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Electron spectroscopy study of Pu and Pu compounds

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Abstract

Core-level and valence-band spectra of Pu and the other early actinide compounds show remarkable systematics, which can be understood in the framework of final state screening. For 4f core-level spectra, approaching 5f localization results in a change of screening mechanism of the core-hole, from f- to d-screening. In the transition region, both screening types coexist, leading to two-peak spectra with d- and f-screened components. A similar mixed-final-state-configuration is observed in the valence band spectra. Here the transition from itinerant to localized 5f character is observed as transition from band-like f-spectra (like in U) to f-screened and finally d-screened final state multiplet peaks of localized f-states. Observed multiplets resemble atomic multiplets, $5f^{n-1}$ for the d-screened, $5f^{n}$ for the f-screened. This interpretation can be extended to the neighbouring actinide elements (Am and Np) and gives a consistent interpretation of spectra of many actinide compounds.

Keywords: Surfaces and interfaces; Electronic band structure; Electronic states (localized); Photoelectron spectroscopies

1. Introduction

Study of the electronic structure of Pu and its alloys has to face the complex nature of the 5f states. Because of the proximity to the localization–delocalization transition, strong electron–electron correlations represent an important energy scale [1]. Over the last 20 years, photoelectron spectroscopy has been used to obtain information on the density of states (DOS) of Pu [2–5]. Yet, it is not a ground state technique, and in highly correlated systems, the system may be left in an excited state after photoemission and the electron removal function differs significantly from the ground state DOS [6]. Current interpretation of photoemission data is therefore controversial, and ranges from direct comparison with ground state DOS calculations [7] (and references therein) to approximated electron removal data in the DMFT calculation [1]. Alternative calculations of the spectral function, as done for other highly correlated materials [8], are not available for the actinides. The different excited states, which are reached with specific transition probability, can result in complex multiplet structures in the valence band spectra. The multiplet nature is clearly indicated by the astonishing similarity of photoemission spectra of Pu systems with very different band structure, proving the atomic origin of the spectral features [9]. Recently, a new theoretical model was proposed, the mixed level model (MLM), stating that the ground state consists of integral number of 5f electrons in localized, atomic-like, states plus a variable number of itinerant, band-like, 5f states. Photoemission spectra of various Pu systems, as $PuCoGa_5$, $PuIn_3$ and δ-Pu [10] were interpreted in this framework. This model with two separated types of states has indeed the variability to explain both the typical strong 5f emission below the Fermi energy, E_F, and simultaneous presence of the 5f emission at or near to E_F. But the question is whether one can expect that the ground state characteristics (density of states) can be directly compared with experimental spectra. For localized 5f states this is definitely not the case. A simple analogy of lanthanides in the metallic state reveals, that the 4f emission from the $4f^n$ state adopts the pattern of the $4f^{n-1}$ multiplet [11], because the 4f hole cannot be re-occupied within the time of the photoemission event. In the case of a weak but non-negligible hybridisation of the 5f states with conduction band or ligand states, interpretation is less clear. This is why a systematic data set covering various regimes of the 5f states has to be collected and compared with existing theories, to capture the so-called final state effects. This article concentrates on the first part of the task—to introduce and review experimental photoelectron spectra in systems of Pu and few

