

## 5*f* Electron Localization-Delocalization Transition from UPd<sub>3</sub> to UPt<sub>3</sub>

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The electronic structures of URh<sub>3</sub>, UPd<sub>3</sub>, UPt<sub>3</sub>, and UAu<sub>3</sub> are calculated with the self-interaction corrected local-spin-density approximation. We find that only in URh<sub>3</sub> the *f* electrons are fully delocalized. UPt<sub>3</sub> has one *f* electron localized at each U site, while a localized *f*<sup>2</sup> configuration of the U ion is found for UPd<sub>3</sub>. It is predicted that, upon application of a pressure of 25 GPa, UPd<sub>3</sub> will acquire the *f*<sup>1</sup> configuration and possibly exhibit heavy-fermion behavior. We find that UAu<sub>3</sub> is characterized by the same mixed localized-delocalized *f*-electron manifold as UPd<sub>3</sub>.

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In order to predict the electronic properties of the actinide intermetallics, it is crucial to understand the nature of the 5*f*-electrons involved. Whether the *f* electrons are localized, itinerant, or in between, depends on the actinide separation and the specifics of the alloying element [1]. Consequently, even slight changes in the chemical compositions can lead to quite significant changes in electronic structure. With respect to the electronic configuration of its constituent atoms, UPd<sub>3</sub> and UPt<sub>3</sub> are very similar compounds. Apart from the chemically inactive core electrons, Pd ([Kr]4*d*<sup>10</sup>5*s*<sup>0</sup>) and Pt ([Xe]4*f*<sup>14</sup>5*d*<sup>10</sup>6*s*<sup>0</sup>) are isoelectronic. However, experimental measurements show that UPd<sub>3</sub> and UPt<sub>3</sub> have dramatically different electronic properties. UPt<sub>3</sub> has an enhanced linear specific heat coefficient  $\gamma$ , characteristic of heavy fermion materials, and has been shown to become superconducting at low temperatures [2]. The large specific heat coefficient is correlated to a large density of states (DOS) at the Fermi level, implying a narrow *f* band, i.e., itinerant *f* electrons. In UPd<sub>3</sub>, on the other hand, the experimental studies clearly indicate that the *f* electrons are localized on the U sites [3,4]. URh<sub>3</sub> (Rh has one *d* electron *less* than Pd) is metallic, and the susceptibility and resistivity measurements suggest a broad band crossing the Fermi level [5]. In UAu<sub>3</sub>, with Au having one *d* electron *more* than Pt, the XPS spectra have been interpreted in terms of itinerant 5*f* electrons [6].

Heavy fermion behavior can be studied by applying pressure or by alloying, say UPt<sub>3</sub> with Pd, i.e., by going from a well-known heavy fermion system to a normal state behavior. In this work we argue that a reverse route to explore heavy fermion behavior is possible, where a normal system may become a heavy fermion one through the application of pressure. In particular, we predict that UPd<sub>3</sub> and UAu<sub>3</sub> could become heavy fermion systems at pressures of 25 and 13 GPa, respectively. Specifically, in this Letter we evaluate the energy for *f*-electron localization in the above mentioned U *f*<sup>2</sup> compounds. This then allows us to predict the pressure at which the localized *f* electron would become delocalized and hence possibly acquire heavy fermion character.

We use the self-interaction corrected (SIC) local spin-density (LSD) theory [7] to describe the *f*-electron localization, without adjustable parameters. This method has been successfully applied to describe the valency of rare-earth compounds [8,9] and of Am and Pu chalcogenides and pnictides [10]. In rare-earth compounds such as Ce monopnictides [11] and monochalcogenides [12] SIC-LSD calculations obtained accurate predictions for the transition pressure between phases with one and no localized *f* electrons on Ce. In the case of elemental Ce [13] those calculations described all features of the  $\gamma$  to  $\alpha$  transition such as transition pressure, volume collapse, and loss of magnetic moment. The valency transition in YbS was also well described [9], proving that the method is not restricted to systems with one *f* electron.

The transition pressure is determined by the common tangent construction between two total energy versus volume curves corresponding to two different valencies. Valencies are defined as  $N_{\text{val}} = Z - N_{\text{core}} - N_{\text{SIC}}$  where  $N_{\text{val}}$  is the number of valence electrons available for band formation,  $Z$  is the atomic number,  $N_{\text{core}}$  is the number of core states,  $N_{\text{SIC}}$  the number of self-interaction corrected states (i.e., localized states, which in the present case are states of predominantly *f* character). Therefore the calculations of transition pressures imply an accurate determination of total energies for *two* different valency configurations and hence also their energy differences.

