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Nature of the 5*f* States in the U--Pu System

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The volume collapse between δ- and α-Pu exemplifies a dramatic change of the character of the 5*f* states at the verge of localization. Any purely band description of the 5*f* states in δ-Pu fails badly, yielding a magnetic state in contrast to weak paramagnetism seen in reality. It was shown recently using the LSDA+U approach that the partly localized 5*f* states indeed turn non-magnetic if the occupancy Pu-n_{5f} increases above ≈ 5.3 [1]. This approach turned similarly successful in describing ground state properties as well as excitations in Am metal and broad variety of Pu-based systems [2]. This includes also Pu-Am alloys, which preserve the δ-Pu *fcc* structure while further expanding it. Similarly interesting is to alloy Pu and earlier actinides, namely Np and U. U exhibits practically no solubility in α-Pu, but about 10% Pu can be dissolved on orthorhombic α-U. In addition, a mysterious ζ-U-Pu phase exists over a certain composition range (35-70 % U) around the middle of the U-Pu phase diagram [3]. Here we describe a XPS and UPS study of U-Pu alloys prepared by co-sputtering of U and Pu.

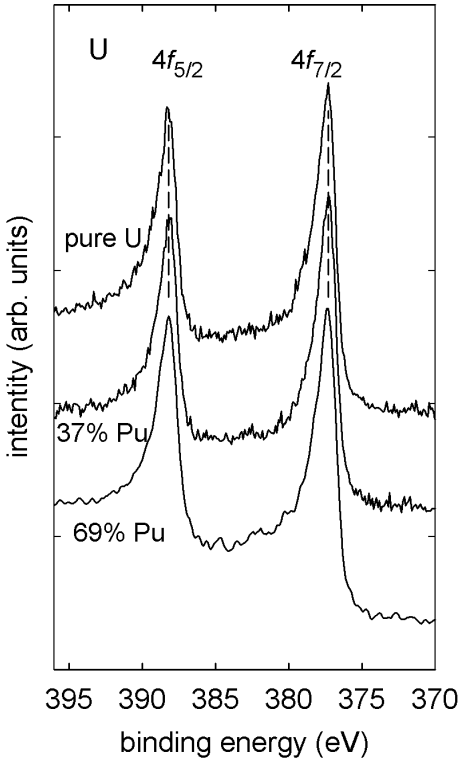

Fig.1: U-4*f* core-level spectra (spin-orbit split $4f_{5/2}$ and $4f_{7/2}$) reveal an invariable character throughout the phases, proving that the 5*f* states do not undergo any noticeable change between pure U metal (top) and the ζ-phase.

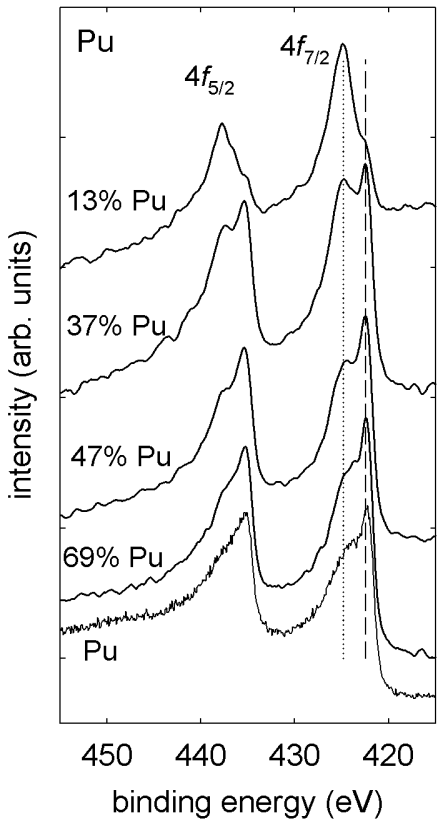

Fig.2: Pu undergoes a dramatic change from ≈ 50% dilution (i.e. within the ζ-phase). The poorly screened features (marked by the dotted line) start to dominate on the account of well-screened one (dashed line).