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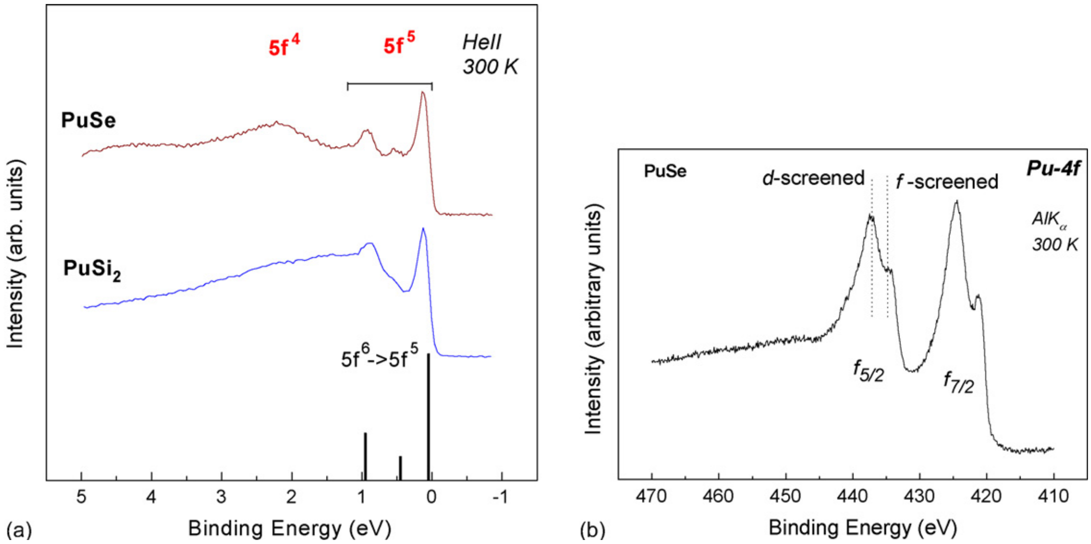

Fig. 1. PuSe spectra: (a) 5f valence-band spectrum and (b) 4f core-level (data from Ref. [12]).

neighbour actinides, and to discuss them on a simple qualitative level.

2. Results

The features which we attribute to such a final state multiplet for Pu are clearly apparent in Pu chalcogenides (PuSe [12]). These compounds are weakly magnetic and semi metallic, with a very low density of conduction states at E_F. They resemble rare-earth intermediate valence systems and are often presented as having a mixed $5f^5/5f^6$ ground state configuration. Intermediate valence comes from the fluctuation of an electron between the well localized 5f level and the conduction band ($5f^6CB^m \leftrightarrow 5f^5CB^{m+1}$). Photoemission from these $5f^5/5f^6$ levels then gives characteristic final state multiplet structures, as typical for localized states. Valence-band spectra (Fig. 1a) indeed show a well resolved three-peak structure at the Fermi-level, attributed to the $5f^5$ final state (reached from the $5f^6$ ground state by $5f^6 \rightarrow 5f^5$ transition) and the $5f^4$ final state at higher binding energy (reached from the $5f^5$ ground state by $5f^5 \rightarrow 5f^4$ transition). The $5f^5$ structure is very well described by an atomic multiplet structure [13], deduced from optical emission spectra and assuming intermediate coupling for the 5f states. Attempts to explain spectra in terms of LS multiplets were not successful, proving the strong spin orbit coupling typical for the actinides. The $5f^4$ is less well resolved, because of the shorter life-time of this final state. Similar spectra with similar difference in peak resolution have been observed for the rare earth chalcogenides [14]. The higher binding energy of the $5f^4$ multiplet is due to the lowered screening of the photohole by a small 5f count. The position of the $5f^5$ multiplet right at the Fermi-level is due to the mixed-valent nature. This final state configuration is equivalent to one of the ground state configuration ($5f^5/5f^6$). Recently a full account of these features was given by the DMFT theory constructed to reflect multiplet excitations as well as hybridisation with conduction electrons [15]. Not surprisingly the presence of two different final state multiplets was also observed for rare-earth compounds with (4f) valence fluctuations (e.g. SmS) [11].

Photoemission from the 4f core levels (Fig. 1b) leads to the two spin-orbit 4f peaks ($f_{5/2}$ and $f_{7/2}$). Each peak is again split into two components, which are associated with two types of final states. The peak at low binding energy can be attributed to the $4f^{13}5f^6$ final state, and the peak at high binding energy is due to the $4f^{13}5f^5$ final state. The $5f^6$ configuration is more stable than the $5f^5$, because the core-hole is more efficiently screened by a local f-state ($5f^6$) rather then a ds conduction band state ($5f^5$ ds).

