PHYSICA B

# Fermi level tuning and the Kondo resonance in $Y_{1-x}U_xPd_3$

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This paper presents a review of the electronic structure of $Y_{1-x}U_xPd_3$, along with new data on Fermi level tuning in this alloy and in $Th_{1-x}U_xPd_3$.

## 1. Introduction

In the past year $Y_{1-x}U_xPd_3$ has emerged as an exciting alloy system from at least two viewpoints [1–3]. First, we have found [1] that the Kondo effect that is observed for $x < 0.3$ has special properties implying non-Fermi liquid behavior. Thus this system joins the high temperature superconducting cuprates as a possible example of a new paradigm for condensed matter physics. It appears that the basic origin of the non-Fermi liquid behavior is the quadrupolar Kondo effect [4], which is a special case of the n-channel Kondo model known theoretically to lead to a local non-Fermi liquid [4,5]. It may also be that intersite interactions are important in determining the properties observed [2]. Second, we have found [3] that the transport and electron spectroscopy properties of the 5f electrons vary with $x$ in a way that is qualitatively consistent with the Kondo regime of the impurity Anderson model. This is the first uranium system in which the picture that works semiquantitatively for cerium [6,7] can be demonstrated even qualitatively, and it provides some insight into the difficulty of interpreting electron spectroscopy data for heavy Fermion uranium systems.

This paper focuses on electron spectroscopy studies of this alloy system, relevant largely to the second of

these two aspects. These studies show that the Fermi energy shifts considerably with $x$, a phenomenon we have called "Fermi level tuning", and which we believe is the major mechanism for the variation of the transport properties with $x$. They also provide evidence for the observation of the Kondo resonance for $x < 0.3$. A review of recent published work is given, along with some previously unpublished data concerning Fermi level tuning in both $Y_{1-x}U_xPd_3$ and the related system $Th_{1-x}U_xPd_3$.

## 2. Electronic structure of the 5f electrons of $Y_{1-x}U_xPd_3$

Figure 1 provides an overview of our findings [3] concerning the electronic structure of the 5f electrons of $Y_{1-x}U_xPd_3$, through a comparison of the 5f spectra for $x = 1$ and $x = 0.1$ with that for the heavy fermion compound $UPt_3$. The portions of the spectra below the Fermi energy $E_F$ have been obtained by resonant photoemission spectroscopy (RESPES), which exploits a large enhancement of the 5f emission for the photon energy $h\nu$ around the uranium $5d \rightarrow 5f$ absorption edge, 90 eV $< h\nu <$ 110 eV, to extract the 5f emission from the rest of the valence band. This is essential even for $x = 1$ due to the large emission from the Pd 4d states. The portions of the spectra above $E_F$ are obtained from Bremsstrahlung isochromat spectroscopy (BIS) performed at $h\nu = 1486.6$ eV. For the top two curves, the 5f BIS spectra have been extracted by subtracting out the BIS spectrum for $x = 0$. Although this is essential for $x = 0.1$, it is less important for $x = 1$ because the large number of 5f holes, and the

large 5f cross-section for $h\nu = 1488.6$ eV, make the 5f contribution the dominant one. For the $UPt_3$ curve at the bottom, only a flat background has been removed.

The top curve of fig. 1 shows the 5f spectrum of $UPd_3$. $UPd_3$ is not a heavy fermion material, but it is the only uranium intermetallic with a 5f spectrum which suggests an Anderson model. The spectrum has a gap around $E_F$ with peaks below and above $E_F$, which are interpreted [8], respectively, as a $5f^2 \rightarrow 5f^1$ ionization peak and a $5f^2 \rightarrow 5f^3$ affinity peak, separated by a Coulomb energy $U_{ff} \sim 2$ eV. This assignment is supported by experimental and theoretical evidence [9–13].

