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# Photoelectron spectroscopy of $\text{NpPd}_3$ and $\text{PuPd}_3$

M D Le<sup>1,2</sup>, H C Walker<sup>1,2</sup>, K A McEwen<sup>1,2</sup>, T Gouder<sup>3</sup>,  
F Huber<sup>3</sup> and F Wastin<sup>3</sup>

<sup>1</sup> Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

<sup>2</sup> London Centre for Nanotechnology, University College London, Gower Street, London WC1E 6BT, UK

<sup>3</sup> European Commission, Joint Research Centre, Institute for Transuranium Elements, Post Box 2340, D-76125 Karlsruhe, Germany

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## Abstract

We present the results of x-ray and ultraviolet photoelectron spectroscopy of  $\text{NpPd}_3$  and  $\text{PuPd}_3$ . The spectra indicate that for both compounds, the 5f electrons are well localized on the actinide sites. Comparison with bulk measurements indicates that for  $\text{NpPd}_3$  the electrons have a valence of  $\text{Np}^{3+}$  and thus a ground state  $5f^4$  with a Hund's rules  $^5I_4$  configuration. Similarly for  $\text{PuPd}_3$ , we find a  $\text{Pu}^{3+}$  valence,  $5f^5$  ground state and a Hund's rules  $^6H_{5/2}$  configuration.

## 1. Introduction

$\text{NpPd}_3$  crystallizes in the cubic  $\text{AuCu}_3$  and double-hexagonal close-packed (dhcp) structures, whereas  $\text{PuPd}_3$  crystallizes only in the cubic  $\text{AuCu}_3$  structure. Both compounds have been studied using bulk measurements and neutron diffraction [1, 2]. These measurements show that the cubic compounds are antiferromagnetic,  $\text{NpPd}_3$  below  $T_N = 55$  K with an ordered moment of  $2.0 \mu_B/\text{Np}$  atom, whilst  $\text{PuPd}_3$  orders below  $T_N = 24$  K with a moment of  $0.8 \mu_B/\text{Pu}$  atom. The lattice parameter and actinide–actinide distances in both cubic (4.095 Å) and dhcp (4.072 Å)  $\text{NpPd}_3$  and  $\text{PuPd}_3$  (4.105 Å) are similar, and above the critical distance at which the 5f moments are expected to be localized [3].

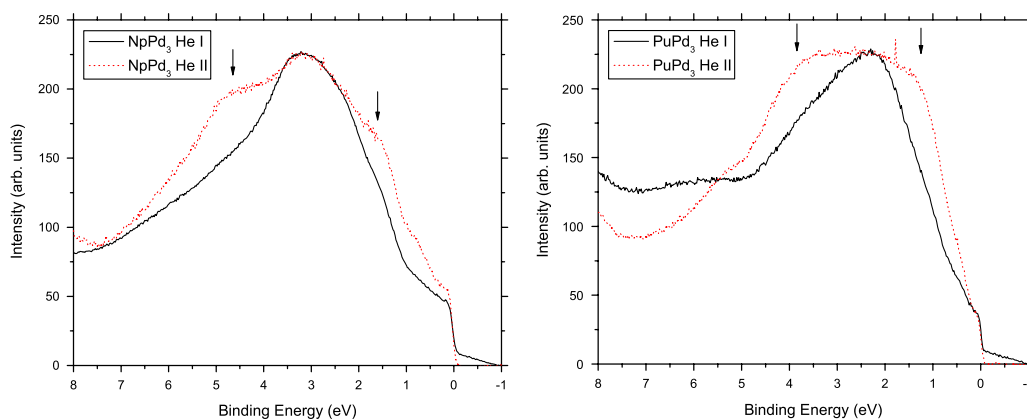
The measured paramagnetic effective moments of  $2.74 \mu_B/\text{Np}$ -atom for cubic  $\text{NpPd}_3$  and  $2.83 \mu_B/\text{Np}$ -atom for dhcp  $\text{NpPd}_3$  suggests that the ground state is  $5f^4$ , whereas for  $\text{PuPd}_3$ , the measured paramagnetic effective moment of  $1.06 \mu_B/\text{Pu}$ -atom suggests that the ground state is probably  $5f^5$ . We have performed photoelectron spectroscopy on thin film samples, prepared *in situ* by sputter deposition from  $\text{NpPd}_3$  and  $\text{PuPd}_3$  targets made by arc-melting at the ITU. The target samples had been used to measure the bulk properties of these systems and synthesis details may be found in [2, 4].

