS of X-ray emission uranium lines for UO_3 with respect to UO_2 . This coincidence of patterns suggests that the *intra-atomic relativistic* $\text{U}5f_+ \leftrightarrow \text{U}5f_-$ transition is possible.

5. Conclusion and outlook

On the basis of the above experiments and calculations it can be concluded that the relativistic component of CS is determined by the intra-atomic relativistic redistribution between split $5f_-$ - and $5f_+$ -orbitals of uranium atom fine structure when its valence state is changed. Its analogue is to a certain extent the non-relativistic $\text{Th}6d \leftrightarrow \text{Th}5f$ transition in thorium compounds with which the beginning of $5f$ -levels filling in the actinides series is related [16]. It may be suggested that the $\text{U}5f_+ \leftrightarrow \text{U}5f_-$ transition is a *fine energetic tuning* to specific chemical state. Apart from the SOS effect it is of interest to investigate the effect of ‘*f*-elements contraction’ and finally to consider the evolution of relativistic effects on chemical properties of atoms in the Th, U, Np – series.

Hence, we have shown that uranium chemical bonding (possibly, also that of other actinides) includes two processes:

1. *Inter-atomic distribution* of valence electron density between chemical bond participants. In other words, the non-relativistic removal of electrons from split valence orbitals is proportional to their statistical weights. This process leads to the appearance of the charge component of CS, which is the CS of the center of gravity of the whole multiplet.
2. Relativistic *intra-atomic redistribution* of electron density between split $5f_-$ - and $5f_+$ -components of uranium atom fine structure. This process does not change the charge on the uranium atom and is reflected in relativistic component of CS.

An important problem also arises about the correlation of these two processes: distribution and redistribution of electron density on valence levels of the actinide atom during the chemical bonding.

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References

- [1] J.J. Katz, G.T. Seaborg, L.R. Morss, 2nd ed, The Chemistry of the Actinide Elements, 2, Chapman and Hall, New York, 1986, pp. 1131–1165.