The middle curve of fig. 1 shows the spectrum of $Y_{0.9}U_{0.1}Pd_3$. The ionization peak has shifted from its position about 1 eV below $E_F$ in $UPd_3$ to being very near $E_F$. This shift of the 5f photoemission peak was observed in our first RESPES work [14] on this alloy system and was interpreted as a shift, or "tuning", of the Fermi level because $U^{4+}(5f^2)$ is replaced by $Y^{3+}$. In the Anderson model, the Kondo temperature $T_K \sim \exp(-1/J)$ with the Kondo coupling constant $J \sim 1/|\epsilon_f|$, where $|\epsilon_f|$ is the 5f ionization energy. Thus $T_K$ is expected to increase as $|\epsilon_f|$ decreases, providing the motivation for our transport and additional electron spectroscopy studies. The new photoemission studies, some of which are presented in the next section, provide strong confirmation of the Fermi level tuning picture. The transport and BIS data also sup-

port the Fermi level tuning picture, and provide strong evidence for the Kondo effect.

The BIS spectra of this alloy system have been presented and discussed in detail in ref. [3], focusing on our interpretation that they provide evidence for the first observation of the Kondo resonance in a uranium material. For large $x$, they also confirm the Fermi level tuning picture in that the peak above $E_F$ shifts further away from $E_F$ relative to its position in $UPd_3$, as expected if $E_F$ is in fact shifting towards the ionization peak in the photoemission spectrum. For $x < 0.3$, the spectra reveal a new and very interesting feature, namely a growth of weight near $E_F$ which tends to fill in the gapped spectrum of $UPd_3$. This new weight can be seen clearly in the $Y_{0.9}U_{0.1}Pd_3$ spectrum of fig. 1 above $E_F$. As reported in ref. [3], the resistivity $\rho$ as a function of temperature $T$ for $x = 0.1$, 0.2 and 0.3 displays a logarithmic increase with decreasing temperature, which is a well known signature of the Kondo effect. $T_K$ can be estimated as the temperature where $\rho$ begins to saturate and it is found that $T_K$ increases as $x$ decreases, consistent with the expectations based on the Fermi level tuning picture and the impurity Anderson model. In analogy to the weight which builds as $T_K$ increases in the BIS spectra of cerium materials [6,7], we interpret the growing BIS weight near $E_F$ in $Y_{0.9}U_{0.1}Pd_3$ as the Kondo resonance. A further presentation of the BIS data is given later in this paper, in the course of discussing the BIS spectra of $Th_{1-x}U_xPd_3$.

The bottom curve of fig. 1 shows that the 5f spectrum of $Y_{0.9}U_{0.1}Pd_3$ is very similar to that of the heavy fermion uranium compound $UPt_3$. This $UPt_3$ spectrum is typical of 5f spectra for these materials. It has been a puzzle [15,16] that these materials, for which $T_K$ would be very small in the Anderson model, do not display a cerium-like spectrum with small weight around $E_F$ and separated ionization and affinity peaks that would provide a measure of $U_{ff}$. Indeed, the rather band-like appearance of the spectrum has caused doubt that the Anderson model could be a useful starting point for discussing these materials. The fact that the gapped spectrum of $UPd_3$ evolves, upon dilution of U, into a spectrum like that of $UPt_3$ is very strong evidence against a band model, and in favor of an Anderson model, as a starting point for discussing heavy fermion 5f materials. Within the Anderson Hamiltonian framework, the absence of an $E_F$ peak in $UPd_3$ must be attributed to the very small value of $T_K$ which occurs as $|\epsilon_f|$ increases with $x$. This value can be estimated by extrapolating from the measured small-$x$ values of $T_K$ to be 0.1 K at $x = 1$.

It is important to rationalize, at least qualitatively, the differences between the f spectra of cerium and
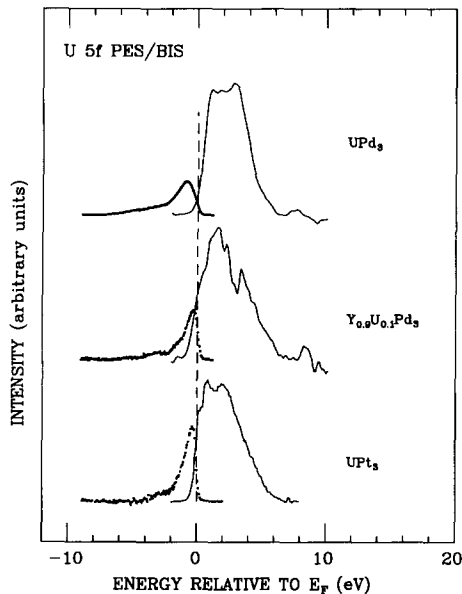


