CHEMICAL SHIFT OF URANIUM L X-RAY LINES UPON $5f$-ELECTRON REMOVAL ($5f$-ELECTRON "FACSIMILE")

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The X-ray lines shift method is successfully applied to study electronic structure of rare-earth (r.e.) elements, electronic phase transition and intermediate valence state in r.e. compounds (see, for example, [1, 2]). It is connected with a fact, that X-ray line shifts upon $4f$-electron removal are anomalously large (they exceed by a factor 10–15 effects due to valence electrons). Moreover the $4f$-electron removal gives a characteristic V-shaped shift — dependence on the line type ("facsimile"). Those two peculiarities permit to determine the $4f$-shell population of r.e. elements with sufficient accuracy.

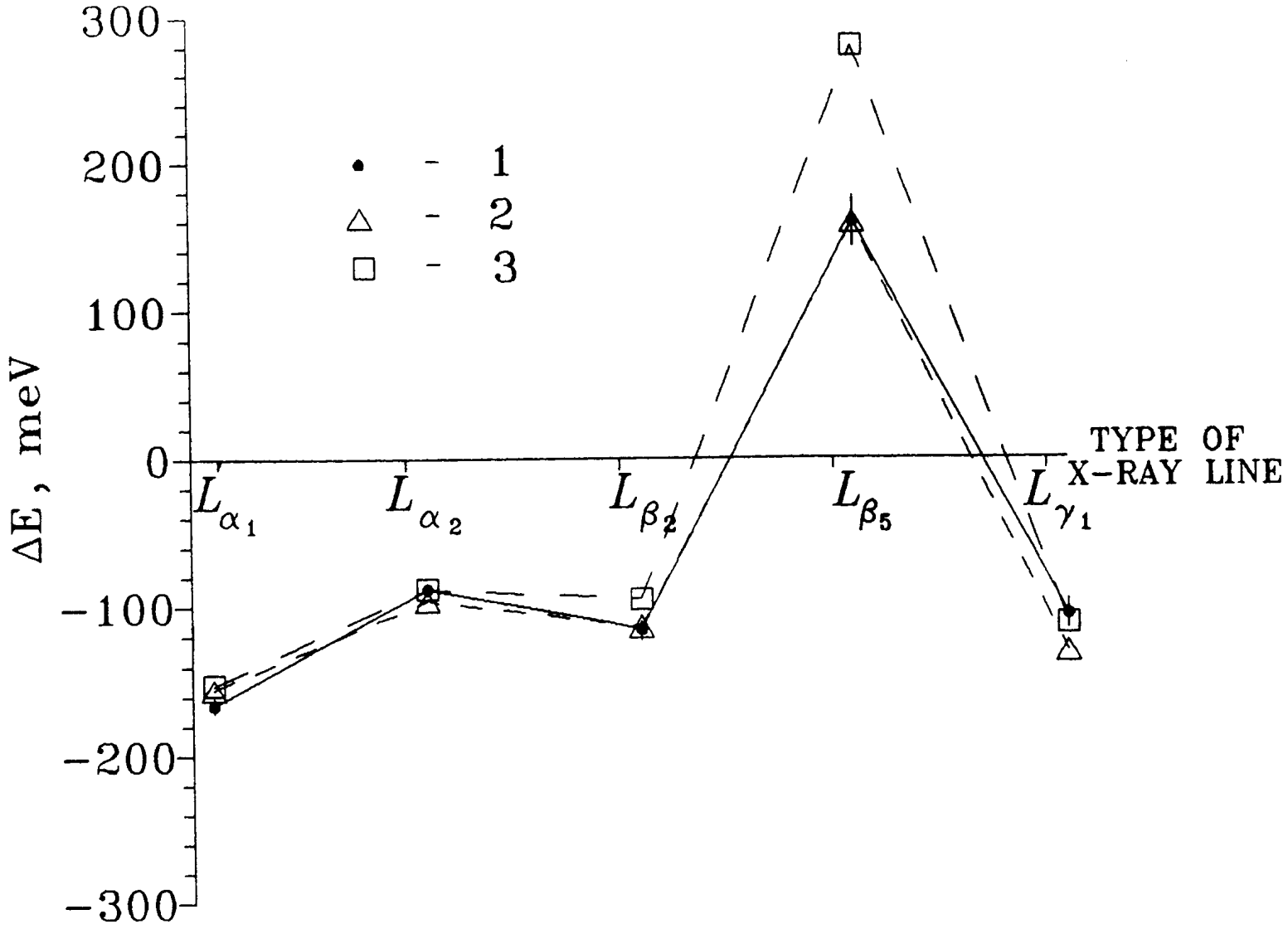

Fig. Experimental and theoretical "facsimile" of the $5f$-electron:
1 are experimental shifts of uranium X-ray lines for pair compounds UF_4–UF_3;
2 and *3* are theoretical differences of the X-ray lines energy for configurations $U^{(3+\eta)+}[Rn]5f^{3-\eta}$, calculated by DF method at Koopmans theorem *(2)* and at the total energies calculation *(3)*

Actinide elements have a partially filled f-shell like r.e. ones, but they are not full r.e. analogs. The cause of this is a peculiar nature of the $5f$-electrons, whose properties are intermediate between d-electrons of transition metals and $4f$-electrons of r.e. elements [3]. A large radial extension of $5f$-electron wave function (in comparison with $4f$-electron) permits it to display apparently a band character (in "light" actinides) and participate in the chemical bond formation [3]. In this work comparison of experimental shifts of five uranium L-series X-lines for a pair of ionic compounds $UF_4 - UF_3$ with theoretical calculations by Dirac-Fock (DF) method is conducted. The calculations were fulfilled in two versions: with a Koopmans theorem use and according to total energies, i.e., in assumption of a full relaxation of the atomic shells after a vacancy generation in the L-shell.

