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Fermi-level tuning in $Y_{1-x}U_xPd_3$

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The $5f$ -electron photoemission peak 1 eV below the Fermi energy E_F in UPd_3 is generally assigned as a $5f^2 \rightarrow 5f^1$ transition, consistent with other evidence of a stable U^{4+} valence state. We report resonant photoemission spectra for the system $Y_{1-x}U_xPd_3$ which show that the peak narrows and shifts to the Fermi level as x decreases from 1. We hypothesize that the shift arises from a decrease in the Fermi energy as Y^{3+} replaces U^{4+} , and therefore expect interesting changes in transport properties as E_F is tuned in this way.

The diverse ground-state properties of uranium compounds, especially heavy-fermion magnetism and superconductivity,¹ have stimulated much work aimed at developing a unified understanding of their spectroscopic and low-energy electronic properties.²⁻⁹ However, most uranium compounds do not show a correlation between the measured uranium $5f$ -electron spectrum and the ground-state properties. Their spectra have in common much f weight around the Fermi energy, although the ground-state properties are different from compound to compound. Further, for uranium compounds^{10,11} studied to date, it has been found that the major large-energy-scale features of the $5f$ -electron spectrum change only slightly or not at all with uranium dilution. In this paper, we report a departure from this unenlightening pattern, namely, the observation that significant changes occur in the $5f$ -electron photoemission spectrum of $Y_{1-x}U_xPd_3$ as x is varied between 0.02 and 1.0.

UPd_3 was chosen for this dilution study because it plays a special role as the one intermetallic material where all properties seem to be consistent with a localized description of the $5f$ electrons. Neutron scattering is observed, which is consistent with crystal-field levels of an f^2 singlet ground state.¹²⁻¹⁵ The Fermi-surface electron masses measured in de Haas-van Alphen experiments are not large,¹⁶ and the T -linear specific-heat coefficient is typical of a normal metal,¹⁷ suggesting negligible $5f$ -electron density of states at the Fermi level E_F . A large disagreement between calculated and experimental values of the volume of UPd_3 (Ref. 18) suggests that the $5f$ electrons do not contribute to the cohesive energy. Finally, UPd_3 is the only uranium intermetallic compound for which the $5f$ -electron spectral weight, determined by photoemission spectroscopy (PES) and bremsstrahlung isochromat spectroscopy (BIS), shows a gap around E_F , with peaks below and above E_F .¹⁹⁻²² The PES and BIS spectra are inter-

puted to show, respectively, the $f^2 \rightarrow f^1$ and $f^2 \rightarrow f^3$ transitions expected for a stable f^2 valence, and the separation between the two spectra is taken as a measure of the Coulomb interaction U_{ff} .^{19–21}

In the rest of the paper we describe the highly interesting finding that uranium dilution in $Y_{1-x}U_xPd_3$ causes the $5f$ -electron PES peak to narrow and move from being about 1 eV below E_F to being very near E_F . This peak shift occurs gradually and is not correlated with a crystal structure change that takes place between $x=0.5$ and 0.9, as discussed further below. Our explanation of the peak shift, also presented below, retains the $f^2 \rightarrow f^1$ identification of the peak. Within this framework, implicitly that of an Anderson model, we expect, by analogy to rare-earth mixed-valence and Kondo systems, that as the $5f$ -state energy moves toward E_F , there will be an increase in the magnitude of the $5f$ -electron virtual charge fluctuations and hence in the spin fluctuations which control ground-state and low-energy transport properties. Thus we expect that the transport properties of the system will change, offering an all too rare opportunity to correlate the spectroscopic and transport behaviors of a uranium system.

Polycrystalline samples were prepared by arc-melting stoichiometric amounts of the constituent elements in an arc furnace and characterized by x-ray diffraction. In the alloy system $Y_{1-x}U_xPd_3$, there is a change in crystal structure with a rather broad mixed-phase region from $x=0.5$ to 0.9. From $x=0$ to 0.5 the compounds have the cubic Cu_3Au -type crystal structure,²³ and from $x=0.9$ to 1.0, the hexagonal Ni_3Ti type.²⁴ The lattice parameter of the cubic phase varies from 4.074 Å for $x=0$ to 4.080 Å for $x=0.5$. We consider that the change in the lattice parameter is too small to be the direct cause of spectral changes as the uranium is diluted.

Resonant photoemission spectroscopy (RPES) was performed on beam line III-1 at the Stanford Synchrotron Radiation Laboratory, by using photons obtained from the beam line's grasshopper monochromator. A recent critical evaluation²⁵ has confirmed the applicability of RPES to $5f$ -electron spectra. The samples were cleaved and measured at a temperature of about 200 K in a vacuum of 8×10^{-11} Torr. The primary purpose of cooling the sample is to slow the diffusion of oxygen from the bulk to the cleaved surface, thereby prolonging the lifetime of the clean surface. The Fermi level of the system was determined from the valence-band spectrum of a gold sample evaporated onto a stainless-steel substrate *in situ*. A commercial cylindrical mirror analyzer (CMA) was used to measure electron kinetic energies. With the CMA operated to obtain a good signal-to-noise ratio, its resolution was poorer than that of the photon monochromator, and thus largely determined the overall resolution of 0.5 eV for the data presented here. A resolution of 0.35 eV did not reveal additional structure. For normalization of the spectra, the photon flux was monitored by the yield from a stainless-steel target. Inelastic backgrounds were removed from the spectra by a standard method.²⁶