## 2. Experimental details and results

The photoelectron spectroscopy was performed in a spectrometer equipped with a Leybold LHS 10 hemispherical analyzer,

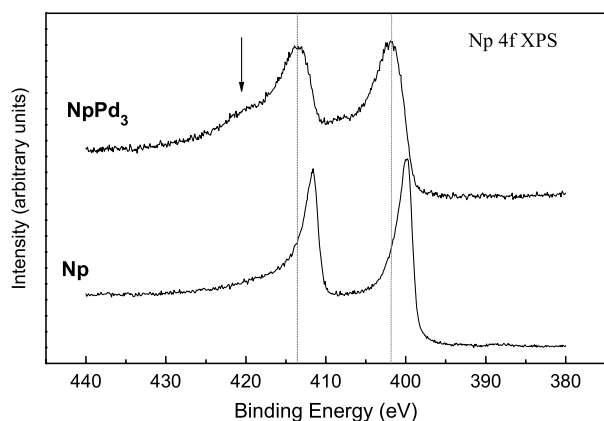
placed in a dedicated transuranium glovebox. The analysis chamber (base pressure  $4 \times 10^{-10}$  mbar) is connected to the preparation chamber (base pressure  $3 \times 10^{-9}$  mbar) within the glovebox and samples were analysed as soon as the deposition was complete. Figure 1 shows the ultraviolet photoelectron spectra (UPS) obtained from He I and He II excitation radiation ( $h\nu = 21.22$  and  $40.81$  eV respectively) produced by a windowless UV rare-gas discharge source. The energy resolution is approximately 45 meV. He II radiation is more sensitive to the 5f photoexcitation, whereas this cross-section is relatively weak for He I radiation. Thus the extra bulge in the  $\text{PuPd}_3$  He II spectra at around 1 eV binding energy with respect to the He I spectra shows that this emission is of 5f origin. If the 5f electrons in  $\text{NpPd}_3$  and  $\text{PuPd}_3$  were itinerant, we should expect to observe significant spectral weight in the He II spectra at the Fermi energy. This is not observed in the data. Instead the 5f emissions are shifted to approximately 1.5 eV binding energy in  $\text{NpPd}_3$  and 1 eV in  $\text{PuPd}_3$ , indicating that they are well localized. This is in agreement with previous studies of 5f localization in Pu metal [5].

The shoulders at 5 eV in the  $\text{NpPd}_3$  valence band spectra and at 4 eV in the  $\text{PuPd}_3$  spectra are attributed to the 2p emissions from surface oxygen impurities, due for example to the adsorption of water or CO, because their intensity grows with time and with non-optimal deposition conditions. The emission is larger in He II than in He I, despite the lower O-2p cross-section for He II radiation [6]. This may be explained by the enhanced surface sensitivity of He II radiation which has an attenuation length of 1 monolayer versus 3–5 monolayers for

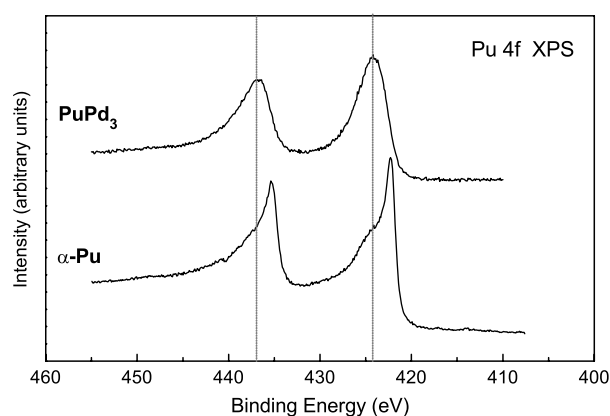


**Figure 1.** Valence band structure of  $\text{NpPd}_3$  and  $\text{PuPd}_3$  for photon energy  $h\nu = 21.22$  eV (He I, solid black line) and  $h\nu = 40.81$  eV (He II, dotted red line). The arrows indicates features in the He II spectra discussed in the text.

(This figure is in colour only in the electronic version)



**Figure 2.** Np-4f spectra for  $\text{NpPd}_3$ . The two peaks represent transitions from the  $4f_{5/2}$  and  $4f_{7/2}$  core levels at binding energies 413.8 eV and 402.3 eV respectively. The dotted line is a guide to the eye. The arrow indicates a feature discussed in the text.



**Figure 3.** Pu-4f spectra for  $\text{PuPd}_3$ . The two peaks represent transitions from the  $4f_{5/2}$  and  $4f_{7/2}$  core levels at binding energies 437.7 eV and 424.9 eV respectively. The dotted line is a guide to the eye.

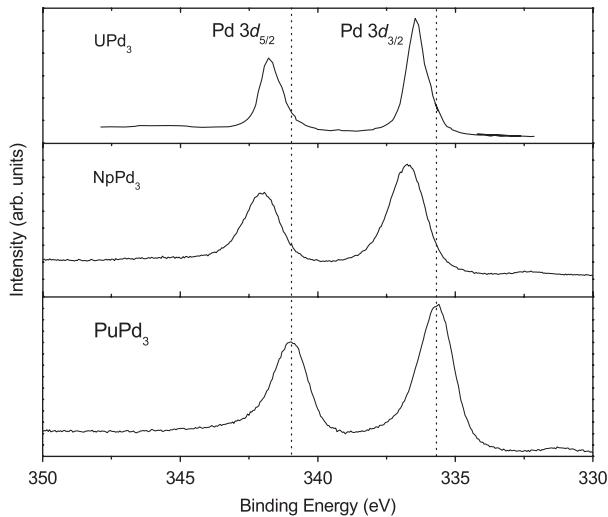
He I radiation and thus probes preferentially adsorbed species. There is no evidence of any oxide formation on the surface and we did not detect any higher binding energy satellites in the core level 4f spectra of  $\text{NpPd}_3$  and  $\text{PuPd}_3$  similar to those observed in the actinide oxides [7]. The broad maximum around 3 eV binding energy, present in both He I and He II spectra, is due to the Pd 3d excitations.