Fig. 1. U 5f spectral weight of (a) $UPd_3$, (b) $Y_{0.9}U_{0.1}Pd_3$, and (c) $UPt_3$ (from ref. [15]). Entire figure from ref. [3].

uranium materials. Within the Anderson Hamiltonian framework, two factors act to obscure the high energy scales of the model, and give the rather bandlike appearance. First, $U_{ff}$ for uranium, $\sim$2 eV, is smaller than the 6-eV value for cerium, which results in a much smaller separation between the ionization and affinity peaks. Second, the $U^{4+}$ $f^2$ state has multiplet splittings which spread over more than 2 eV, while for the $Ce^{3+}$ $f^1$ state, the largest splitting is the spin-orbit splitting of $\sim$0.28 eV. For Ce, this splitting is known [6,17,18] to produce spin-orbit sidebands on the Kondo resonance which extend it away from $E_F$ and contribute considerable extra weight. As pointed out previously [15,16], for uranium the additional multiplet splittings are expected to result in a much broader sideband spectrum and much more total weight associated with the resonance than occurs for a cerium material with a similar $T_K$. Another very important issue, discussed by Cox [4], is that uranium materials with smaller $U_{ff}$, smaller $|\epsilon_f|$, and larger hybridization, because their 5f wave functions are more extended than the 4f wave functions of Ce, can nonetheless have equally small values of $T_K$. Cox has calculated for $U^{4+}$ the configuration overlap factor [19] which enters the hybridization parameter $V$ in the Anderson model, and finds that its smallness more than compensates the other differences.

## 3. Further evidence for Fermi level tuning in $Y_{1-x}U_xPd_3$

In this section we present previously unpublished photoemission spectra which provide strong support

for Fermi level tuning in $Y_{1-x}U_xPd_3$. These data are presented in figs. 2, 3 and 4. The figures also show, for comparison, data for the system $Th_{1-x}U_xPd_3$, discussed in the next section.

Figures 2 and 3 show, respectively, the Pd 3d and Y 3d core level spectra obtained by X-ray photoemission spectroscopy (XPS) performed at $h\nu = 1486.6$ eV. Both core levels shift towards $E_F$ as $x$ decreases, by amounts that are similar to each other and to the shift of the 5f valence band feature, as would be expected in the Fermi level tuning picture. As will be discussed in more detail in a future paper, there are differences of the order of 10–20% in the magnitudes of the



Fig. 3. XPS core level spectra of Y 3d in $Y_{1-x}U_xPd_3$ (left panel) and Th 4d and U 4d in $Th_{1-x}U_xPd_3$ (right panel). Note presence and absence of shifts in the left and right panels, respectively.
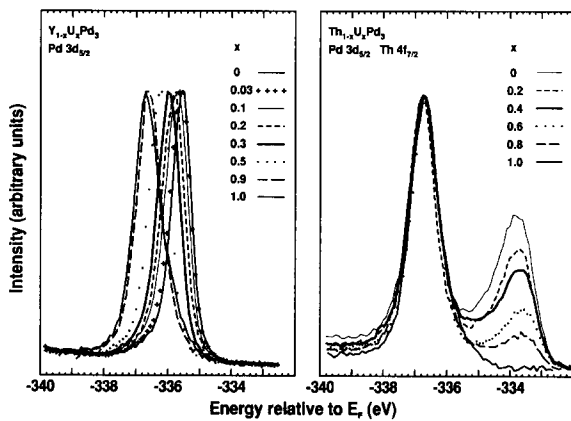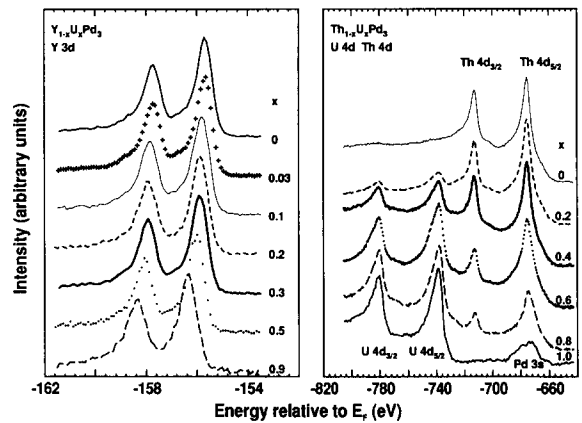