Figure 1 shows the normalized valence-band spectra of UPd_3 for $h\nu=102$ and 108 eV, where the U $5f$ emission is resonantly suppressed and enhanced, respectively, due to a

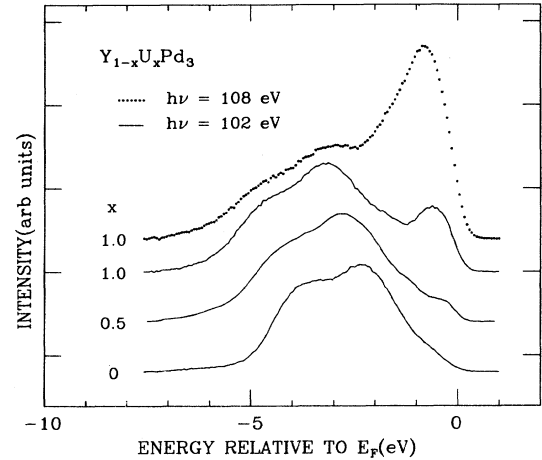


FIG. 1. Normalized energy distribution curves for $Y_{1-x}U_xPd_3$ with $h\nu=102$ eV for $x=0, 0.5,$ and 1.0 and $h\nu=108$ eV for $x=1.0$. Note the resonant enhancement of U $5f$ emission and the shift of the Pd $4d$ emission between -2 and -6 eV toward E_F as x decreases.

Fano resonance in the $5f$ -electron cross section at the U $5d$ edge.²⁰ The more extreme minimum and maximum which occur for $h\nu=92$ and 98 eV, respectively, are not used in this study because the shape of the Pd $4d$ emission from -2 to -5 eV is more nearly constant between 102 and 108 eV than between 92 and 98 eV. The other $h\nu=102$ eV spectra in Fig. 1 show that for decreasing x in $Y_{1-x}U_xPd_3$ the two Pd $4d$ peaks move toward E_F with their separations remaining more or less the same. The emission nearer E_F in these spectra is an uncertain mix of U $6d$ and incompletely suppressed U $5f$. The U $5f$ spectral weight was extracted by subtracting the 102 eV spectrum from the 108 eV spectrum, after scaling the former by a factor of 0.47 to account for the $h\nu$ dependence of the non- $5f$ -electron emission, determined from the $h\nu$ dependence of the Pd $4d$ peaks for $x=0$. For $x=0.02$, the effect of the Pd $4d$ shape change is large enough to produce a substantial non- $5f$ -electron contribution in the energy range between -2 and -5 eV and therefore the $h\nu=108$ eV spectrum for $x=0$ was subtracted from that for $x=0.02$, after scaling determined by matching the $h\nu=102$ eV spectra for $x=0$ and 0.02.

Figure 2 compares the extracted $5f$ -electron spectra for $x=1.0, 0.9, 0.5,$ and 0.1 , scaled to have the same magnitude at the peak. The relative areas under the $5f$ -electron spectra, when normalized by taking the $h\nu=102$ eV spectra to have the same magnitudes, are satisfactorily close to the ratios of the corresponding uranium concentrations, i.e., $A(x=1.0):A(0.9):A(0.5):A(0.1)=10.0:9.3:5.1:1.4$. The $5f$ -electron spectrum for $x=1.0$ is essentially the same as previously reported in the literature.^{19,20} The inset shows the full width at half maximum (FWHM) of the U $5f$ spectral distribution versus x . Figure 3 compares the extracted $5f$ -electron spectra for $x=0.02$ and 0.1, scaled to have the same peak intensities. Before the scaling, the ratio of the areas under the extracted $5f$ -electron curves is $A(x=0.02)/A(x=0.1)=0.21$, again very close to the ratio of the x values.

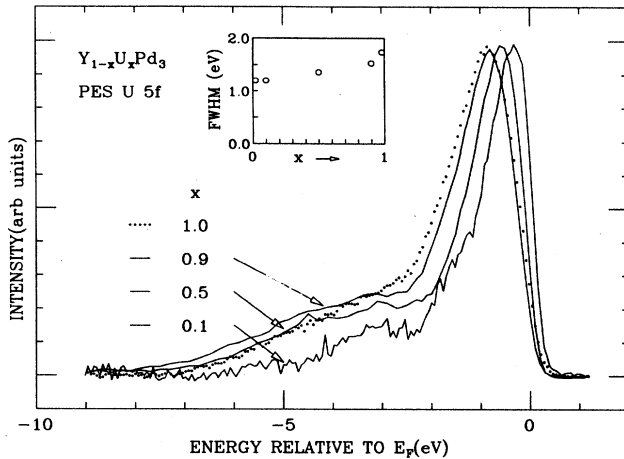


FIG. 2. U 5f spectral weight for $x=0.1, 0.5, 0.9,$ and 1.0 in the $Y_{1-x}U_xPd_3$ system, obtained as described in the text. Note that the 5f-electron peak moves to the Fermi energy as x decreases. Inset shows that the U 5f FWHM decreases as x decreases.