Uranium L-series X-ray line shifts were measured with a focusing Cauchois spectrometer, which parameters were described in [5]. A measurement procedure was described in detail in [1]. The shifts of the following X-ray lines were measured: L_{α_1} (transition $2p_{3/2} - 3d_{5/2}$), L_{α_2} $(2p_{3/2} - 3d_{3/2})$, L_{β_2} $(2p_{3/2} - 4d_{5/2})$, L_{β_5} $(2p_{3/2} - 5d_{5/2})$ and L_{γ_1} $(2p_{1/2} - 4d_{3/2})$. The experimental results are shown in Figure. The theoretical values of the shifts (upon $5f$-electron part η removal) are also represented in the same Figure, i.e., the X-ray lines energy differences for configurations $U^{(3+\eta)+}[Rn]5f^{3-\eta}$ and $U^{3+}[Rn]5f^3$, calculated by DF method [4]. The η value was determined in accordance with minimum of the M value:

$$M = \sum_i (\Delta E_{Li}^{ex} - \Delta E_{Li}^{th})^2 / \sigma_i^2,$$

where ΔE_{Li}^{ex} is the experimental shift of the uranium L_i-line for a pair of the compounds $UF_4 - UF_3$, ΔE_{Li}^{th} is the theoretical shift of the uranium L_i-line for configurations $U^{(3+\eta)+}[Rn]5f^{3-\eta}$, $U^{3+}[Rn]5f^3$, σ_i is the experimental error in the ΔE measurement. The η value was varied. A fitstep was equal to 0.01. It led the ΔE_{Li}^{th} to change no more than σ_i value. One can see, that the experimental and theoretical "facsimile" agree well, but η is not equal to unit ($\eta = 0.51$ at Koopmans theorem calculations and $\eta = 0.41$ at total energies calculations).

In ionic compounds of r.e. elements for unit change of rare-earth valence X-ray lines shifts correspond to the full $4f$-electron removal independently from the ionicity of given compound, because the strongly localized $4f$-electron cannot participate in a chemical bond and for forming bond it must be converted to the valent state.

The η inequality to unit in our case may be explained with an assumption that $5f$-electron (owing weak radial localization in comparison with $4f$-electron) may participate in the chemical bond formation. Then η will be a certain analog of the ionicity degree, i.e., will indicate the $5f$-electron part drawn to the ligands.

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