We now turn our attention to the itinerant Pu systems. From all, α-Pu is presumably the most itinerant, having the smallest atomic volume from all Pu phases. Its spectrum (Fig. 2a) shows strong similarity with Np and U metal [16]. The triangular peak starting at about 4 eV binding energy (BE) and the maximum right at the Fermi-level is attributed to the 5f band. Fine details of band structure are not seen because of the polycrystalline nature of the sample and angle-integrated mode of measurement. That is why the spectra of U and Np are featureless (the small structure at 2 eV binding energy is due to 6d states). In α-Pu, a new, weak structure appears in the vicinity of E_F (at 1 eV BE), superimposing on the pure band signal. In δ-Pu it develops into a three peak structure with energies conspicuously identical to those in PuSe. This change is obviously associated with the shift of the 5f states towards localization. The atomic volume of δ-Pu is about half-way between that of the *f*-itinerant α-Pu and f-localized Am. The similarity of the emerging structure to PuSe with the $5f^5$ final state multiplet suggests, that δ-Pu can be described as superposition of the triangular band signal and the multiplet signature of a discrete $5f^5$ final state. While in a (f) band system, the photohole is fast re-occupied and the observed spectrum copies the occupied part of the ground state density of states, substantial (f) band narrowing (the band width becomes smaller than Coulomb correlation energy) in actinides means, that the band picture no longer describes the situation entirely. In addition, creation of the photohole perturbs the peri-

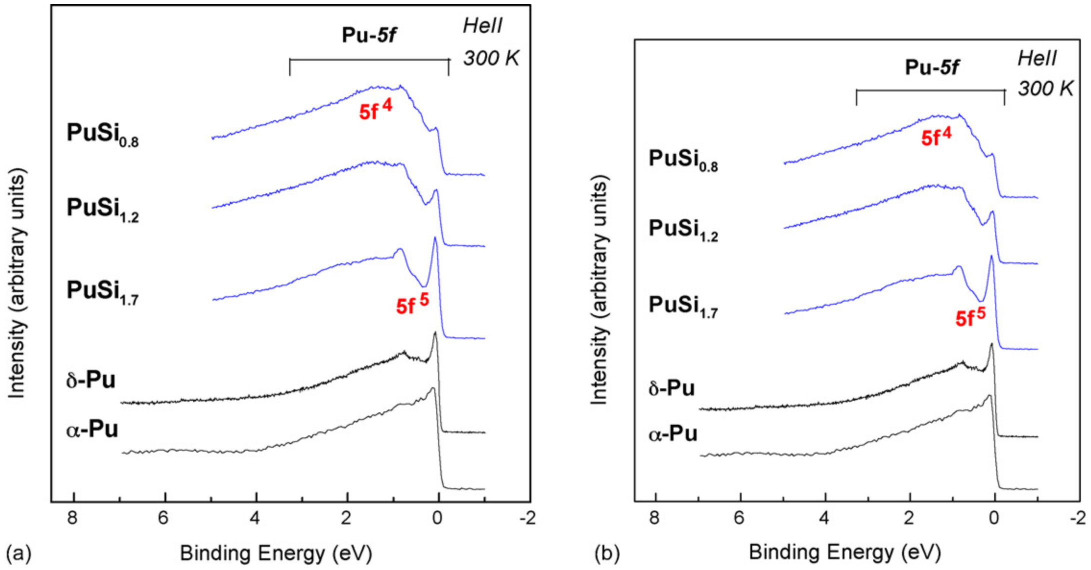

Fig. 2. Spectra of α- and δ-Pu (1 wt% Ga) and Pu silicides: (a) 5f valence-band spectrum and (b) 4f core-level (data from Ref. [9]).

odicity, which may emphasize the local atomic aspects even more. In an intermediate-localization situation, one may expect two types of responses to the photohole creation: (i) the hole is refilled due to the promotion of electrons in the 5f band or due to 5f-ligand hybridisation, but the dynamical processes lead to appearance of the whole $5f^n$ multiplet (broadened by a short lifetime) and (ii) the hole is not re-occupied and the $5f^{n-1}$ multiplet appears in the spectrum. Therefore we expect that individual multiplets appear in valence-band spectra long before a real localization. The weight of each multiplet is then affected not only by the probability of re-occupation of the photohole, but also by the actual f count in the ground state, which is a non-integral variable number and differs between various materials. In the mixed level model, nothing of the final-state effects mentioned above has been applied when interpreting valence-band spectra of Pu systems. In principle, the presence of localized $5f^4$ states would have to lead to a $5f^3$ final state multiplet, which is distinctly different form both $5f^4$ and $5f^5$ final state multiplets [13].