- [2] K. Balasubramanian, Relativistic effects and electronic structure of lanthanide and actinide molecules, in: K.A. Gschneidner, L. Eyring, G.R. Choppin, G.H. Lander (Eds.), Handbook of Physics and Chemistry of Rare Earth, 18, Elsevier, Amsterdam, 1994, pp. 29–50, Chap. 119.
- [3] P. Pyykko, Relativistic effects in structural chemistry, Chem. Rev. 88 (1988) 563–594.
- [4] W.H.E. Schwarz, E.M. van Wezenbeek, E.J. Baerends, J.C. Snijders, The origin of relativistic effects of atomic orbitals, J. Phys. B.: At. Mol. Opt. Phys. 22 (1989) 1515–1529.
- [5] M. Pepper, B.E. Bursten, The electronic structure of actinide-containing molecules: a challenge to applied quantum chemistry, Chem. Rev. 91 (1991) 719–741.
- [6] Y. Gohshi, A. Ohtsuka, The application of chemical effects in high resolution X-ray spectrometry, Spectrochim. Acta Part B 28 (1973) 179–188.
- [7] L.L. Makarov, X-ray emission effects as a tool to study light actinides, Czech. J. Phys. 49 (1999) 610–616.
- [8] O.I. Sumbaev, The effect of the chemical shift of the X-ray K lines in heavy atoms, Phys. Lett. A 30 (1969) 129–130.
- [9] O.I. Sumbaev, Crystal-diffraction Gamma-spectrometers, GosAtomIzdat, Moscow, 1963, pp. 110–111, (in Russian).
- [10] Y. Cauchois, Spectrographie des rayons x par transmission d'un faisceau noncanalise' a travers un cristal courbe' (I), J. Phys. Rad. 3 (1932) 320–332.
- [11] S.I. Salem, F. Boehm, P.L. Lee, Instrumental line width of a bent crystal spectrometer and measurement of the K β X-ray width, Nucl. Instr. Methods 140 (1977) 511–514.
- [12] S.B. Mamedov, N.D. Aksenov, L.L. Makarov, Yu.F. Batrakov, X-ray emission study of the system Ge–Se in glassy and crystal states, J. Non-cryst. Solids 195 (1996) 272–278.
- [13] R.L. Barinsky, V.I. Nefedov, Röntgenspektroskopische Bestimmung der Atomladungen in Molekülen. Leipzig 1969 (in German).
- [14] R.I. Karazija, D.V. Grabauskas, A.A. Kiselev, Litov. Fizich. Sborn. 14 (1974) 235–246, in Russian.
- [15] L.L. Makarov, A.B. Nikolskiy, Yu.M. Zaitsev, Ju.F. Batrakov, Ju.I. Djatchenko, A.K. Morozov, Evaluation of the effective charges of atoms from combination of the X-ray K α_1 chemical shifts and the isomer shifts of the NGR spectra, J. Res. Inst. Catalysis Hokkaido Univ. 24 (1976) 102–126.
- [16] L.L. Makarov, R.I. Karazija, Yu.F. Batrakov, N.P. Chibisov, A.N. Mosevich, Yu.M. Zaytsev, A.I. Udriš, L.V. Shishkunova, Chemical effects in the Th L-spectra, Radiokhimiya (Radiochemistry) 20 (1978) 116–124, (in Russian).
- [17] L.L. Makarov, B.F. Myasoedov, Yu.P. Novikov, Yu.F. Batrakov, R.I. Karazija, A.N. Mosevich, V.B. Gliva, Shifts in X-ray emission Np L-lines, J. Neorg. Khim. (Soviet Union J. Inorg. Chem.) 24 (1979) 1014–1024, (in Russian).
- [18] M.A. Blokhin, Physics of X-rays, GITTL Publishing, Moscow, 1957, (in Russian).
- [19] M.A. Blokhin, Methods of X-Ray Spectroscopic Research, Pergamon Press, Oxford, 1965.
- [20] J. Kawai, E. Nakamura, Y. Nihei, M. Fujisawa, Y. Gohshi, Sc K α , and K β X-ray fluorescence spectra, Spectrochim. Acta Part B 45 (1990) 463–479.
- [21] L.L. Makarov, Yu.F. Batrakov, N.D. Aksenov, State of copper atom in oxides and HTSC systems YBaCu and BiPbSrCaCu, Sverhprovodimost': Fizika, Khimija, Tehnika (Superconductivity: Physics, Chemistry Technics) 6 (1993) 1247–1260, (in Russian).
- [22] J. Kawai, T. Konishi, A. Shimohara, Y. Gohshi, High resolution titanium K α X-ray fluorescence spectra, Spectrochim. Acta Part B 49 (1994) 725–738.
- [23] Yu.F. Batrakov, N.O. Sablina, L.L. Makarov, State of atoms of 4d-elements Mo–Tc–Ru and cluster compounds by the data of X-ray emission spectroscopy, Koord. Khim. (Russian Coord. Chem.) 21 (1995) 642–650, (in Russian).
- [24] L.L. Makarov, Yu.F. Batrakov, M.A. Myaghkova-Romanova, I.I. Tupitsyn, State of an extrinsic Cu $^{2+}$ ion in crystal lattices of oxides of nickel, magnesium and zinc according to X-ray emission spectroscopy, Koord. Khim. (Russian Coord. Chem.) 22 (1996) 853–860, (in Russian).
- [25] A.V. Legin, D.L. Baidakov, Yu.F. Batrakov, Yu.G. Vlasov, The state of copper in the CuI–As $_2$ Se $_3$ and CuI–PbI $_2$ –As $_2$ Se $_3$ chalcogenide films prepared by chemical deposition, Glass Phys. Chem. 23 (1997) 429–432.
- [26] I.I. Tupitsyn, L.L. Makarov, Ju.F. Batrakov, Sign of the spin-polarized effects in the chemical shift of the X-ray Cu K $\alpha_{1,2}$ emission transitions, J. Phys. Chem. Solids 59 (1998) 809–817.
- [27] T. Konishi, J. Kawai, M. Fujisawa, T. Kurisaki, H. Wakita, Y. Gohshi, Chemical shift and lineshape of high-resolution Ni X-ray fluorescence spectra, X-Ray Spectrom. 28 (1999) 470–477.
- [28] Yu.F. Batrakov, E.V. Puchkova, Effect of the L $_{III}$ absorption edge of uranium on chemical shifts of the L β_1 line of uranium in UO $_{2+x}$, Radiochemistry 45 (2003) 25–27.