

Localized U 5*f* electrons in UPd₃ from LDA+*U* calculations

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A generalization of the local-density approximation + *U* (LDA+*U*) method which takes into account that in the presence of spin-orbit coupling the occupation matrix of localized electrons becomes nondiagonal in spin indices is used to study the electronic structure of UPd₃ and UPd_{1.5}Pt_{1.5}. For both compounds LDA+*U* calculations give a solution with two localized U 5*f* electrons. Their energy position agrees well with the binding energy of a U 5*f* peak observed in photoemission experiments. The calculations also reproduce the shift of the peak position toward the Fermi level upon Pt substitution. The LDA+*U* results are compared to the results of LDA calculations for ThPd₃ and ThPd_{1.5}Pt_{1.5} and their dependence on the crystal structure is analyzed.

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I. INTRODUCTION

An interest in uranium compounds has recently been renewed, especially after the discovery of such unusual effects as heavy fermion superconductivity and coexistence of superconductivity and magnetism. To a large extent compounds exhibit a rich variety of properties because of the complex behavior of 5*f* electrons, which is intermediate between the itinerant behavior of 3*d* electrons in transition metals and the localized behavior of 4*f* electrons in rare-earth compounds. The dual character of 5*f* electrons in addition to the presence of strong spin-orbit (SO) coupling make the determination of the electronic structure of U compounds a challenging task because in many of them the width of 5*f* bands, their spin-orbit splitting, and the on-site Coulomb repulsion in the partially filled 5*f* shell are of the same order of magnitude and should be taken into account on the same footing.

UPd₃ is the only uranium-based intermetallic compound in which 5*f* electrons are known to be localized, as determined by low-temperature specific heat¹ and inelastic neutron scattering^{2,3} data. This is also confirmed by de Haas-van Alpern (dHvA) measurements^{4,5} in which no orbits with heavy effective masses were found. According to photoemission spectroscopy (PES) experiments⁶⁻⁸ localized U 5*f* electrons form a peak at a binding energy of about -0.8 eV and there is no 5*f* spectral weight at the Fermi level. The study of the electronic structure of UPd₃ is interesting not only because of the localized character of 5*f* electrons but also because it can help to understand the intriguing properties of an isoelectronic uranium compound UPt₃, which exhibits a heavy fermion behavior and becomes superconducting at low temperatures. In U(Pd_{1-x}Pt_x)₃ alloys U 5*f* electrons remain localized for *x* smaller than 0.9 whereas a heavy quasiparticle peak develops at larger Pt concentrations. PES experiments⁶ show that the U 5*f* peak shifts to higher energies with the

increase of Pt content and at *x*>0.9 a second peak is formed just below the Fermi level (E_F), indicating that 5*f* spectral weight appears at E_F . To our knowledge, the shift of the U 5*f* peak position is not yet understood.

The calculations of the electronic structure of UPd₃ performed using the local-density approximation (LDA) either for the experimentally observed double hcp (dhcp) or for fcc crystal structures⁹⁻¹¹ place partially occupied U 5*f* states exactly at the Fermi level and, thus, disagree qualitatively with the experimental data. Compared to the experimental values calculated cyclotron masses and the coefficient of the electronic specific heat are too high. On the other hand, a reasonably good agreement between calculated and experimental angular dependence of dHvA frequencies is found in Ref. 12 in which two U 5*f* electrons were treated as core states. Recently, the electronic structure of UPd₃ has been calculated using self-interaction corrected local spin-density approximation (LSDA) and a solution with two localized 5*f* electrons has been found.¹³

The aim of the present work is to study the effect of the Coulomb repulsion in the U 5*f* shell on the electronic structure of UPd₃ and UPd_{3-x}Pt_x. This is achieved by using the LDA+*U* method¹⁴⁻¹⁷ which has been successfully applied to study the electronic structure of many compounds with strongly correlated 3*d* and 4*f* electrons. In the conventional LDA+*U* scheme it is usually supposed that the spin is a good quantum number and the occupation matrix of the localized electrons is diagonal in spin indexes. This approximation is justified for 3*d* and to a less extent 4*f* compounds, in which the spin-orbit coupling is rather strong but still much weaker than the on-site Coulomb repulsion. In the case of uranium compounds, however, the relativistic effects are of the same order of magnitude as the Coulomb interaction and the occupation matrix of localized electrons becomes nondiagonal in spin indices which should be taken into account when constructing the LDA+*U* potential.^{18,19} Evi-

dently, LDA+ U is too crude an approximation to describe the heavy fermion behavior of UPt₃ and we will not discuss it in the present work. Instead we refer to Ref. 20.

The paper is organized as follows. In Sec. II we present the generalization of the LDA+ U method regarding the case of compounds with strong spin-orbit coupling. The details of the calculations are given in Sec. III. The results of the LDA calculations of the electronic structure of UPd₃ in different crystal structures are described in Sec. IV. They are also compared to the results calculated for ThPd₃. In Sec. V we present the LDA+ U band structure of UPd₃. The effects of Pt substitution are studied in Sec. VI and a summary is given in Sec. VII.

II. “RELATIVISTIC” LDA+ U METHOD

In order to account better for strong correlations in the partially filled d or f shell, in the LDA+ U method^{14–17} a new total-energy functional is introduced,

$$E^{\text{LDA}+U}(\rho, \hat{n}) = E^{\text{L(S)DA}}(\rho) + E^U(\hat{n}) - E^{\text{dc}}(\hat{n}), \quad (1)$$

where $E^{\text{L(S)DA}}(\rho)$ is the LSDA [or LDA (Ref. 14)] functional of the total electron-spin densities, $E^U(\hat{n})$ is the electron-electron interaction energy of the localized electrons, and $E^{\text{dc}}(\hat{n})$ is the so-called “double-counting” term that approximately cancels a part of an electron-electron energy which is already included in E^{LDA} . The last two terms are functions of the occupation matrix \hat{n} of the local orbitals $\{\phi_{m\sigma}\}$. In the conventional LDA+ U method the localized orbitals are labeled by their spin σ and azimuthal m quantum numbers and it is usually assumed that the occupation matrix $\hat{n} = n_{m,m}^{\sigma}$ is diagonal in spin indices σ . The assumption that the occupation matrix is diagonal in σ is, however, no longer valid for compounds containing heavy $4f$ or $5f$ elements because a relatively strong SO coupling in the f shell intermixes majority- and minority-spin states. Then, in the basis of local orbitals $|lm\sigma\rangle$ the occupation matrix for an l channel becomes $n_{\sigma m, \sigma' m'}$ and additional exchange terms between non-diagonal in σ elements of the occupation matrix appear in the expression for $E^U(\hat{n})$,^{18,19}

$$E^U = \frac{1}{2} \sum_{\sigma, \sigma', \{m\}} (n_{\sigma m_1, \sigma m_2} U_{m_1 m_2 m_3 m_4} n_{\sigma' m_3, \sigma' m_4} - n_{\sigma m_1, \sigma' m_2} U_{m_1 m_4 m_3 m_2} n_{\sigma' m_3, \sigma m_4}), \quad (2)$$

where $U_{m_1 m_2 m_3 m_4}$ are the matrix elements of screened on-site Coulomb interaction.