Fig. 2. XPS core level spectra of Pd $3d_{5/2}$ in $Y_{1-x}U_xPd_3$ (left panel) and Pd $3d_{5/2}$ and Th $4f_{7/2}$ in $Th_{1-x}U_xPd_3$ (right panel). Note presence and absence of shifts in the left and right panels, respectively.
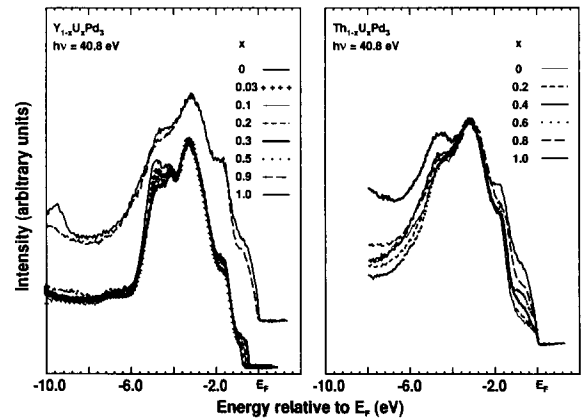


Fig. 4. UPS valence band spectra for $Y_{1-x}U_xPd_3$ (left panel) and $Th_{1-x}U_xPd_3$ (right panel). The left panel spectra are shifted to align the main valence band features, showing the shifting Fermi edge clearly. The right panel spectra are unshifted.

shifts, especially at values of $x < 0.3$. These differences indicate that there is some charge redistribution among the various sites, in addition to the shift of $E_F$. These effects may well be important for interpreting transport data at a more detailed level in the future. It is important to note that none of the core levels show any tendency to be split, which enables us to rule out surface phase separation for this alloy system.

Figure 4 shows the valence band spectra obtained with ultraviolet photoemission spectroscopy (UPS) measured with a laboratory helium lamp for $h\nu = 40.8$ eV. The resolution is about 80 meV. At this photon energy, the U 5f states are hardly observable, and cannot be seen for $x \leq 0.5$. In the figure, the data has been shifted to line up the main features of the valence band, which are essentially unchanged with $x$. It is clear that $E_F$ shifts toward the large peaks of the Pd 4d states with decreasing $x$. Note that the shape of the density of states around $E_F$ is rather flat, and that the magnitude hardly changes with $x$. Further details of these data will be published elsewhere. Taken together with the XPS spectra, these data make the case for our Fermi level tuning picture in this alloy series unambiguous.

## 4. $Th_{1-x}U_xPd_3$

Another way to test the entire picture that has been presented for $Y_{1-x}U_xPd_3$ is to study the alloy series $Th_{1-x}U_xPd_3$. Th is expected to take the 4+ valence state so that $E_F$ should not shift with $x$ in this alloy, since U and Th would have the same valence. This section presents UPS and BIS data for $Th_{1-x}U_xPd_3$ and compares them with the data for $Y_{1-x}U_xPd_3$.

Figure 2 shows the Pd 3d and Th 4f XPS core level spectra, which overlap, and fig. 3 shows the Th 4d XPS spectra. It is clear that these spectra do not shift with $x$, as we expect if $E_F$ does not shift. Figure 4 shows the valence band UPS spectra for the alloy. In contrast to the UPS spectra shown in fig. 4 for $Y_{1-x}U_xPd_3$, $E_F$ does not shift and the spectra themselves are presented in the figure unshifted.