Here we present the first study of pressure induced valency transitions for actinide compounds. In actinides the *f*-electron localization energy is typically less than half the value found in the rare earths ( $\sim 30$  mRy versus  $\sim 80$  mRy). This is a consequence of the 5*f* states being less tightly bound than the 4*f*'s. However, the physical effects of *f*-electron localization-delocalization in the 5*f*'s and the 4*f*'s are similar. In the following we will be concerned with discovering possibly new heavy fermion materials by applying external pressure.

The SIC-LSD approach has been implemented in the tight-binding linear muffin-tin orbital (LMTO) method [14]. Since we are dealing with U compounds we have included the spin-orbit interaction in the Hamiltonian [15].

The SIC-LSD approach allows one to selectively localize a chosen number of  $f$  electrons by correcting for the resulting unphysical self-interaction energy [16]. In this way the total energies of all different  $f$ -electron configurations can be compared. Those  $f$  electrons that are not self-interaction corrected are allowed to form bands and hybridize with the  $s$ ,  $p$ , and  $d$  conduction electrons, giving rise to a nonintegral number of itinerant  $f$  electrons. Thus two types of  $f$  electrons coexist in this approach: itinerant and localized. For each  $U$  compound, the  $f^2$ ,  $f^1$ , and  $f^0$   $U$ -ion configurations have been investigated. In terms of the number of the  $U$  valence electrons, i.e., the  $7s$ ,  $6d$ , and those  $5f$  electrons that are left itinerant, we refer to these configurations, respectively, as tetravalent, pentavalent, and hexavalent [8]. In the hexavalent configuration all the  $f$  electrons are treated as itinerant, which is equivalent to the LSD calculation.

In Fig. 1a, we show the total energies calculated with the SIC-LSD approach for different  $f$  configurations of the  $U$ -ion in  $UPd_3$ . The global energy minimum is found for the tetravalent configuration, with two SIC-localized  $f$  electrons. The corresponding equilibrium volume,  $V_{\text{tetv}} = 474.1 \text{ (a.u.)}^3$ , is in good agreement with the experimental

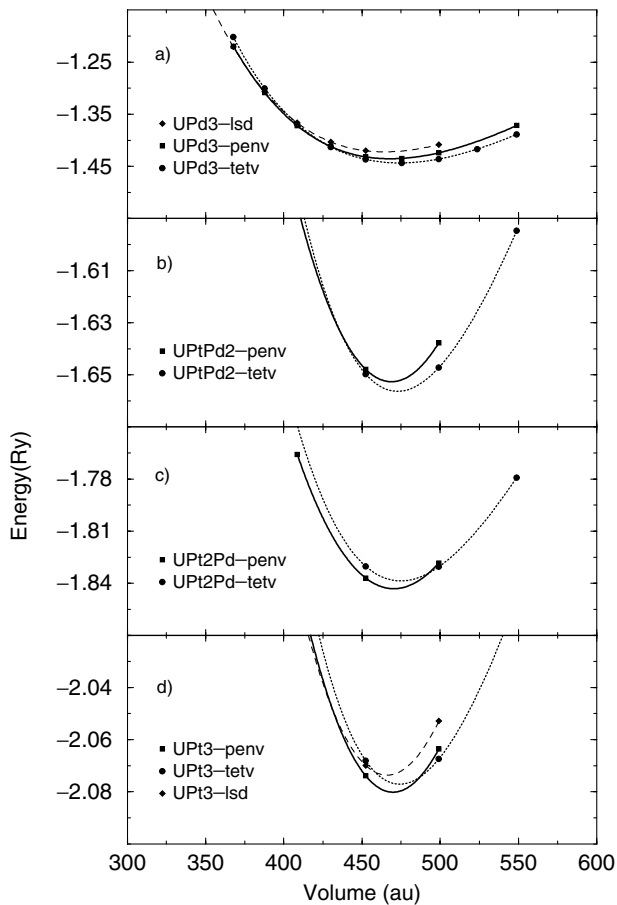


FIG. 1. Total energy (in Ry/f.u.) versus volume [in  $(\text{a.u.})^3$ ] for (a)  $UPd_3$ , (b)  $UPtPd_2$ , (c)  $UPt_2Pd$ , and (d)  $UPt_3$ .