For the double-counting term we adopted the expression proposed in Ref. 15

$$E^{\text{dc}} = \frac{1}{2} U n(n-1) - \frac{1}{2} J \sum_{\sigma} n_{\sigma} (n_{\sigma} - 1), \quad (3)$$

where n_{σ} is the number of localized electrons with the spin σ given by a partial trace of the occupation matrix $n_{\sigma} = \sum_m n_{\sigma m, \sigma m}$, $n = n_{\uparrow} + n_{\downarrow}$, and U and J are averaged on-site Coulomb and exchange integrals, respectively.¹⁴

Because of the term $E^U - E^{\text{dc}}$ in Eq. (1) the effective one-electron potential acquires an additional orbital-dependent contribution $V_{\sigma m_1, \sigma' m_2}$. The Appendix shows the way in which the matrix elements of $V_{\sigma m_1, \sigma' m_2}$ enter the Hamiltonian of the linear-muffin-tin orbitals (LMTO) method.

To analyze the results of LDA+ U calculations based on Eqs. (1)–(3) it is helpful to consider the density of states (DOS) projected onto new local orbitals,

$$|li\rangle = \sum_{\sigma, m} |lm\sigma\rangle d_{\sigma m, i}, \quad (4)$$

where the matrix $d_{\sigma m, i}$ diagonalizes the occupation matrix for the l shell so that

$$\sum_{\sigma m} \sum_{\sigma' m'} d_{\sigma m, i}^* n_{\sigma m, \sigma' m'} d_{\sigma' m', j} = \delta_{ij} n_i. \quad (5)$$

In this representation the occupation matrix is diagonal and the eigenvalues n_i represent orbital occupation numbers for the $|li\rangle$ local orbitals.

The “relativistic” generalization of the LDA+ U method outlined above is formulated in terms of the occupation matrix nondiagonal in spin indices and can be used to account for the effects of strong electronic correlations between $5f$ electrons in U compounds in which the value of the screened Coulomb integral U (~ 2 eV) is of the same order as the SO coupling strength.

III. COMPUTATIONAL DETAILS

UPd₃ crystallizes in the hexagonal (dhcp) TiNi₃ type structure with the $P6_3/mmc$ (No. 194) space group.²¹ Each of two inequivalent U atoms occupying pseudocubic $2a(D_{3d})$ and hexagonal $2c(D_{3h})$ positions is surrounded by 12 Pd atoms, six of them being situated in the same and another six in the adjacent UPd₃ planes. The UPd₃ planes form a $abac$ sequence in the c direction. The calculations were also performed for hcp and pseudocubic fcc-derived crystal structures with $abab$ and abc stacking of UPd₃ planes, respectively. In these calculations the in-plane lattice constant and interplane spacing were kept the same as in the original dhcp structure, which required the application of a small trigonal distortion to the fcc structure.

The calculations were performed for the experimentally observed lattice constants $a = 5.769$ Å and $c = 9.640$ Å using the LMTO method²² in the atomic sphere approximation (ASA) with the combined correction term taken into account. The radii of U and Pd atomic spheres (AS) were chosen to be equal to 3.3794 and 2.9019 a.u., respectively. The LMTO basis functions were constructed by solving the scalar relativistic radial equation and the matrix elements of the spin-orbit interaction were included in the Hamiltonian matrix at the variational step. To check the validity of this approximation the LDA band structure was compared to that calculated with the fully relativistic LMTO method.²³

We used the von Barth–Hedin parametrization²⁴ for the exchange-correlation potential. Brillouin-zone integrations were performed using the improved tetrahedron method.²⁵

Screened Coulomb U and exchange J integrals enter the LDA+ U energy functional as external parameters and have to be determined independently. In principle, their values can be obtained from LDA calculations using Slater's transition state approach as described in Ref. 26. For UPd₃ with the specified above AS radii such calculations, in which an f^2 configuration of the U ion is assumed and the hoppings of $5f$ states to all other states are suppressed, give the values of $U=4.4$ eV and $J=0.5$ eV. The same value of U was also obtained from constrained LDA calculations using the scheme proposed in Ref. 27. This value of averaged Coulomb interaction is significantly higher than U of ≈ 2 eV estimated from x-ray photoemission spectroscopy (XPS) and bremsstrahlung isochromat spectroscopy (BIS) experiments⁸ and those extracted from optical data for various U ions in Ref. 28. If, however, in the transition state calculations unoccupied U $5f$ states are kept in the basis and allowed to take part in the screening the value of U decreases to 2.6 eV. Because of the screening by two corelike U $5f$ electrons $5f$ derived bands are found well above the Fermi level in this case. As, according to the transition state procedure, the number of the former is varied the latter remain above E_F but their energy position changes. As a result the U $5f$ contribution to the wave functions of the occupied states formed predominantly by Pd $4d$ electrons also changes and this change of f -electron density in U atomic spheres provides additional screening of the corelike U $5f$ electrons. In order to model the conditions which occur in LDA+ U calculations, U of 4.4 eV was applied to the unoccupied f states. Then, the calculations were repeated until "self-consistency" in U was achieved with U obtained on the previous step acting on the unoccupied states. The exchange integral J was not affected by the additional screening. This procedure implies that U $5f$ states can be subdivided into localized and delocalized ones. Recently, such a possibility has been widely discussed in connection with another U intermetallic compound UPd₂Al₃ which displays both pronounced local-moment and heavy-mass itinerant behavior.²⁹ Of course, there is no experimental evidence that some U $5f$ electrons in UPd₃ are delocalized and the results of the above-mentioned calculations using Slater's transition state approach should only be considered as an indication that the screening of localized U $5f$ electrons by delocalized f density can bring the calculated value of $U=4.4$ eV closer to the value of 2 eV derived from photoemission experiments. Since in this work we focus our attention on comparison with PES spectra we present in the following sections LDA+ U results calculated for $U=2$ eV derived from XPS measurements and $J=0.5$ eV.

In order to determine $U_{m_1 m_2 m_3 m_4}$ we first calculated the ratios F^4/F^2 and F^6/F^4 of Slater's integrals directly using the radial solution $\phi_v(r)$ of the Schrödinger equation for $5f$ electrons. Then, these ratios were fixed and F^2 , F^4 , and F^6 themselves were determined from the well-known expression for the average J in terms of Slater's integrals.²⁸

IV. LDA RESULTS

The LDA band structures calculated for UPd₃ in different crystal structures agree well with the results of previous