Figure 5 shows the BIS spectra for both $Th_{1-x}U_xPd_3$ and $U_{1-x}U_xPd_3$. We discuss first the latter BIS data, which have already been published in ref. [3], and analyzed there to extract the U 5f emission. As $x$ decreases, the U 5f intensity decreases, and for $x \geq 0.5$, it is clear that the peak shifts away from $E_F$ with decreasing $x$, as expected. The $x = 0$ spectrum is well understood [20] to reflect the band structure [21] of $YPd_3$. The peak centered at 2.7 eV arises from antibonding states of Y and Pd 4d character and is generic to a broad class of similar intermetallics. In
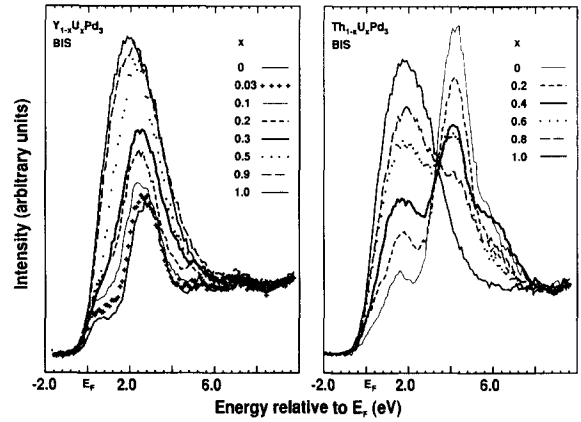


Fig. 5. BIS spectra for $Y_{1-x}U_xPd_3$ (left panel) and $Th_{1-x}U_xPd_3$ (right panel).

extracting the 5f emission by subtracting the spectrum for $x = 0$ from the spectrum for some nonzero value of $x$ [3], it was assumed that the antibonding feature persisted in the alloy series, but with its energy shifted relative to $E_F$ due to the shift in $E_F$. Thus, before the subtraction, the $E_F$ of the $x = 0$ spectrum was shifted toward the antibonding peak by an amount taken from the UPS spectra shown in fig. 4, and then cut off at the new $E_F$ with a step function broadened by the experimental resolution.

The BIS spectra for $Th_{1-x}U_xPd_3$ substantiate our analysis of the spectra for $Y_{1-x}U_xPd_3$. As $x$ decreases from 1, the uranium 5f peak near $E_F$ decreases without shifting, as expected if $E_F$ does not shift. The Th $5f^0 \rightarrow 5f^1$ transition grows at 4.2 eV, also without shifting. The peak in the $x = 0$ spectrum centered at 1.6 eV is assigned as the antibonding peak. That it is shifted about 1.1 eV nearer $E_F$ than the corresponding peak in $YPd_3$, an amount of the same order as the $E_F$ shift in $Y_{1-x}U_xPd_3$, is again consistent with our Fermi level tuning picture, and our BIS data analysis in $Y_{1-x}U_xPd_3$, since $Th^{4+}$ and $Y^{3+}$ have different valances. The difference between the 1.1 eV shift from $YPd_3$ to $ThPd_3$ and the 0.8 eV shift in the $Y_{1-x}U_xPd_3$ series is probably a measure of the modest error involved in assuming that the Y 5d, U 6d and Th 6d states are perfectly isoelectronic in the formation of the antibonding peak.

## 5. Summary

In summary, as $Y^{3+}$ replaces $U^{4+}$ in the alloy system $Y_{1-x}U_xPd_3$, $E_F$ moves towards all the peaks of the XPS, UPS and RESPES spectra, and away from the BIS 5f peak. For $x \leq 0.3$, the transport properties

show Kondo behavior and the BIS spectrum displays a growth of weight at $E_F$, which we interpret as the Kondo resonance. The XPS, UPS and BIS spectra of the alloy system $Th_{1-x}U_xPd_3$, for which we expect U and Th both to take the 4+ valence state, support this picture in that $E_F$ does not shift, and that transport properties, which will be reported elsewhere, do not display Kondo behavior for any value of $x$.

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