value,  $V_{\text{exp}} = 469.5 \text{ (a.u.)}^3$  [17]. The total DOS for both the hexavalent and tetravalent configurations are shown in Fig. 2a. Only the states of itinerant character are shown, since the SIC-LSD approach, being a one-electron ground-state theory, does not give accurate removal energies of localized states, due to screening and relaxation effects [18]. The main difference between the respective two curves can be seen at the Fermi level, where in the  $f^2$  configuration most of the  $f$  weight has been transferred from the bottom of the  $f$  bands into the two localized states. Hence the density of states at the Fermi energy has become vanishingly small, in agreement with the results from XPS studies which have established the absence of noticeable  $f$  features at the Fermi level [3].

In  $URh_3$  we obtain the hexavalent configuration to be energetically most favorable. The calculated equilibrium volume  $V_{\text{hexv}} = 436.0 \text{ (a.u.)}^3$ , is in good agreement with the experimentally determined volume  $V_{\text{exp}} = 428.0 \text{ (a.u.)}^3$  [17], thus confirming the results from earlier LSD calculations [19]. In the corresponding DOS, the Fermi level

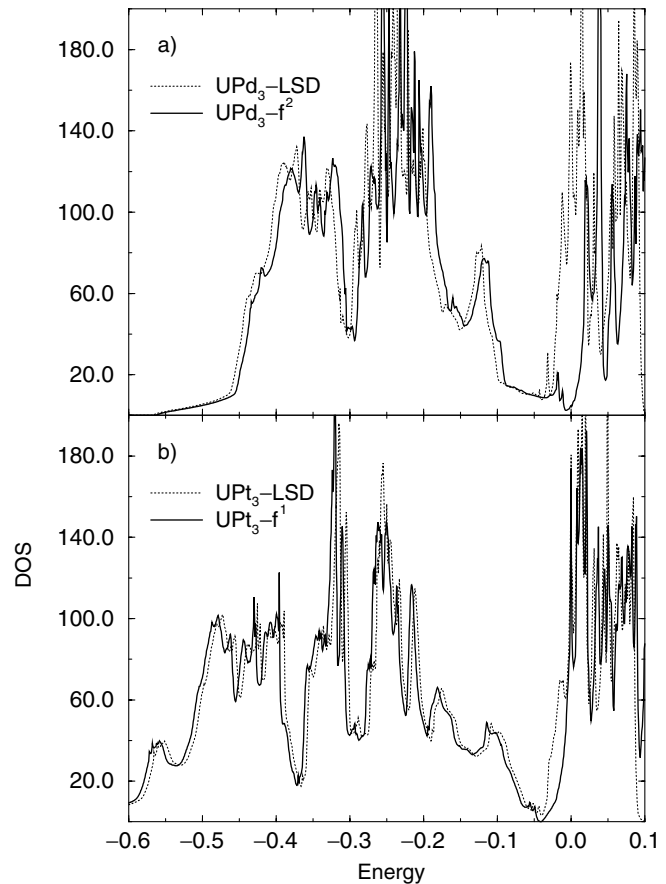


FIG. 2. (a) Total DOS of  $UPd_3$  (in states/Ry·f.u.) in the hexavalent (dotted line) and tetravalent (solid line) configurations, respectively. (b) Total DOS of  $UPt_3$  in the hexavalent (dotted line) and pentavalent (solid line) configurations, respectively. The energy zero (in Ry) marks the Fermi level. All the DOS are obtained with a volume of  $450 \text{ (a.u.)}^3$ .

is situated below the  $f$  peak, and crosses a strongly hybridized  $fd$  band. In UPd<sub>3</sub>, on the other hand, the increased nuclear charge leads to  $d$  bands that lie lower in energy, being well separated from the  $f$  peaks, as can be seen from the LSD curve of Fig. 2a. The extra  $d$  electron in Pd, gives rise to an increased filling of the bands, and the Fermi level is now situated in the  $f$  peak. This combination of decreased  $fd$  hybridization and increased filling of the  $f$  peak in UPd<sub>3</sub> results in a situation where the  $f$  electrons prefer to localize since the gain in hybridization energy is not sufficient to overcome the strong correlations. Consequently, the tetravalent SIC configuration becomes the preferred ground state for UPd<sub>3</sub>.