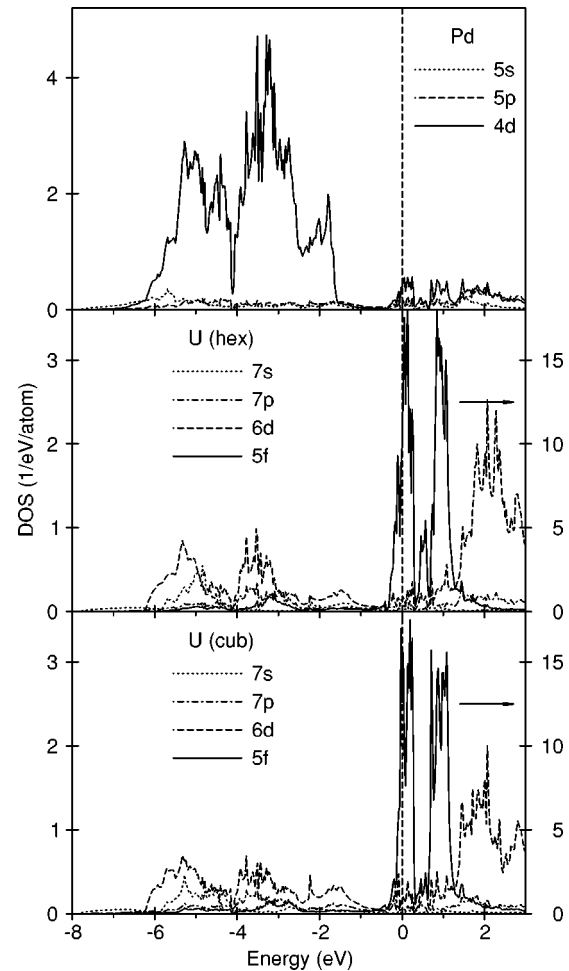


FIG. 1. Partial DOS for Pd and two inequivalent pseudocubic (D_{3d}) and hexagonal (D_{3h}) U sites calculated within the LDA for UPd₃.

calculations.^{9–11} Figure 1 shows l projected densities of U and Pd states calculated for dhcp UPd₃. The occupied part of the valence band is formed predominantly by Pd $4d$ states. The characteristic feature of the LDA band structure is a narrow peak of U $5f_{5/2}$ states situated just at the Fermi level 1.5-eV above the top of Pd $4d$ states. U $5f_{7/2}$ states are split off by strong SO coupling and form another narrow peak 1-eV above E_F . It is important to note that U $5f$ states are situated in a low DOS region between Pd $4d$ and U $6d$ states^{11,10} and hybridize only weakly with the former. Because of this weak hybridization the width of the U $5f_{5/2}$ and $5f_{7/2}$ peaks is ~ 0.5 eV which is smaller than both the SO splitting and the value of their on-site Coulomb repulsion $U=2$ eV derived from XPS and BIS spectra.⁸ LDA calculations performed for UPd₃ in fcc and hcp structures also place the U $5f_{5/2}$ states just at E_F , the width of the peak being almost the same as for dhcp UPd₃. It seems that from the LDA point of view the localized behavior of U f electrons in UPd₃ is mainly caused by their very peculiar energy position which results in the weak hybridization with other conduction states.

The calculated occupation of U $5f$ states (2.924 for pseudocubic and 2.955 for hexagonal sites; see Table I) is

TABLE I. The comparison of d and f charges in U and Th atomic spheres calculated for UPd_3 and ThPd_3 in different crystal structures.

Structure	Th d	Th f	U d	U f	U f - Th f
fcc	1.759	0.900	1.723	2.997	2.097
dhcp (cubic)	1.802	0.877	1.804	2.924	2.046
dhcp (hexagonal)	1.778	0.886	1.756	2.955	2.069
hcp	1.824	0.879	1.824	2.893	2.014

significantly larger than one would expect for a U ion with an f^2 configuration. From Fig. 1 one can notice, however, that apart from the two peaks of U $5f$ states at E_F there is a significant U $5f$ contribution to the DOS in the energy range between -6 and -2 eV which shows an energy dependence similar to that of Pd $4d$ DOS. These states are apparently the so-called “tails” of Pd $4d$ states and arise as a result of the decomposition of the wave function centered at Pd atoms inside U atomic spheres. It is worth recalling that in ASA-based calculations partial charges are defined as integrals of electron density over the volume of the AS surrounding the atom. In order to estimate the share of the Pd $4d$ “tails” in the calculated U $5f$ charges we performed calculations of the electronic structure of a model ThPd_3 compound keeping the lattice parameters and atomic sphere radii the same as for UPd_3 . The band structure of ThPd_3 seems to provide a reasonable approximation for that of UPd_3 with two localized $5f$ electrons because the Th atom has two valence electrons less than U and Th $5f$ states in ThPd_3 are above E_F .

Calculated Th and U partial charges are summarized in Table I and the densities of Th $4d$ and $5f$ and Pd $4d$ states calculated for ThPd_3 in distorted fcc, dhcp, and hcp crystal structures are shown in Fig. 2. Note that Pd $4d$ DOS is multiplied by a factor of 0.5 and its scale is shown at the right-hand side of Fig. 2. The energies are given with respect to the muffin-tin zero. For all three structures the peak of atomiclike Th $5f$ states appears above E_F whereas the occupied Th states of f character are the above-mentioned “tails” of predominantly Pd $4d$ states. Nevertheless, they sum up to give the $5f$ occupation of 0.9 electrons inside the Th sphere, most of it acquired in the energy range below 8 eV, corresponding to the top of Pd $4d$ DOS. It is interesting to note that the difference between f charges in U and Th spheres is only slightly larger than 2, i.e., the occupied part of the U $5f_{5/2}$ peak found at E_F in UPd_3 contains exactly the number of $5f$ electrons which, according to available experimental data, is supposed to be localized.

Comparing the DOS curves calculated for different structural modifications of ThPd_3 one can note that the strongest changes are observed in the low DOS region lying above the top of Pd $4d$ and below the steep slope of unoccupied “atomiclike” Th $5f$ states. Because of the low DOS in this energy range the position of the Fermi level is found to be very sensitive to the crystal structure. When going from fcc to dhcp, E_F shifts downward by as much as -0.73 eV and the transition from dhcp to hcp causes a further shift of -0.31 eV. A structure consisting of a mixture of dhcp and hcp phases was experimentally determined in a $\text{UPd}_{3-x}\text{Pt}_x$

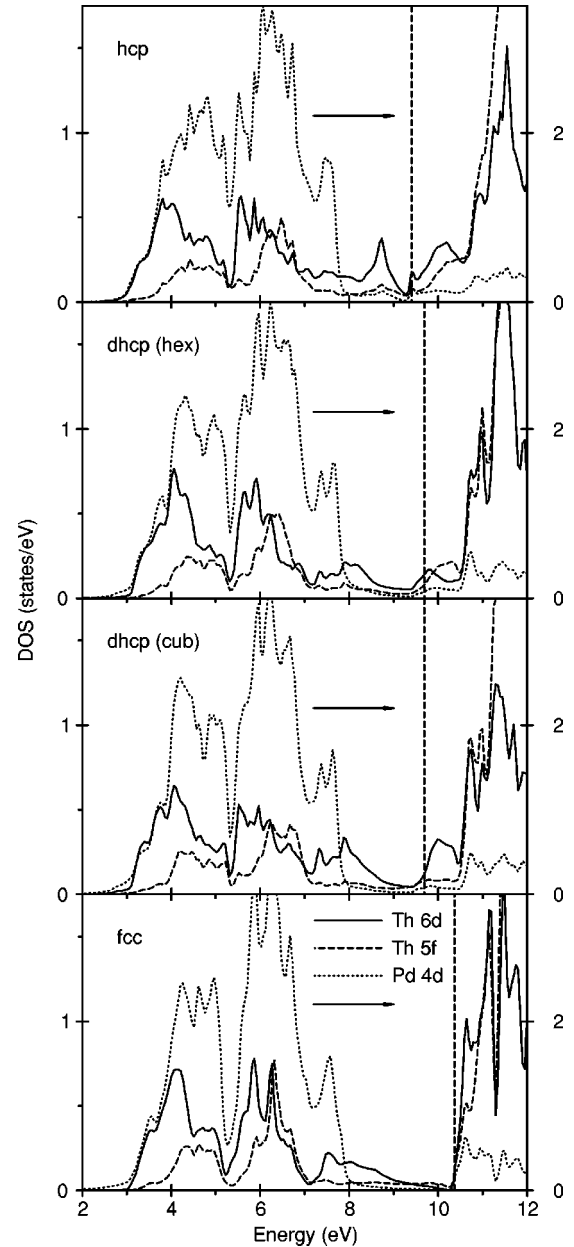


FIG. 2. LDA partial DOS of calculated for ThPd_3 in different crystal structures.

