Vol. 34 (2003) *ACTA PHYSICA POLONICA B* No 2

PHOTOELECTRON SPECTROSCOPY STUDY OF Pu AND Pu-BASED SYSTEMS*

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(Received July 10, 2002)

Photoelectron spectra of various Pu-based systems are discussed from the point of view of variations of the 5*f* localization.

PACS numbers: 71.20.Gj, 71.28.+d, 79.60.–i

1. Pu — the end of 5*f* delocalization

Elements at the beginning of the actinide series exhibit band-like 5*f* states. The bonding tendency persists up to Pu. From Am onwards, the 5*f* states withdraw from the bonding similar to rare-earths. So as to investigate variations of electronic structure across the Mott transition, one way is to deal with a light actinide — typically U — and to try to suppress the 5*f* bonding tendency by increasing the interatomic spacing in a compound. But the hybridization of the 5*f* states with ligand electronic states causes that the localization is achieved only in few singular cases. A stronger tendency to localization appears also with increasing Z, so another option is to proceed to Np and especially to Pu, as Am exhibits the localized $5f^6$ state. Pu systems provide therefore a large variability of the delocalization in compounds and abundant Pu allotropic phases with strikingly different atomic volume. The δ-Pu phase can be taken, due to its volume being in about the middle between α-Pu and Am, already half way towards the localization. Photoelectron spectroscopy can bring a straightforward information on the situation of the 5*f* electronic states. Here we review results of X-ray

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* Presented at the International Conference on Strongly Correlated Electron Systems, (SCES 02), Cracow, Poland, July 10–13, 2002.

photoelectron Spectroscopy (XPS) and High-Resolution Ultraviolet Photoelectron Spectroscopy (HRUPS) studies of various Pu systems spanning the the cross-over between localized and itinerant behaviour of the $5f$ states.

2. Valence-band photoemission spectra

Photoemission studies have been so far performed for two of the allotropic modifications, namely α-Pu (monoclinic), which can be described as a $5f$-band system, and for δ-Pu (cubic), which has the largest volume (by 20% larger than α-Pu). It is normally stable between 592 and 724 K, but can be stabilized to much lower temperatures by doping.

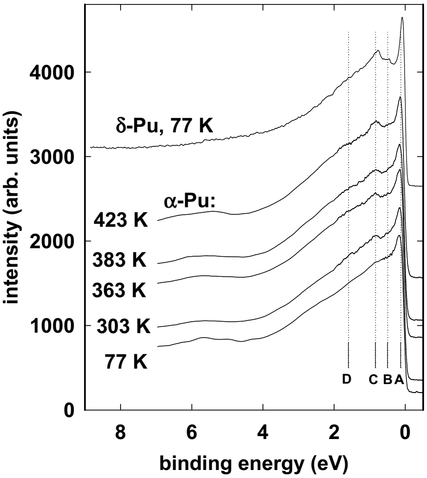

Fig. 1. Valence-band spectra of α-Pu surface prepared at various temperatures.

α-Pu spectra, described in [1], exhibit a triangular spectral intensity increasing up to the Fermi level without sharp distinct features, and are not qualitatively different from the picture of U or Np. Quite different spectra, displaying a satellite maximum around 0.8 eV binding energy, were reported in [2]. The latter type is more reminiscent of δ-Pu (stabilized by Ga) [1]. Trying to specify reasons for such disagreement, we were experimenting with surface treatments. We found that using the standard Ar-ion bombardment technique, temperature is a crucial parameter. As seen in Fig. 1, low-T bombardment leads to spectra identical to those in [1]. The bombardment at elevated temperatures (or annealing) leads to irreversible changes amounting to some δ-Pu features, similar to [2], where a laser ablation was used. The findings point to a reconstruction of a freshly prepared surface into a phase, which may be associated with δ-Pu. This interpretation has support in electronic structure calculations, predicting a large increase of atomic volume at the Pu surface due to lower coordination at the surface [3].