UPt<sub>3</sub> and UPd<sub>3</sub> are isoelectronic as far as the valence electrons are concerned. The  $5d$  electrons are, however, less tightly bound to the nucleus than the  $4d$  electrons, which results in an increased overlap of the U  $f$  and the transition metal  $d$  orbitals in UPt<sub>3</sub>. Band structure calculations of UPt<sub>3</sub> based upon the LSD approximation result in a DOS where the Fermi level is situated in a narrow  $f$  peak, and where there is at the same time significant  $fd$  and  $fp$  hybridization [20]. The DOS of UPt<sub>3</sub>, as calculated with the SIC-LSD method, for both the hexavalent and pentavalent configurations, is shown in Fig. 2b. Both curves show a large DOS at the Fermi level, and thus are consistent with XPS measurements [6]. According to the total energy calculations in Fig. 1d, it is, however, the pentavalent configuration that becomes energetically most favorable. The theoretical equilibrium volume,  $V_{\text{penv}} = 469.7$  (a.u.)<sup>3</sup>, compares well with the experimental values,  $V_{\text{exp}} = 463.7$  (a.u.)<sup>3</sup> ([21], at 130 K) and  $472.9$  (a.u.)<sup>3</sup> [17]. The measured specific heat coefficient is a factor of 20 larger than the one calculated from the LSD result [22]. From the height of the  $f$  peaks at the Fermi level for both configurations (Fig. 2b), we calculate the specific heat coefficients to be nearly the same, in both the pentavalent, and the LSD scenario, i.e., considerably smaller than the experimental value. Therefore, our calculations indicate that  $f$ -electron localization cannot explain the electron mass enhancements as deduced from specific heat measurements, and reinforce further that the origin of these mass enhancements lies in the spin fluctuations [22,23].

In both UPd<sub>3</sub> and UPt<sub>3</sub>, the small energy differences between the tetravalent and pentavalent configurations indicate near degeneracy (within  $\sim 5$  mRy), rather than a clearly preferred  $f^2$  ground state for UPd<sub>3</sub> and an  $f^1$  ground state for UPt<sub>3</sub>. The SIC-LSD calculations, performed for both UPd<sub>3</sub> and UPt<sub>3</sub> in the Cu<sub>3</sub>Au structure, seem to suggest that the  $f$ -electron localization-delocalization transition between the two compounds is related to small changes in their electronic structures. In reality, UPt<sub>3</sub> [21] crystallizes in the hexagonal (trigonal) structure, and UPd<sub>3</sub> in the dhcp TiNi<sub>3</sub> structure. Therefore, one has to consider the possible influence of the change of structure on the behavior of the  $f$  electrons.

The theoretical Cu<sub>3</sub>Au structure and the observed crystal structure differ in the stacking of the planes of atoms, but not in the nearest neighbor environment. The respective densities of states show small differences, especially at the Fermi level [20,24], that are associated with changes in the  $fd$  and  $fp$  hybridization. However, the global features appear to be the same for both structures. In addition, the energy differences between the pentavalent and tetravalent UPd<sub>3</sub> are identical for both the experimental TiNi<sub>3</sub> and theoretical Cu<sub>3</sub>Au structure, indicating that structural effects have no influence on the determination of the ground-state configuration of the U ions. Alloying experiments on UPt<sub>3-x</sub>Pd<sub>x</sub> [25], show an increase in specific heat for concentrations up to  $x = 0.1$ . Above this value, the specific heat decreases rapidly. The structural change to dhcp occurs only at  $x = 0.3$ . As can be seen in Figs. 1a-d, we have applied the SIC-LSD approach to some of the UPt<sub>3-x</sub>Pd<sub>x</sub> alloys in the Cu<sub>3</sub>Au structure. Moving from Fig. 1d to Fig. 1a, gradually substituting Pt by Pd, leads to a transition from the pentavalent to tetravalent ground state between UPt<sub>2</sub>Pd and UPtPd<sub>2</sub>, i.e., an  $f$  electron gets localized. This transition appears to be driven mainly by changes in the electronic structure, and not by the lattice parameter. The changes occurring when replacing Pt by Pd in the U compounds are related to the decreasing  $fd$  hybridization. The opposite effect is obtained by putting UPd<sub>3</sub> under pressure. The total energy calculations for UPd<sub>3</sub> in Fig. 1a show that the pentavalent configuration becomes energetically favorable for volumes below 425 (a.u.)<sup>3</sup>. The latter corresponds to a pressure of approximately 25 GPa, at which we predict a delocalization of the  $f$  electrons to occur. Likewise, we also obtain in UPtPd<sub>2</sub> a transition, from tetravalent to pentavalent configuration, at a pressure of 16 GPa. In Fig. 3, the DOS calculated in the pentavalent UPd<sub>3</sub> configuration is presented for two different volumes, illustrating the effect