alloy for $1.0 < x < 2.0$ which then becomes hcp for $x > 2.0$.^{6,30} We can speculate that the shift of the U $5f$ peak observed in resonant photoemission experiments on $\text{UPd}_{3-x}\text{Pt}_x$ (Refs. 31 and 6) can be partially caused by different positions of the Fermi level in the hcp and dhcp phases. However, this change of the E_F position is not sufficient to account for the whole shift, nor can the shift of the U $5f$ peak for $x < 1.0$ be explained where the alloy has dhcp structure.

The lowest DOS in the energy range 8–10 eV is found for the fcc structure. The density of Th $6d$ states increases in the dhcp one and, finally, a peak of Th $6d$ states develops at 8.5 eV in hcp ThPd_3 . These changes of DOS are reflected in a small increase of the Th $6d$ charge (see Table I). The density of $5f$ “tails” in the vicinity of the Fermi level also increases upon a transition from the dhcp to the hcp structure. This can

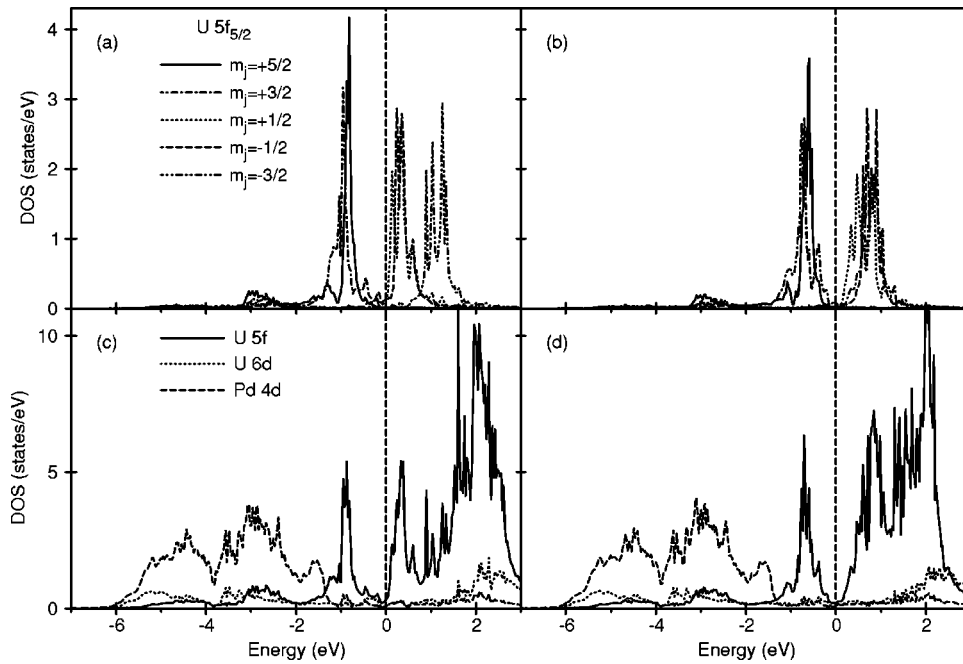


FIG. 3. U 5f DOS projected onto the states which diagonalize the 5f occupation matrix (a) and (b) and the U and Pd partial DOS (c) and (d) calculated for hcp UPd₃ using the LDA+U method. DOS curves in (a) and (c) are calculated with nonspherical corrections to Coulomb matrix elements whereas those in (b) and (d) are calculated with averaged U and J .

lead to an increase of the hybridization between the localized 5f and conduction electrons and may therefore be responsible for the delocalization of the former in hcp UPt₃.

V. LDA+U RESULTS

The results of LDA calculations (see Fig. 1), with U 5f states forming the huge peak just at E_F , contradict drastically the available experimental data which show that the electronic states at the Fermi level have relatively low effective masses whereas the U 5f states are localized and situated according to the XPS data^{6,31} at about 0.7-eV below E_F . This discrepancy between the calculations and experimental data is apparently due to the underestimation of the Coulomb repulsion between rather localized 5f electrons. In order to account for the electronic correlations in the 5f shell we calculated the band structure of UPd₃ using the modification of the LDA+U approach outlined in Sec. II with the averaged Coulomb and exchange integrals being equal to $U=2$ eV and $J=0.5$ eV.

The density of U 5f and 6d and Pd 4d states calculated for hcp UPd₃ are shown in Fig. 3(c). The Coulomb repulsion splits partially occupied U 5f_{5/2} states and the LDA+U calculations give a solution with two localized 5f electrons. These localized 5f states are situated in the region of low DOS above the top of Pd 4d and form a rather narrow peak at 0.8 eV below E_F . The position of the peak agrees well with the results of recent resonant PES (Ref. 6) and angle-resolved PES (ARPES) measurements.⁷ U 5f states just above the Fermi level are formed by the remaining 5f_{5/2} states whereas the peak of 5f_{7/2} states is pushed from its LDA position at 1-eV above E_F to 2.2 eV. This shift brings the DOS of unoccupied U 5f states to a much better agreement with the BIS spectrum of UPd₃ which has a maximum at ~ 2.6 eV.⁸

The orbital character and occupation of the localized U 5f

states can be determined by diagonalization of the 5f occupation matrix as described in Sec. II. From the analysis of the matrix $d_{\sigma m, i}$ [see Eq. (5)] it follows that each of the six orbitals with largest occupation numbers is predominantly formed by one of the $|\frac{5}{2}, m_j\rangle$ states (see Table II) in which we use the notation $|j, m_j\rangle$ for the state with the total momentum j and its projection m_j . Since the states with $m_j = \pm \frac{1}{2}$ and $m_j = \pm \frac{3}{2}$ transform according to different irreducible representations of the D_{3h} symmetry group the expectation value of the z projection of the total momentum $\langle j_z \rangle$ calculated for these orbitals is equal to m_j . The spin-dependent part of the exchange-correlation potential couples $|\frac{5}{2}, \pm \frac{1}{2}\rangle$ and $|\frac{5}{2}, \pm \frac{3}{2}\rangle$ states to $f_{7/2}$ states with the same m_j but because of the strong spin-orbit interaction the contribution of $f_{7/2}$ states is very small. As for $|\frac{5}{2}, \pm \frac{5}{2}\rangle$ states, the local symmetry of the U site allows their mixing not only with $|\frac{7}{2}, \pm \frac{5}{2}\rangle$ but also with $|\frac{7}{2}, \mp \frac{7}{2}\rangle$. However, a substantial contribution of $f_{7/2}$