The corresponding 4f spectra for α- and δ-Pu (Fig. 2b) support this view. The spectrum of α-Pu is similar to that of U and Np. The peaks are sharp and asymmetrical, pointing a high DOS at the Fermi-level. In δ-Pu, a broad high satellite appears on the high binding energy side. As in PuSe, there are now two components, even though there is only one 4f level in the ground-state. An explanation is provided by the simple, qualitative screening model. While in α-Pu, the 4f core hole is screened by the 5f electrons, with decreasing 5f bandwidth (hybridization) in δ-Pu, this screening mode becomes difficult and alternative screening by 6d7s (broad band) electron sets on. This leads thus to two possible final states in δ-Pu: the f-screened $4f^{13}5f^{n+1}6d7s^m$ and the d-screened $4f^{13}5f^n6d7s^{m+1}$. The f-screened peak appears at lower binding energy because the closer proximity of the hole and f screening electron yields a lower final state energy, allowing a higher kinetic energy of the photoelectron. There are thus two final states with different energies, both for core-level and for valence-band spectra, simply due to competitive screening mechanisms.

The development of valence-band spectra with further 5f band narrowing can be well followed in the Pu–Si system [9]. Photoemission spectra were recorded on thin Pu–Si films with decreasing Pu concentrations, and data compared to the two stable solid state compositions PuSi and $PuSi_2$. PuSi orders ferromagnetically around 72 K and has an effective moment $\mu_{eff} = 0.72\mu_B$/Pu in the paramagnetic state. $PuSi_2$ remains paramagnetic and its effective moment is reduced to $0.54\mu_B$/Pu. Pu–Pu interatomic spacings in PuSi and $PuSi_2$ are 0.364 and 0.397 nm, respectively, which is far above the Pu–Pu spacing in δ-Pu (0.292 nm). This would be generally favourable for the 5f localization, but the 5f hybridisation with the Si-2p states becomes the main delocalising mechanism. The presence of magnetic moment shows, that the ground-state configuration should be close to $5f^5$—the $5f^6$ configuration is a non-magnetic singlet. Yet the moment is reduced compared to the theoretical value of $0.86\mu_B$. Stronger suppression of the local moment in the more dilute $PuSi_2$ relative to PuSi points to a stronger hybridization in $PuSi_2$. The valence band (Fig. 2a) spectra of near stoichiometric films are dominated by multiplet-like structures, and the early actinide-like 5f conduction band peak, which would be reminiscent of early actinide metals, is missing. In $PuSi_2$ ($PuSi_{1.7}$ film), the $5f^5$ final state multiplet appears, together with a weak $5f^4$ final state multiplet at higher binding energies. In PuSi ($PuSi_{0.7}$ film), the $5f^5$ final state multiplet disappears, and only the $5f^4$ multiplet structure is observed. As it is unlikely that the charge state of Pu in PuSi and $PuSi_2$ would be very different (in both cases the ground state configuration is $5f^5$), we have to assume that the re-occupation of the 5f hole in PuSi is much less probable than in $PuSi_2$. Consequently the $5f^4$ final state dominates in PuSi, whereas the $5f^5$ final state still manifests in $PuSi_2$ due to a stronger hybridisation. This model also explains why the $5f^4$ multiplet is shifted towards higher binding energies comparing to the $5f^5$ multiplet. The reason is