Figures 2 and 3 show the x-ray photoelectron spectra (XPS), taken using Al  $K\alpha$  radiation with the same spectrometer described above. The energy resolution is  $\approx 1.0$  eV. Figure 2 shows the neptunium 4f core level transitions, whilst figure 3 shows the plutonium 4f transitions.

For comparison, the figures also show reference spectra for Np and  $\alpha$ -Pu which are the delocalized cases. The spectra of both compounds are shifted to about 3 eV higher binding energy, compared to the metallic cases. A similar behaviour was observed for  $\text{UPd}_3$  and U, which was taken as evidence for 5f localization and explained by the screening model [7]. In this model, the 5f states, upon localization, lose their capability to screen the photohole which is created after emission of the

4f electron. Screening is instead performed by the extended ds states. However, this screening is less efficient, due to the larger size of the ds orbitals, and results in a displacement of the photoemission line to higher binding energy (BE). Close to the localization threshold (for weakly hybridized f states) both screening types may co-exist, as e.g. in  $\alpha$ -Pu, where the ds-screened peak appears as a high BE satellite on the f-screened (well screened) main line (figure 3). In Np metal (figure 2), no high BE satellite is observed showing the 5f states to be well delocalized. But in both compounds, all intensity is shifted to the high BE position, which shows the 5f states to be well localized. It is to be noted that the peaks in the 4f core spectra of  $\text{PuPd}_3$  actually coincide quite closely with the poorly screened peaks in  $\alpha$ -Pu.

Supplementary indication for 5f localization is provided by the broadened shape of the 4f emission in the compounds, compared to the pure metals, which is due to exchange splitting between the 4f hole and the localized 5f states that is not resolved. This is analogous to the splitting of the s core levels of the rare earths by the 4f states [8]. Similar broadening



**Figure 4.** X-ray photoelectron spectra of the core Pd 3d levels in  $\text{UPd}_3$ ,  $\text{NpPd}_3$ , and  $\text{PuPd}_3$ . Note that  $\text{UPd}_3$  crystallizes in the hexagonal  $\text{TiNi}_3$  structure, whereas the spectra shown for  $\text{NpPd}_3$  and  $\text{PuPd}_3$  are from samples with the cubic  $\text{AuCu}_3$  structure.

is observed between U and Am, and explained by the 5f localization in Am metal [9]. In addition, the 4f peaks in both Np and  $\alpha$ -Pu show an asymmetric shape which is due to e-h pair formation of conduction electrons from scattering by the core-hole potential [10]. This is directly proportional to the density of states at the Fermi level. Thus the symmetrical shape of the 4f emission in the compounds compared to the metal shows that the DOS at  $E_F$  is drastically reduced. This directly correlates with 5f localization and is consistent with the valence band spectra in figure 1, where the 5f states are shown to be shifted away from the Fermi level.

The 4f XPS spectra in  $\text{NpPd}_3$  also exhibits a satellite at about 7 eV higher binding energy than the main  $4f_{5/2}$  peak as indicated by the arrow in figure 2. Similar satellites for both the  $4f_{5/2}$  and  $4f_{7/2}$  spin orbit components were also observed in many localized uranium compounds [11], including  $\text{UPd}_3$  [12], and also in  $\text{NpO}_2$  [13]. Using the Anderson impurity model, the satellites may be attributed to a final state which is an antibonding mixture of the  $4f^{13}5f^n$  and  $4f^{13}5f^{n+1}$  configurations ( $n = 4$  for Np), mixed by fd hybridization, whereas the main line is due to a bonding mixture. That satellites are not observed in the 4f spectra in  $\text{PuPd}_3$  may indicate that the  $4f^{13}5f^n$  ( $n = 5, 6$ ) configurations in  $\text{PuPd}_3$  have larger energy separations and so are more weakly mixed.

Finally, figure 4 shows the Pd 3d core levels for  $\text{UPd}_3$ ,  $\text{NpPd}_3$  and  $\text{PuPd}_3$ , and the chemical shift in energies between the different compounds. There is a shift of  $\approx 1$  eV between the levels of  $\text{NpPd}_3$  and  $\text{PuPd}_3$ , and a shift of  $\approx 0.3$  eV between

$\text{NpPd}_3$  and  $\text{UPd}_3$ . These small shifts in the binding energy may indicate slight changes of screening of the core Pd electrons in the different compounds.

In conclusion, we have measured the photoelectron spectra of  $\text{NpPd}_3$  and  $\text{PuPd}_3$ , showing that the valence and core level spectra are both consistent with a picture of localized 5f electrons, in agreement with measurements of the bulk properties of these compounds.

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