TABLE II. The occupation numbers n and the expectation values of the z projection of the total ($\langle j_z \rangle$) momentum, spin ($\langle s_z \rangle$), and angular ($\langle l_z \rangle$) momentum calculated for the local orbitals diagonalizing the U 5f occupation matrix. The states that provide the dominant contribution to the orbitals are listed in the rightmost column.

n	$\langle j_z \rangle$	$\langle s_z \rangle$	$\langle l_z \rangle$	
0.988	2.497	-0.416	2.913	$0.99 \frac{5}{2}, +\frac{5}{2}\rangle + 0.09 \frac{7}{2}, +\frac{5}{2}\rangle$
0.982	3/2	-0.298	1.798	$0.99 \frac{5}{2}, +\frac{3}{2}\rangle + 0.10 \frac{7}{2}, +\frac{3}{2}\rangle$
0.152	-1/2	-0.219	-0.281	$0.96 \frac{5}{2}, -\frac{1}{2}\rangle + 0.29 \frac{7}{2}, -\frac{1}{2}\rangle$
0.125	1/2	-0.264	0.764	$0.98 \frac{5}{2}, +\frac{1}{2}\rangle + 0.21 \frac{7}{2}, +\frac{1}{2}\rangle$
0.081	-3/2	-0.212	-1.288	$0.91 \frac{5}{2}, -\frac{3}{2}\rangle + 0.43 \frac{7}{2}, +\frac{3}{2}\rangle$
0.072	-1.947	0.375	-2.322	$0.95 \frac{5}{2}, -\frac{5}{2}\rangle - 0.30 \frac{7}{2}, +\frac{7}{2}\rangle$

states is found only for the local orbital originating from a $|\frac{5}{2}, -\frac{5}{2}\rangle$ state for which $\langle j_z \rangle = -1.95$ deviates strongly from the corresponding m_j value. The admixture of the $|\frac{7}{2}, -\frac{7}{2}\rangle$ state to the $|\frac{5}{2}, \frac{5}{2}\rangle$ orbital turns out to be very small so that $\langle j_z \rangle \approx \frac{5}{2}$ in this case. In the following we will refer to these orbitals by their m_j value. It is worth pointing out that the fact that the orbitals which diagonalize the $5f$ occupation matrix almost coincide with the eigenfunctions of j and j_z shows the importance of taking into account the nondiagonal in spin terms of the occupation matrix when constructing the LDA+ U potential.

An orbital resolved DOS corresponding to the orbitals with the largest occupation numbers is shown in Fig. 3(a). From the comparison to U $5f$ DOS shown in the lower panel one can see that the peak at -0.8 eV is formed by $5f_{5/2}$ states with $m_j = \frac{5}{2}$ and $m_j = \frac{3}{2}$. Their occupation numbers are $n_{5/2} = 0.988$ and $n_{3/2} = 0.982$, which corresponds to a f^2 configuration of the U ion. The total $5f$ charge in the U atomic sphere is, however, equal to 2.881 which is very close to the LDA value of 2.893. The excessive $5f$ charge of 0.9 electrons comes mainly from the “tails” of Pd $4d$ electrons distributed over the energy range -6 to -2 eV.

A peak of U $5f$ states just above the Fermi level is formed predominantly by $|\frac{5}{2}, \pm\frac{1}{2}\rangle$ states with $n_{1/2} = 0.125$ and $n_{-1/2} = 0.152$. Two remaining $f_{5/2}$ states with $m_j = -\frac{3}{2}$ ($n_{-3/2} = 0.081$) and $m_j = -\frac{5}{2}$ ($n_{-5/2} = 0.072$; not shown in Fig. 3) are shifted to ~ 1 -eV above E_F . This rather large splitting of the unoccupied $f_{5/2}$ states is caused by strong anisotropy of the on-site Coulomb interaction because of which the states having the same $|m_j|$ as the occupied ones experience much stronger repulsion than $|\frac{5}{2}, \pm\frac{1}{2}\rangle$ states.

It should be mentioned that depending on the starting conditions another self-consistent LDA+ U solution with close total energy can be obtained for hcp UPd₃. This solution also results in two localized U $5f$ electrons but in this case the occupied states are $|\frac{5}{2}, \frac{5}{2}\rangle$ and $|\frac{5}{2}, \frac{1}{2}\rangle$. The existence of two almost degenerated solutions can be understood if one compares the matrix elements of Coulomb interaction U_{m_j, m'_j} calculated between $f_{5/2}$ states with different m_j . The matrix elements $U_{5/2, 3/2}$ and $U_{5/2, 1/2}$ are equal and the energy difference is caused not by the on-site Coulomb interaction but instead by the difference in the hybridization between U $f_{5/2}$ and conduction electrons. Also, the lowest unoccupied $5f$ state, which is either $|\frac{5}{2}, \frac{1}{2}\rangle$ or $|\frac{5}{2}, \frac{3}{2}\rangle$, feels the same Coulomb repulsion of the localized electrons.

From Fig. 3 one can notice that U $|\frac{5}{2}, \pm\frac{1}{2}\rangle$ states are situated very close to the Fermi level and are partially occupied due to hybridization with the delocalized states. Unfortunately, because of the presence of the narrow $5f$ peak just above E_F we could not obtain a stable self-consistent LDA+ U solution for dhcp UPd₃ with two inequivalent U atoms per unit cell. It seems, however, that the splitting between unoccupied U $f_{5/2}$ states with $m_j = \pm\frac{1}{2}$ and $m_j = -\frac{3}{2}$ and $\frac{5}{2}$ is overestimated in the LDA+ U calculations. The arguments for this are the following: the wave function of the ground-state multiplet of a U ion in an f^2 configuration with the total

angular momentum $J=4$ is formed by linear combinations of products of all $f_{5/2}$ states and results in more or less uniform occupation of one-electron $|\frac{5}{2}, \pm\frac{1}{2}\rangle$ states. In the Hartree-Fock-like LDA+ U solution, however, two particular $f_{5/2}$ states ($m_j = \frac{5}{2}$ and $m_j = \frac{3}{2}$) are occupied which leads to (i) large spin ($1.45\mu_B$) and orbital ($-4.33\mu_B$) magnetic moments of the U atom and (ii) strongly anisotropic Coulomb interaction of the remaining $5f$ electrons with the occupied ones. The fact that there exists another solution with the close total energy with occupied $m_j = \frac{5}{2}$ and $m_j = \frac{1}{2}$ states suggests that the “true” ground state should be a superposition of these two solutions and of another two with $m_j \rightarrow -m_j$. If it were possible to construct such a solution then unoccupied U $5f$ electrons would feel a much more isotropic repulsive potential. The effect of a less asymmetric density of the localized $5f$ electrons can be simulated by replacing in Eq. (2) the matrix elements $U_{mm'm'm'}$ and $U_{mm'm'm}$ by averaged Coulomb U and exchange J integrals, respectively, and setting all other matrix elements to zero. In the nonrelativistic limit this would correspond, except for the approximation to the double-counting term, to the original version of the LDA+ U method proposed in Ref. 32. In this case all unoccupied U $5f$ electrons independently of their angular momentum, experience the same Coulomb repulsion as the localized ones.