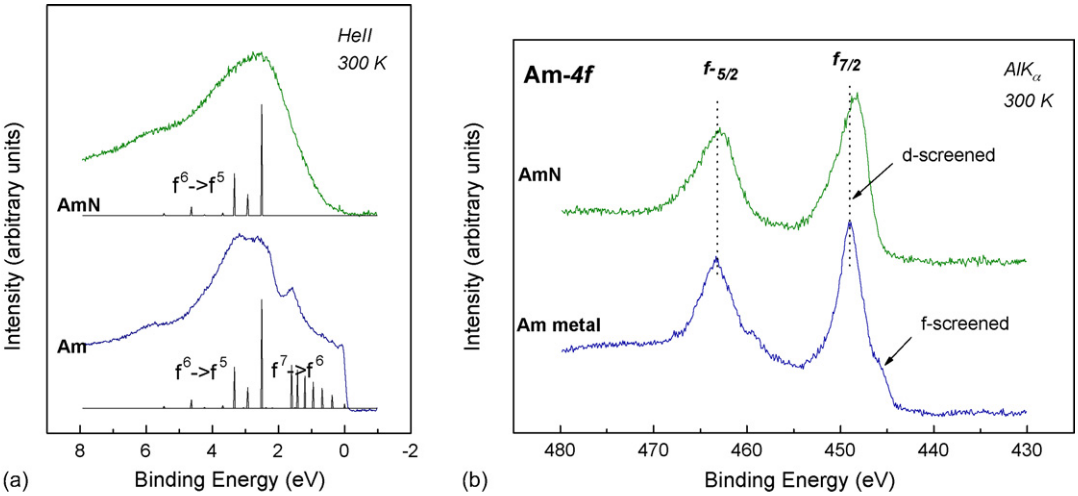

Fig. 3. Spectra of Am and AmN: (a) 5f valence-band spectrum and (b) 4f core-level (data from Ref. [17]).

the less effective 5f photohole screening by non-f electrons. Naturally, if there is the ground-state 5f occupancy higher than 5, the $5f^5$ final state would be even more emphasized due to the $5f^6 \rightarrow 5f^5$ transitions.

Core level data (Fig. 2b) support the above-mentioned view. They also show, for $PuSi_2$ ($PuSi_2$ film), the very much suppressed f-screened peak together with the dominating ds-screened peak: 5f hybridization is significantly weaker than in δ-Pu, where the f-screened peak was the most intense. This is also consistent with the absence of the f-conduction band peak in the valence-band spectra. In PuSi ($PuSi_{0.7}$ film), the f-screened peak completely vanishes pointing to an even weaker f-hybridization. Both, valence band and core-level spectra of PuSi are similar to those of PuSb [12], which is the prototype of a localized 5f system with a $5f^5$ ground-state configuration.

It appears, that Pu systems of very different degree of hybridization (5f bandwidth) are successfully described by the final-state screening model. While this model is only qualitative and therefore necessarily speculative, it catches already the development of the valence-band spectra representing the spectral density from the band-like form, to a weakly localized form still screened by 5f states, and finally to a strongly localized form where screening is performed by 6d7s electrons. The examples show that the multiplet structure emerges long before the full localization is reached. The complex valence-band spectra are always accompanied by complex core-level spectra. The experimental facts, taken not for one individual case, but in the systematic covering different regimes, are quite selective as to the possible theoretical models. They definitely disqualify, for comparison with experimental spectra, both purely band models and mixed-level models, as none of them explains the systematically observed features attributed to atomic multiplets.

Pu plays no special role within the actinide series. The same rules can also be applied to its direct neighbours in the actinide series (Am, Np and U). In Am metal, the 5f states are localized in the ground-state, which in the Hubbard models means, that the 5f hybridization becomes too weak to overcome the on-site f–f correlation energy (U). The ground state is undoubtedly

