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Electronic structure of $PuSi_x$ films studied by photoemission

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The electronic structure of Pu and its compounds is dominated by the *5f* states, which are close to the localization-delocalization threshold. The delicate balance between itinerancy and localisation is quite sensitive to slight variations in the chemical environment. *5f* localization is favoured by reduced bonding (lower coordination, small overlap of the *5f*-orbitals). *5f* itinerancy is favoured by hybridisation, either direct by *5f-5f* overlap or mixing with the states of ligand atoms.

In this context, we studied $PuSi_x$ systems with x=4 down to 0.5. The electronic structure of $PuSi_x$, prepared as thin films (1 μg, 50 atomic layers) by sputter deposition, has been studied by photoelectron spectroscopy (Fig. 1). The question was how the bonding properties of the Pu-*5f* states evolve as Pu becomes diluted in the Si matrix. In pure (α) Pu the *5f* states form a broad conduction band with a maximum at the Fermi-level (E_F). In δ-Pu, a sharp peak appears right at the Fermi-level, separated from the rest of the conduction band by a small gap. This can be qualitatively associated with the narrowing of the *5f* band in δ-Pu.

Adding small amounts of Si disrupts this band. In $PuSi_{0.5}$ the density of states at E_F becomes suppressed and the *5f* spectral weight is shifted to higher BE. In $PuSi_{0.8}$ the intensity at E_F is very small, and the *5f* emission takes the same energy position and shape as in PuSb, which is the prototype of a localized $5f^5$ system [1]. It is concluded that in $PuSi_{0.8}$ (which is close to stoichiometric PuSi), the 5*f* states are mostly localized. Pu-*4f* core-level spectra confirm *5f* localization: for PuSi the well-screened *4f* peak (associated with *5f* hybridization), is almost missing, and the poorly screened peak (associated with *5f* localization) is dominating. In addition PuSi exhibits a strong magnetic character with a local magnetic moment of 0.74 μ_B

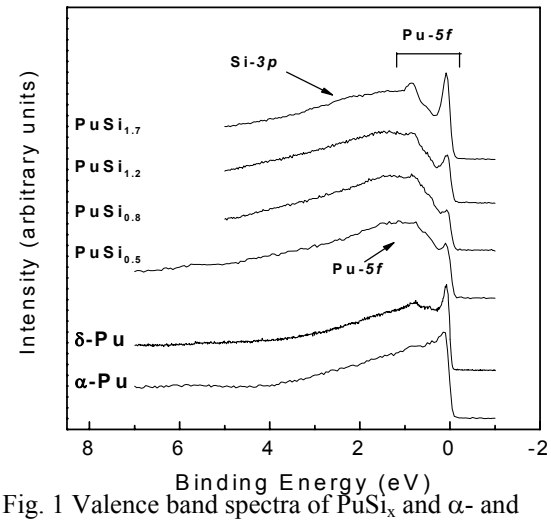

Fig. 1 Valence band spectra of $PuSi_x$ and α- and δ-Pu.

[2] (The local magnetic moment in PuSb ($5f^5$) is 0.75 μ_B). Localization may be attributed to the increased Pu-Pu spacing, interrupting the direct *5f-5f* orbital overlap, or possibly to the bonding interaction between Pu and Si.

Quite surprisingly, at even higher Pu dilution, the 5*f* electrons regain some of their bonding properties: in $PuSi_{1.7}$ photoemission spectra show an increased intensity at the Fermi-level. This can be attributed to the hybridization between the Pu (*5f*) and the Si ligand states. Pu-*4f* core level spectra confirm the increased *5f* hybridization: in $PuSi_2$ the well-screened peak becomes more pronounced than in PuSi. Very clearly $PuSi_2$ is a less localized system than PuSi. Interestingly, magnetic measurements of bulk $PuSi_2$ reveal a sizeable local magnetic moment of 0.54 μ_B. This shows that even in $PuSi_2$ the *5f* states must be localized. However the

reduction of the moment, compared to PuSi (0.74 μ_B), points to the presence of a ground state different from a pure $5f^5$ configuration.