DOS curves calculated for hcp UPd₃ using spherically averaged U and J are shown in Figs. 3(b) and 3(d). The main effect of this approximation on the electronic structure is that the lowest unoccupied $|\frac{5}{2}, \pm\frac{1}{2}\rangle$ states feel a more repulsive LDA+ U potential. As a result they are shifted further away from E_F and their contribution to the bands crossing the Fermi level decreases.

The site and orbital resolved densities of state for two inequivalent U sites with pseudocubic and hexagonal symmetries calculated for UPd₃ in an experimentally observed dhcp crystal structure using spherically averaged Coulomb matrix elements are shown in Fig. 4. Occupied U $5f$ states with $m_j = \frac{5}{2}$ and $\frac{3}{2}$ produce almost dispersionless bands at about -0.8 eV which is close to the binding energy of one of the bands ascribed to the localized U $5f$ electrons in ARPES measurements.⁷ However, in contrast to the experimental data in which three groups of flat bands separated by ~ 0.3 eV were observed, only one bunch of $5f_{5/2}$ bands is found in the calculations. The bands located in the energy window between the split by the on-site Coulomb interaction $5f_{5/2}$ states show that the dispersion is very similar to the dispersion of the bands crossing the Fermi level in dhcp ThPd₃. It is worth mentioning that the Fermi-surface cross sections obtained from LDA calculations for dhcp ThPd₃ reproduce very well those derived from the ARPES experiment.⁷

The above-mentioned self-consistent LDA+ U solutions are magnetic with a rather large U magnetic moment. This contradicts the experimental data which show that the ordered magnetic moment in UPd₃ is only $0.01\mu_B$ per U atom.³³ This extremely small U magnetic moment is explained by the fact that according to a crystalline electric field (CEF) levels scheme derived from neutron-scattering

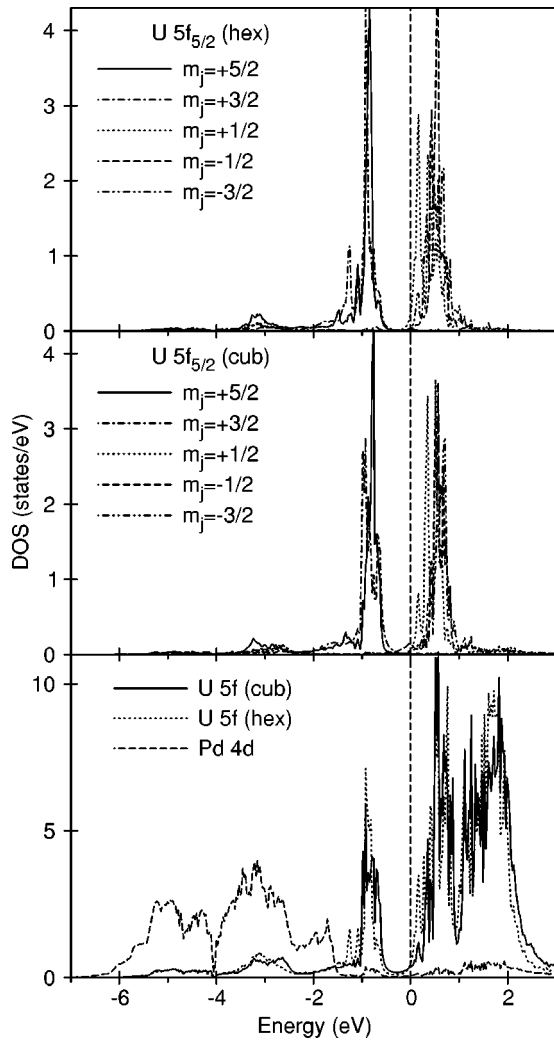


FIG. 4. Partial DOS calculated for dhcp UPd₃ using LDA+U method with spherically averaged U and J (lower panel). Orbital resolved density of $5f$ states for two inequivalent U atoms in pseudocubic (middle panel) and hexagonal (upper panel) environment.

experiments the lowest CEF level of the U⁴⁺ ion in both hexagonal and quasicubic sites is a singlet³⁴ which leads to a nonmagnetic ground state of UPd₃. The LDA+U is still a one-electron approximation and cannot fully account for the subtle many-body effects responsible for the small value of the U magnetic moment in UPd₃. It tries to obey the Hund's rules in the only way that it is allowed, i.e., by producing a magnetic solution. A possible way to overcome this discrepancy between the calculations and the experiment is to force a nonmagnetic ground state in LDA+U calculations as was done by Harima *et al.* in Refs. 19 and 33. We have verified, however, that this leads to an increase of the total energy as compared to magnetic calculations.

VI. THE EFFECT OF Pt DOPING

In order to study the effect of Pt doping on the electronic structure of UPd_{3-x}Pt_x alloys we performed LDA and LDA+U calculations for the model UPd_{1.5}Pt_{1.5} compound in

dhcp and hcp crystal structures. The lattice constants and sphere radii in these calculations were kept the same as that for UPd₃. The desired composition was obtained by replacing one of the inequivalent Pd atoms with Pt accompanied in the case of the hcp structure by a lowering of the crystal symmetry to $P\bar{6}m2$. This results in an alloy which consists of alternating UPd₃ and UPt₃ planes, forming *abc* or *abab* sequences along the crystallographic *c* direction. Two different compounds with the dhcp structure can be produced in this way. From the comparison of the LDA total energies it was found that Pt substitution into the planes containing U atoms with the hexagonal local symmetry is more favorable and in the following only this compound will be considered.

The LDA density of U $5f$ states in dhcp UPd_{1.5}Pt_{1.5} is similar to that of UPd₃. However, Th f charges calculated for a reference ThPd_{1.5}Pt_{1.5} compound show an average increase of 0.09 electrons as compared to ThPd₃ because of the larger spatial extent of Pt $5d$ states. In UPd_{3-x}Pt_x alloys this leads to increased screening of the localized U $5f$ electrons which is confirmed by LDA+U calculations for dhcp and hcp UPd_{1.5}Pt_{1.5}. These calculations were performed using the same values $U=2.0$ eV and $J=0.5$ eV of the averaged Coulomb and exchange matrix elements as were used for the calculations of UPd₃ described in Sec. V. Figure 5 shows U $5f$, Pd $4d$, and Pt $5d$ DOS (lower panels) together with orbital resolved DOS projected onto the orbitals with the dominating contribution of U $5f_{5/2}$ states with $m_j = \frac{5}{2}, \frac{3}{2},$ and $\pm \frac{1}{2}$ (middle and upper panels). Comparing these results to those calculated for dhcp UPd₃ and presented in Fig. 4 one notices a shift of two localized U $5f$ states from -0.8 to -0.6 eV in dhcp UPd_{1.5}Pt_{1.5}. This shift is apparently caused by stronger screening of the localized states by a part of the f -electron density coming from the d "tails," which increases due to the larger contribution of extended Pt $5d$ states. The increased screening manifests itself in a 0.5-eV increase of ϵ_v for U $5f$ electrons upon Pt substitution. The U f charge calculated for dhcp UPd_{1.5}Pt_{1.5} is 0.06 of an electron larger than that in UPd₃. The excessive charge is provided by the small increase of the occupation numbers of $5f$ states lying above the Fermi level. These unoccupied states participate in the augmentation of the "tails" in the energy range -6 to -2 eV and, as a consequence, have nonzero occupation numbers which sum up to a difference of about 0.9 electrons between the total f charge in U AS and the sum of the occupations of localized $|\frac{5}{2}, \frac{5}{2}\rangle$ and $|\frac{5}{2}, \frac{3}{2}\rangle$ states.