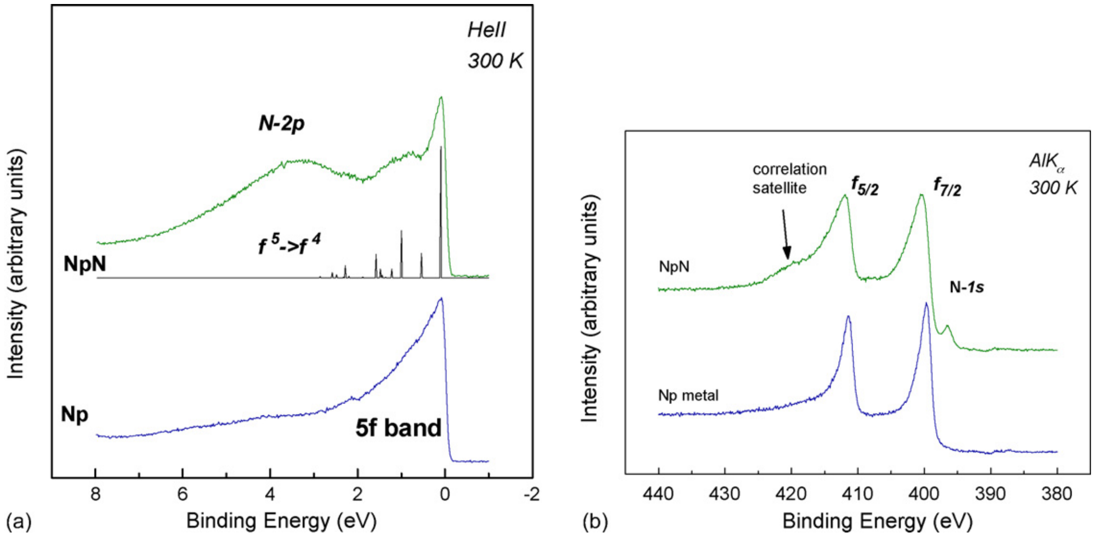

Fig. 4. Spectra of Np and NpN: (a) 5f valence-band spectrum and (b) 4f core-level.

the $5f^6$ singlet. But photoemission spectra still registers a weak residual hybridization and demonstrated by the finite size of the well-screened final state. It is unambiguously demonstrated by presence of a shoulder in the Am-4f spectra on the well-screened positions (Fig. 3), which means that there is a weak but non-zero probability that one extra 5f electron is attracted to screen the 4f hole [17]. This would not be possible without the 5f-ligand hybridisation. Correspondingly, we attribute to such effects also a weak $5f^6$ multiplet resulting from the f-screened $5f^6 \rightarrow 5f^5f = 5f^6$ transition, which is responsible for the weak 5f intensity at 1.8 eV BE. The dominating structure above 2 eV BE is attributed to the $5f^5$ multiplet, resulting from the d-screened $5f^6 \rightarrow 5f^5d = 5f^5$ transition [17,18]. In AmN, the f-screened peak disappears both in core level and valence band spectra, due to the still reduced 5f hybridization. In addition AmN is an insulator, as shown by the disappearance of the 6d–7s conduction band.

Neptunium is the neighbour of Pu on the itinerant side. The 5f spectrum of the valence band shows no multiplet-like structures (Fig. 4a). The 4f spectrum shows only the f-screened peak, proving the 5f-states to be itinerant (Fig. 4b). But like for Am, the 5f character varies in the nitride NpN. In the valence band spectrum, sharp features appear, which can be very well described by final-state multiplet structures (Fig. 4a). From observation of the spectra one would conclude that the degree of localization is intermediate between δ-Pu and $PuSi_2$. The valence-band spectrum shows sharp features at the Fermi-level, which are similar to the $5f^4$ multiplet structure—to be compared with the $5f^5$ multiplet structure in δ-Pu. There is still a weak triangular band signal—weaker than in δ-Pu but stronger than in $PuSi_2$. No d-screened peak is observed at higher binding energy—in fact it appears for more localized Np systems. Core-level spectra show a still asymmetrical, but broadened 4f peak (Fig. 4b). A correlation satellite, similar to higher correlated or weakly localized U compounds (UBe_{13}, UPt_3) is observed. The peak is shifted to slightly higher binding energy than the metal, similar to UN [19], but the shift is less pronounced than in PuN [20] where the 5f states are more localized.

3. Conclusions

Photoemission of the early actinide systems reflects the highly correlated nature of the 5f electronic states. The spectral function depends on the complex relaxation behaviour, where the 5f state may or may not participate following their degree of itinerancy or hybridization. In general, with decreasing hybridization 5f tendency for screening disappears and the alternative 6d–7s screening takes place. In a wide regime the PES spectra do not reflect the ground state density of states, but are dominated by pure final-state effects, such as competing screening mechanisms and atomic-like multiplet excitations. For determination of the position of multiplets in the energy spectrum, and of width and intensity of the individual lines, sophisticated methods, which implement local excitations into electronic structure calculations, have to be developed. The presented simple intuitive model is thought to provide a link between experimental spectra and various theories leading to spectral density, as the complexity of the problem has to be reduced only to the most relevant parameters.

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