The important features of Figs. 1 and 2 are that with decreasing x the centroid of the 5f-electron peak moves toward E_F and its width becomes narrower, while the Pd 4d peaks move toward E_F as well. These changes occur without abrupt behavior at any x , including the range of the crystal-structure change. Figure 3 shows that the main features of the spectra for $x=0.02$ are essentially the same as those for $x=0.1$, within the experimental uncertainty. The resolution of these data does not let us know how close to E_F is the $f^2 \rightarrow f^1$ transition peak for small x .

We offer an interpretation of our result which is consistent with evidence summarized above suggesting a stable $5f^2$, i.e., U^{4+} , valence state in UPd_3 . As stated above, the volume change with x is very small. This is explained quite naturally if we assume that uranium is present for $x=0$ as U^{4+} , and that upon dilution it is replaced with Y^{3+} , because the Goldschmidt radius²⁷ of U^{4+} , 1.05 Å, is only 0.01 Å different from that of Y^{3+} . It is significant for this argument that the ionic radius^{27,28} of U^{3+} is much larger than that of U^{4+} . Dilution with Y^{3+} then reduces the number of conduction electrons by 1 per unit cell as x changes from 1 to 0. It is then important that our PES spectrum and the BIS spectrum²⁹ of YPd_3 show very small conduction-band density of states at E_F . Energy-band calculations predict this result and give a value of ~ 1 states per eV cell²³ over the range from E_F to ~ 2 eV above E_F , implying that as x changes from 0 to 1, the Fermi level should shift by ~ 1 eV, increasing its separation from the 5f-electron peak by about the amount observed. The separation between E_F and the Pd 4d states should then increase by a similar amount as x changes from 0 to 1, as observed. This picture also implies that the separation between E_F and the 5f-electron BIS peak should increase as uranium is diluted, so that dilution BIS studies would be useful. Although resonant BIS cannot be performed with the typical fixed photon energy x-ray BIS system, it may be possible to obtain the diluted U 5f spec-

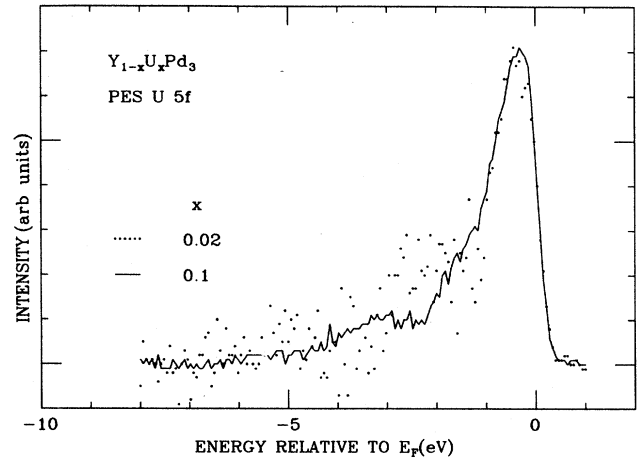


FIG. 3. U 5f spectral weight for $Y_{0.9}U_{0.1}Pd_3$ (solid line) and $Y_{0.98}U_{0.02}Pd_3$ (dotted data), identical within experimental error.

trum by comparing spectra for different x , if a sufficient signal-to-noise ratio can be achieved for small x . We plan to pursue the BIS measurements in the near future, as well as PES measurements to see whether core levels also shift relative to E_F . That the 5f-electron peak narrows with dilution suggests that part of its width in UPd_3 arises from coupling between uranium atoms, either directly or indirectly via U-Pd hybridization.

Before concluding, we remark on the lack of 5f-electron weight around E_F in UPd_3 . In the model employed here, it means that U-Pd hybridization does not result in a large Kondo temperature, which would yield a large Kondo resonance at E_F , as occurs in many cerium-transition-metal intermetallics.²⁶ It is not obvious that U-Pd hybridization should be intrinsically weaker than that between uranium and other transition metals, e.g., the U-Rh hybridization in URh_3 , which has large 5f-electron weight around E_F .⁷ A possible explanation is that the virtual valence fluctuations leading to a Kondo effect are suppressed by a very small conduction-electron density of states at E_F , which is common to YPd_3 and UPd_3 .^{20,23}

To summarize, our major finding is that the centroid of the uranium 5f-electron peak shifts toward E_F by ~ 1 eV as uranium is diluted in the $Y_{1-x}U_xPd_3$ system, while its width becomes narrower. The change is not correlated with a change in the crystal structure. We explain this in a model based on a stable U $5f^2$ valence state and a shift of the Fermi level as x is varied, with the unusually large magnitude of the effect arising from the very small density of conduction electron states at E_F . The resulting picture provides a strong motivation for measuring the transport properties of this system, and such measurements are now in progress.

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