From the comparison of the left and right panels of Fig. 5 one can notice that the change of the UPd_{1.5}Pt_{1.5} crystal structure from dhcp to hcp results in an additional shift of the localized U $5f_{5/2}$ states towards E_F which places them at about -0.4 eV. However, keeping in mind the strong dependence of the Fermi-level position on the crystal structure found for both ThPd₃ and ThPd_{1.5}Pt_{1.5}, it seems better to associate the change in the relative position of the localized U $5f_{5/2}$ states with the downward shift of E_F caused by modification of delocalized non- f states. The width of the occupied U $5f_{5/2}$ states is slightly larger in hcp UPd_{1.5}Pt_{1.5} which is probably a consequence of the higher density of delocalized band states in this energy range.

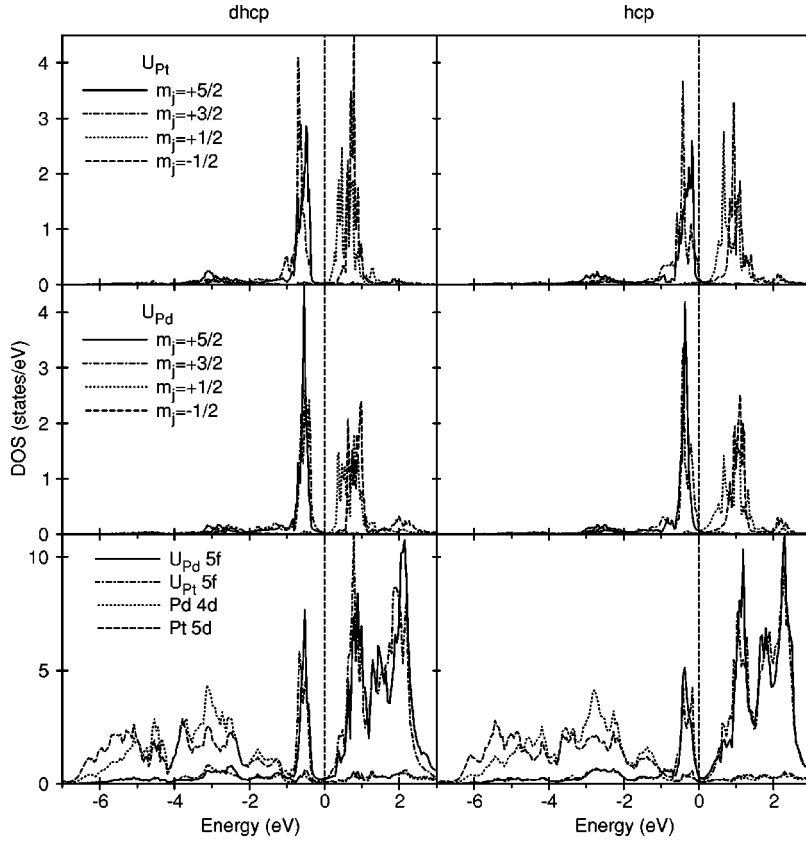


FIG. 5. Partial DOS and orbital resolved densities of U $5f_{5/2}$ states calculated for $\text{UPd}_{1.5}\text{Pt}_{1.5}$ in dhcp (left panels) and hcp (right panels) crystal structures using the LDA+ U method with spherically averaged $U=2$ eV and $J=0.5$ eV.

Substitution of all Pd atoms by Pt leads to a further increase of the Th f charge up to 1.061 in hcp ThPt_3 . Due to stronger screening by the density of the “tail”-like f electrons, the center of gravity of the occupied U $5f_{5/2}$ states in UPt_3 obtained from LDA+ U calculations is pushed even closer to E_F as compared to hcp $\text{UPd}_{1.5}\text{Pt}_{1.5}$. As a result of the shift the bands originating from U $|\frac{5}{2}, \frac{3}{2}\rangle$ states start to cross the Fermi level and these states become only partially occupied with the occupation equal to 0.894. This work is not aimed at the description of the heavy fermion behavior of UPt_3 ,²⁰ and we will not go into further details of the calculations.

In order to check the extent to which the results of the LDA+ U calculations depend on the value of U we also performed calculations with $U=2.6$ eV and $U=4.4$ eV obtained from LDA calculations using Slater’s transition state technique as described in Sec. III. The use of $U=2.6$ eV affects the results only slightly. The DOS peak originating from occupied $5f$ states shifts to lower energies and the agreement with the PES peak position worsens. As U increases to 4.4 eV, occupied U $5f$ states in UPd_3 move down to -3 -eV below E_F and become much wider because of strong hybridization with Pd d states. Unoccupied $5f$ states, however, shift only 0.5-eV upward and remain “pinned” to the Fermi level. Upon Pt substitution split by U , $5f$ states shift as a whole to higher energies.

Summarizing the results of LDA+ U calculations, the following scenario seems to provide a plausible explanation for the dependence of the binding energy of the Uf -derived peak in the $\text{UPd}_{3-x}\text{Pt}_x$ alloy on the Pt content observed in reso-

nant PES experiments.⁶ Because of the larger spatial extent of the Pt $5d$ wave function, an increase in the number of Pt nearest neighbors surrounding the U atom upon Pt substitution causes a proportional increase of the part of f -electron density at the U site provided by the “tails” of Pd and Pt d states. The screening of the localized U $5f$ states by this delocalized density becomes stronger and they shift to higher energy. The change of the structure from dhcp to hcp, which occurs gradually for x between 1 and 2, provokes the increase of the density of band states below E_F , clearly seen from the results of the LDA calculation for $\text{ThPd}_{3-x}\text{Pt}_x$, and a downward shift of the Fermi energy. In the PES experiment this manifest itself in an additional decrease of the binding energy of U $5f$ electrons. In Fig. 6 U $5f$ densities of states calculated for $\text{UPd}_x\text{Pt}_{3-x}$ with $x=0, 1.5,$ and 3 using the LDA+ U method are compared to the resonant PES spectra from Ref. 6. The LDA+ U results reproduce quite well the observed shift of the U $5f$ peak position towards the Fermi level with increased Pt content in the alloy. Considering the calculated density of unoccupied U $5f$ states we can suppose that if the proposed mechanism is correct a shift of a U $5f$ derived peak away from E_F should be observed in BIS spectra.