Establishing thus spectra of the Pu phases, we have to ask about their relation to electronic structure. As to electronic structure calculations, neither LDA calculations with itinerant $5f$ states nor LDA with $5f$ restricted to core give a satisfactory agreement [2]. Why it is the case we understand when we review other Pu systems. We see that for majority of them we can identify the same spectral features, occurring at identical energies. The detailed inspection of the data in [1] and [2] shows that it is not a single satellite maximum, but two features, one at 0.50 eV (denoted as B) and 0.85 eV (C), whereas the Fermi level peak is denoted as A. Their energies coincide with pronounced maxima observed for example for PuSe [4].

An interesting way to tune the localization is to work with thin layers, reducing the thickness of Pu layers down to several monolayers [5]. Fig. 2 shows that the features A, B and C are easily observable for 2–3 monolayers, whereas the progressive localization for 1 monolayer leads to their suppression, and the spectral intensity shifts into a broad maximum D located between 1.5–2.0 eV. A similar character of valence-band spectra was found for PuSb with presumably $5f^5$ localized states [4]. The fact that the peaks A–C appear quite generally is proved in several other studies (PuN, Pu-Si).

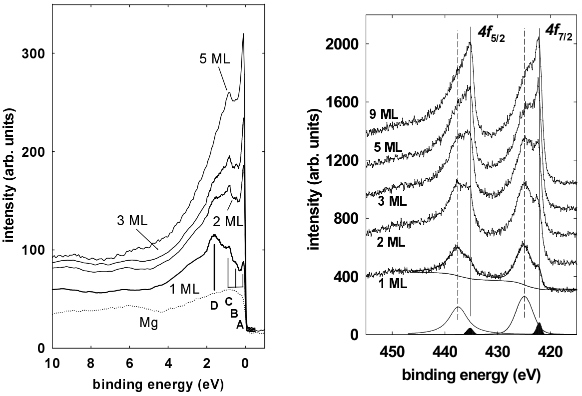

Fig. 2. Valence-band (left) and $4f$ (right) spectra of Pu layers of various thickness.

3. Pu-$4f$ lines

Complementary information can be obtained from the Pu-$4f$ spectra, which consist of two well separated peaks, $4f_{5/2}$ and $4f_{7/2}$. Each peak can exhibit two features appearing at different binding energies, explained on the basis of the two-channel screening model [6]. One channel corresponds to the $4f$ hole screened by $5f$ electrons, and is thus dominating for metallic systems with itinerant $5f$ states. If the probability of the $5f$ screening decreases, the channel based on non-f screening takes over. It results in a final state with a higher energy, and the kinetic energy of photoelectron is by 2.0–2.5 eV lower. Thus "poorly" screened features only appear for PuSb, whereas the 5f screening is strong in α-Pu. The varying weight of the two spectral features can illustrate the localization with decreasing thickness of Pu layers (see Fig.2).

4. Discussion

The 4f-core level spectra exhibit two types of features, their mutual ratio being good indication of the degree of the 5f delocalization. On the other hand, we have three types of valence-band spectra. The spectacular set of three sharp features within 1 eV below the Fermi level vanishes only at the 5f localization limit, at which the spectral intensity moves to the energy range around 2 eV. At the itinerant limit (α-Pu), they vanish in a broader triangular emission peaking at E_{F}. The origin of the 3-peak structure is thus a key to understanding of Pu. It cannot be due to one-electron features, which should differ significantly between various systems, and the sharp peaks (obtained in angle-integrated mode) cannot have much dispersion.

A possible explanation is to associate it with another final-state multiplet ($5f^5$), while the intensity around 2 eV can be related to the $5f^4$ unresolved multiplet, left as final state after excitation from the $5f^5$ states. The larger atomic volume of the $5f^6$ initial state would restrict it first to the surface, and should be supported by enhanced surface roughness, which does not seem to be the case. We can also consider the features to be arising due to a many-body effect, an analogy of Kondo effect in Ce materials. An anomalous temperature dependence of intensities is expected in such case and our recent results prove the presence of such effect.

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