The 4*f* core-level spectra reveal an invariable character of U-5*f* states, which remain practically identical to the situation in α-U. On the other hand, dramatic changes were found for Pu if diluted by U to more than 50%. The changes are not related to the ζ-phase structure (complex low-volume structure [3]). For example, the spectra for 69% Pu are practically identical to pure Pu deposited under the same conditions, and the variation for 47% Pu is only minor. The real dramatic changes come only then. For 37% Pu, i.e. at the U-rich phase boundary of the ζ-phase, the well-screened peak attributed to screening by itinerant 5*f* states is already somewhat suppressed. This tendency continues into the α-U phase with diluted Pu (shown for 13% Pu), where the "poor-screening" peak, located at 2.4 eV higher binding energy, dominates. Such spectrum can be interpreted as result of the loss of the predominance of 5*f* screening, i.e. typically due to 5*f* localization.

Such changes cannot be investigated in detail in valence-band UPS spectra, in which the Pu and U 5*f* states overlap in the vicinity of the Fermi level. Fig.3 shows that variations in the Pu-5*f* emission are only minor comparing to the dominating U emission.

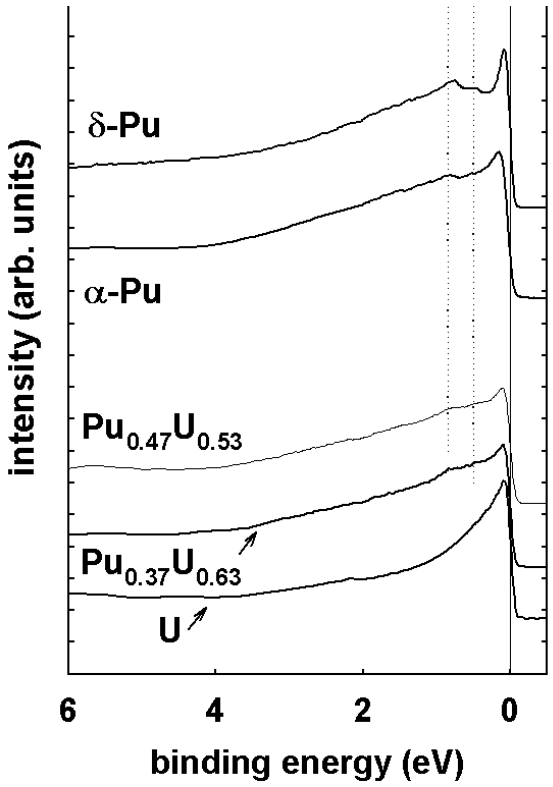

Fig.3: UPS spectra for hν =40.81 eV photo- excitation (5*f* emission dominant). The spectra obtained within this work, complemented by α- and δ-Pu, exhibit the characteristic triplet of peaks close to the Fermi level, supposed to reflect the 5f^5 final-state multiplet [2].

The electronic structure of Pu-U was also tested by LSDA and LDA+U calculations. We used PuU_3 supercell with the lattice parameter of γ-U. The LSDA yields a magnetic solution with total moments M_{Pu} = 2.5 μ_B and $M_{U\text{-}I,II}$ = -0.58, -0.29 μ_B. When Around Mean Field LDA+U is applied, PuU_3 becomes non-magnetic along with an increase of Pu-n_{5f} from 5.1 (LSDA) to 5.3 (LDA+U). For FLL-LDA+U, both Pu and U-atoms stay magnetic, and Pu-n_{5f} = 5.1.

We can conclude that when Pu is diluted in U metal, the character of Pu 5*f* states is rather different than in α-Pu. The 4*f* spectra point to their localization. The same, but to a smaller extent, is true for the ζ-phase, although it belongs to high-density phases similar to α-Pu.

It is very desirable to check for possible Pu magnetic moments by bulk magnetometry in both phases. It will help to clarify the character of Pu ground state at the threshold of localization transition.

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References

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