VII. SUMMARY AND CONCLUSIONS

The relativistic generalization of the LDA+ U method which takes into account that in the presence of spin-orbit coupling the occupation matrix of localized electrons is not diagonal in spin indices is used to calculate the electronic

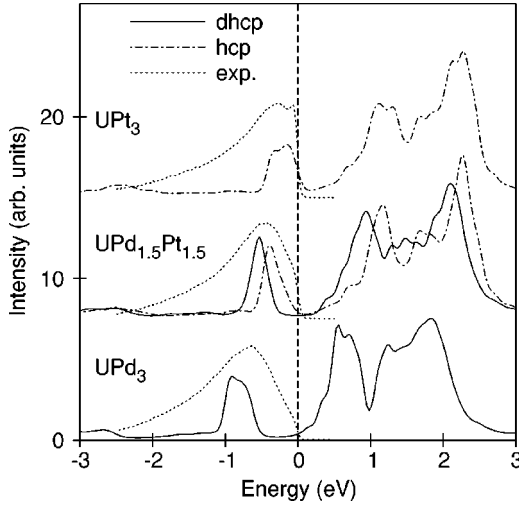


FIG. 6. The comparison of U 5f densities of states calculated for UP_xPt_{3-x} using the LDA+U method to the resonant PES spectra (dotted lines) from Ref. 6. Densities of states calculated for hcp and dhcp structures are shown by solid and dash-dotted lines, respectively.

structure of UPd₃, one of a few U compounds with localized 5f electrons. In contrast to the LDA, which places U 5f_{5/2} bands just at the Fermi level, LDA+U calculations with reasonable values of screened Coulomb $U=2$ eV and exchange $J=0.5$ eV integrals give a solution with two localized 5f electrons. The localized U 5f_{5/2} states form almost dispersionless bands at about 0.8-eV below E_F in good agreement with recent resonant PES and ARPES measurements. The remaining U 5f_{5/2} states form a rather wide peak centered at about 0.5-eV above E_F whereas 5f_{7/2} states are pushed by the on-site Coulomb repulsion to ~ 2 eV. This improves significantly the agreement with the UPd₃ BIS spectrum as compared to LDA calculations.

The dispersion of the bands crossing the Fermi level in the LDA+U calculations resembles strongly that within the LDA for ThPd₃ which suggests that the Fermi surface of ThPd₃ derived from LDA calculations can provide quite a reasonable approximation to the Fermi surface of UPd₃. Also, comparing the band structures of UPd₃ and ThPd₃ one notes that U 5f states are situated in the region of a very low DOS, well above the top of Pd 4d states. This seems to cause their localized nature.

The comparison of the band structures and densities of states calculated for ThPd₃ in pseudocubic, dhcp, and hcp crystal structures shows that the states in the vicinity of E_F and the position of the Fermi level itself are rather sensitive to the crystal structure. The increase of the DOS found for the hcp structure can be one of the reasons for partial delocalization of U 5f electrons in UPd_{3-x}Pt_x alloys with high Pt content. They undergo a dhcp-to-hcp structural transition at large x .

The analysis of the f charges in Th and U atomic spheres shows that about 0.9 of the total of 2.9 f electrons in U comes from the “tails” of Pd 4d states as a result of their decomposition inside U AS. Substitution of Pd atoms by Pt with more extended 5d states results in an increase on the part of

f -electron density at the U site originating from the “tails.” This leads to more effective screening of the localized U 5f electrons and to a shift of their energy position to higher energies. This mechanism, possibly amplified by the shift of the Fermi level upon the change of the crystal structure, seems to be responsible for the shift of the U 5f peak towards E_F with increased Pt content observed in resonant PES experiments.

APPENDIX: VARIATIONAL PRINCIPLE

In order to determine the way in which the LDA+U potential acts on the LMTO basis functions we follow a derivation similar to the one given in Ref. 17. The LMTO wave functions can be written as a one-center expansion²²

$$\Psi_{nk}(r) = \sum_{ilm\sigma} [a_{ilm\sigma}^{nk} \phi_{vl}(r_t) + b_{ilm\sigma}^{nk} \dot{\phi}_{vl}(r_t)] Y_{lm}(\hat{r}_t) \chi_{\sigma}, \quad (\text{A1})$$

where n is the band index, $\phi_{vl}(r_t)$ and $\dot{\phi}_{vl}(r_t)$ are the radial solution of the one-electron equation inside the atomic sphere centered at a site t and its energy derivative, respectively, and the matrices $a_{ilm\sigma}^{nk}$ and $b_{ilm\sigma}^{nk}$ can be expressed in terms of the eigenvectors obtained from the solution of the LMTO eigenvalue problem. Then, the diagonal in t and l index elements of the occupation matrix is given by

$$n_{m\sigma, m'\sigma'} = \sum_{nk} f_{nk} (a_{ilm\sigma}^{nk} a_{ilm'\sigma'}^{*nk} + b_{ilm\sigma}^{nk} b_{ilm'\sigma'}^{*nk} \langle \dot{\phi}_{vl}^2 \rangle), \quad (\text{A2})$$

where f_{nk} is the occupation of the $|nk\rangle$ state and $\langle \dot{\phi}_{vl}^2 \rangle = \int \dot{\phi}_{vl}^2(r) r^2 dr$. Here we have taken into account that ϕ_{vl} is normalized to unity inside its sphere and we dropped the site index t . In order to use the variational principle it is convenient to rewrite Eq. (A2) as

$$n_{m\sigma, m'\sigma'} = \sum_{nk} f_{nk} \left(\langle \phi_{vl} Y_{lm} \chi_{\sigma} | \Psi_{nk} \rangle \langle \Psi_{nk} | \phi_{vl} Y_{lm'} \chi_{\sigma'} \rangle + \frac{1}{\langle \dot{\phi}_{vl}^2 \rangle} \langle \dot{\phi}_{vl} Y_{lm} \chi_{\sigma} | \Psi_{nk} \rangle \langle \Psi_{nk} | \dot{\phi}_{vl} Y_{lm'} \chi_{\sigma'} \rangle \right). \quad (\text{A3})$$

The term $E^U - E^{\text{dc}}$ in the total-energy functional defined by Eq. (1) give rise to the appearance of an additional term in the Kohn-Sham equations,

$$\frac{\delta(E^U - E^{\text{dc}})}{\delta \Psi_n^*} = \sum_{\sigma, m_1, \sigma', m_2} V_{\sigma m_1, \sigma' m_2} \frac{\delta n_{\sigma m_1, \sigma' m_2}}{\delta \Psi_n^*}, \quad (\text{A4})$$

where $V_{\sigma m_1, \sigma' m_2}$ is obtained by taking the derivative of Eqs. (2) and (3) with respect to the elements of the occupation matrix. Finally, using Eq. (A3) one can write

$$\frac{\delta n_{\sigma m_1, \sigma' m_2}}{\delta \Psi_n^*} = [|\phi_{vl} Y_{lm_2} \chi_{\sigma'} \rangle \langle \phi_{vl} Y_{lm_1} \chi_{\sigma} | + \frac{1}{\langle \dot{\phi}_{vl}^2 \rangle} |\dot{\phi}_{vl} Y_{lm_2} \chi_{\sigma'} \rangle \langle \dot{\phi}_{vl} Y_{lm_1} \chi_{\sigma} |] \Psi_n. \quad (\text{A5})$$

Equations (A4) and (A5) specify the way in which the additional LDA+ U potential acts on the projections of the wave function Ψ_n onto $|lm\sigma\rangle$ subspace.

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