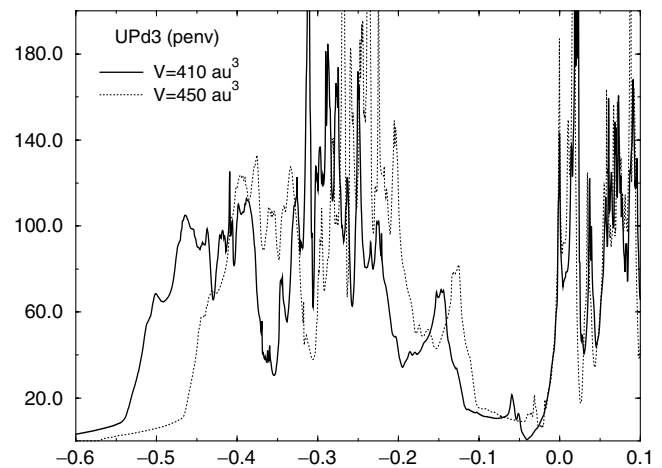


FIG. 3. Total DOS of UPd<sub>3</sub> (in states/Ry·f.u.) in the pentavalent configuration at volumes  $V = 450$  (a.u.)<sup>3</sup> (dotted line) and  $V = 410$  (a.u.)<sup>3</sup> (solid line), respectively. The energy zero (in Ry) marks the Fermi level.

of pressure on the electronic structure of this compound. A considerable broadening of the  $fd$  band under pressure is seen, especially in the low energy area. Furthermore we notice the increased separation between the  $d$  band and the  $f$  peak, and the appearance of the  $d$ - $d$  hybridization-gap [20] below the Fermi level. The broadening of the band brings about the gain in hybridization energy, necessary to overcome the SIC energy. A striking similarity to the pentavalent configuration of  $UPt_3$ , in Fig. 2b, is revealed, i.e., the same opening of a gap and the same width of the  $fd$  band. Given the pentavalent ground state for  $UPd_3$  under pressure, the Fermi level is situated in the narrow  $f$ -peak, suggesting heavy-fermion behavior, similar to the one observed in  $UPt_3$ . Unfortunately, we are not aware of any pressure experiments on  $UPd_3$  to confirm this prediction.

To complete our story on U compounds, we have found the  $f^2$  configuration of  $UAu_3$  to be energetically most favorable. This is the same configuration as seen in  $UPd_3$ . This is at variance with the accepted wisdom of itinerant  $f$  electrons [6], based on the interpretation of XPS experiments. However, the calculation of the XPS spectra by Marksteiner *et al.* [26] making use of the DOS from LSD, yields a peak at the Fermi energy of twice the size of the measured one. Our SIC-LSD calculations of the DOS, for both the hexavalent (LSD) and tetravalent configurations of  $UAu_3$ , also give itinerant  $f$  peaks at the Fermi level. However, in the tetravalent configuration two of the  $f$  levels have become localized, leading to a DOS at the Fermi level only half the size of the hexavalent DOS. This visibly reduced tetravalent DOS peak would give a better explanation of the XPS measurements than LSD (the atomiclike matrix elements will be very similar for both configurations and therefore behave as an energy dependent constant for the XPS spectra of the different configurations). This gives a strong indication that in  $UAu_3$  the U ions have the localized  $f^2$  configuration, rather than delocalized electrons. We have also evaluated a transition pressure of 13 GPa for realizing the  $f^1$  configuration. In this configuration the density of states at the Fermi energy will increase and possibly  $UAu_3$  could also become a heavy fermion system.

We have evaluated the transition pressures for delocalizing one  $f$  electron in  $f^2$  materials  $UPd_3$  and  $UAu_3$  to result in the same  $f^1$  valency as in  $UPt_3$ . These transition pressures lie within the range of 13-25 GPa, well within experimental reach. The question now arises whether both  $UPd_3$  and  $UAu_3$  will be transformed into heavy fermion systems by applying pressure. We would expect  $UPd_3$  to become heavy fermion because of its similarities to  $UPt_3$ .

In any case, an experimental investigation of these issues would no doubt increase our knowledge of heavy fermion systems.

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