The structure of the peak at the Fermi-level is intriguing. While α-Pu just shows the broad (4 eV wide) early actinide like peak at the Fermi-level, characteristic for well itinerant *f*-states, $PuSi_{1.7}$ has a narrow peak separated by a pseudo-gap from the rest of the conduction band. By subtracting HeI from HeII excited UPS spectra, the *f*-fraction can be separated from the rest of the valence band (Fig. 2). The non-*f* fraction consists of the Si-3p valence band

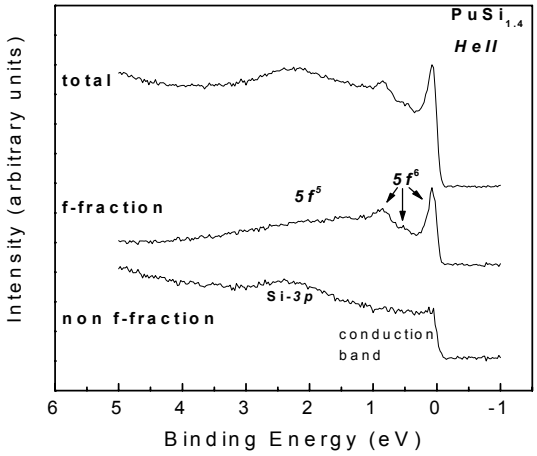

Fig. 2 HeII valence band spectrum decomposed into the *f*- and non-*f* states.

and a flat, featureless conduction band. The *f*-fraction shows a broad and weak $5f^5$ peak (significantly weaker than in $PuSi_{0.8}$), and a three-peak structure close to the Fermi-level. This structure has been observed in a large variety of Pu systems such as thin films of Pu on Al [3], Mg [4], and in PuSe [1] (Fig. 3). In the thin films it appears with approaching localization, with decreasing film thickness. In PuSe, where it was seen most clearly, it could be related to the non-magnetic ground-state of this material, explained by a localized $5f^6$ configuration. In this case it can be attributed to a ($5f^6$ ->$5f^5$) multiplet transition. Calculations of multiplet transition indeed indicate, that the ($5f^6$ -> $5f^5$) transition would give rise to the observed three-peak structure [5]. The position of this structure right at the Fermi-level means, that it can exchange electrons with the conduction band. This is the typical situation of intermediate valence

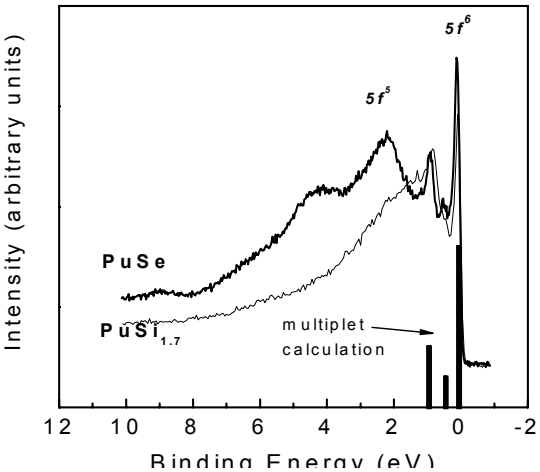

Fig. 3 HeII valence band comparing the three-peak structure in PuSe and $PuSi1_{1.7}$ and the calculated multiplet.

system, which for PuSe has indeed been postulated [6]. The general occurrence of the three-peak structure points to its atomic, (rather than material or structure related) origin. It would also imply that the similar structure in δ-Pu metal does not correspond to ground state DOS features but is related to photoemission final state effects. Pu metal systems thus seem to have three possible ground state configurations: the itinerant *f*-states, the well-localized ($5f^5$) and an intermediated localized ($5f^6$) configuration.

References:

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