Unified character of correlation effects in unconventional Pu-based superconductors and $\delta$-Pu

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Electronic structure calculations combining the local-density approximation with an exact diagonalization of the Anderson impurity model show an intermediate $5f^5$-$5f^6$-valence ground state and delocalization of the $5f^5$ multiplet of the Pu atom $5f$-shell in PuCoIn$_5$, PuCoGa$_5$, and $\delta$-Pu. The $5f$-local magnetic moment is compensated by a moment formed in the surrounding cloud of conduction electrons. For PuCoGa$_5$ and $\delta$-Pu the compensation is complete and the Anderson impurity ground state is a singlet. For PuCoIn$_5$ the compensation is partial and the Pu ground state is magnetic. We suggest that the unconventional $d$-wave superconductivity is likely mediated by the $5f$-states antiferromagnetic fluctuations in PuCoIn$_5$, and by valence fluctuations in PuCoGa$_5$.

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Providing a consistent description of correlation effects in the electronic structure of elemental actinides and their compounds is a complex problem due to the interplay between the localized and the itinerant nature of the 5f electrons. It is commonly accepted that 5f-electrons in light actinides form rather broad conduction bands whereas for the heavy actinides the 5f states are atomic-like. Johansson 1 described this situation as a “Mott transition in the 5f-electron sub-system” taking place between Pu and Am when moving along the Periodic Table. Katsnelson et al. 2 linked the broadening of the 5f band to the “atomic collapse” characterizing the transformation from the high-temperature expanded and the low-temperature compressed phases of Pu.

A quantitative description of the Mott transition in actinides 3 was obtained by the dynamical mean-field theory (DMFT) 3 more than 20 years after the concept was formulated. Further DMFT studies suggested an intermediate-valence nature of the Pu-atom 5f shell 5 and provided justification for the experimentally proved absence of magnetism in $\delta$-Pu 6.

The intermediate-valence and nonmagnetic character of the 5f shell can play an important role in stabilizing the superconducting state exhibited by PuCoGa$_5$ below a critical temperature $T_c$ of 18.5 K. 6,7 The unconventional character of superconductivity in this compound is now generally accepted but the microscopic mechanism responsible for electron pairing remains unknown. The $d$-wave symmetry of the superconducting gap in PuCoGa$_5$ has been proven by point-contact spectroscopy experiments 10 that also provided the first spectroscopic measurements of the gap amplitude and its temperature dependence.

Recently, superconductivity has been discovered also in PuCoIn$_5$ 11, with $T_c = 2.5$ K. The experimental studies of this compound were immediately followed by conventional density functional theory (DFT) calculations in the local-density generalized-gradient approximation (LDA/GGA) 12,13. Keeping in mind a well known failure of DFT in the case of $\delta$-Pu 5, it can be expected that LDA/GGA does not provide an accurate description of the electronic structure for this strongly correlated material. A few static mean-field correlated band theory calculations were also performed 12,14, making use of different flavors of the LDA/GGA plus Coulomb’s $U$ (LDA+$U$) method. While being an improvement over the conventional band theory, the LDA(GGA)+$U$ falls short in describing the itinerant-to-localized crossover of the 5f manifold in $\delta$-Pu 5 and PuCoGa$_5$ 10.

Here, we report electronic structure calculations of PuCoIn$_5$, PuCoGa$_5$ and $\delta$-Pu performed by combining LDA with the exact diagonalization (ED) 15 of a discretized single-impurity Anderson model 10. In this approach, the band structure obtained by the relativistic version of the full-potential linearized augmented plane wave method (FP-LAPW) 17 is consistently extended to account for the full structure of the 5f-orbital atomic multiplets and their hybridization with the conduction bands 18.

The starting point of our approach is the multiband Hubbard Hamiltonian 10 $H = H^0 + H^\text{int}$, $H^0 = \sum_{i,j,\gamma} H_{\gamma i,j}^0 c_{\gamma i}^\dagger c_{\gamma j}$, where $i,j$ label lattice sites and $\gamma = (lm\sigma)$ mark spinorbitals $\{\phi_\gamma\}$, is the
one-particle Hamiltonian found from \textit{ab initio} electronic structure calculations of a periodic crystal; \(H^{\text{int}}\) is the on-site Coulomb interaction describing the \(f\)-electron correlation. We assume that electron interactions in the \(s\), \(p\), and \(d\) shells are well approximated in DFT.

The effects of the interaction Hamiltonian \(H^{\text{int}}\) on the electronic structure are described by a \(k\)-independent one-particle self-energy \(\Sigma(z)\), where \(z\) is a (complex) energy. The self-energy is constructed with the aid of an auxiliary impurity model describing the complete seven-orbital \(5f\) shell. This multi-orbital impurity model includes the full spherically symmetric Coulomb interaction, the spin-orbit coupling (SOC), and the crystal field (CF). The corresponding Hamiltonian can be written as

\[
H_{\text{imp}} = \sum_{kmm'\sigma\sigma'} \left[ \epsilon^k \delta_{m\sigma} \delta_{m'\sigma'} b_{km\sigma}^\dagger b_{km'\sigma'} + \sum_{m} \epsilon_f f_{m \sigma}^\dagger f_{m \sigma} \right]
+ \sum_{mm'\sigma\sigma'} \left[ \xi (1 \cdot s + \Delta_{\text{CF}}) \delta_{m\sigma} \delta_{m'\sigma'} f_{m \sigma}^\dagger f_{m' \sigma'} + h.c. \right]
+ \sum_{mm'\sigma\sigma'} \left[ V^k \delta_{m\sigma} \delta_{m'\sigma'} f_{m \sigma}^\dagger b_{km'\sigma'} + \text{h.c.} \right]
+ \frac{1}{2} \sum_{mm'm''\sigma\sigma'} U_{m'm'm''\sigma\sigma'} f_{m \sigma}^\dagger f_{m' \sigma'} f_{m'' \sigma'} f_{m'' \sigma''},
\]

where \(f_{m \sigma}^\dagger\) creates an electron in the \(5f\) shell and \(b_{km\sigma}^\dagger\) creates an electron in the “bath” that consists of those host-band states that hybridize with the impurity \(5f\) shell. The energy position \(\epsilon_f\) of the impurity level, and the bath energies \(\epsilon^k\) are measured from the chemical potential \(\mu\). The parameter \(\xi\) specifies the strength of the SOC and \(\Delta_{\text{CF}}\) is the crystal-field potential at the impurity. The parameter matrices \(V^k\) describe the hybridization between the \(5f\) states and the bath orbitals at energy \(\epsilon^k\).

The band Lanczos method \cite{13} is employed to find the lowest-lying eigenstates of the many-body Hamiltonian \(H_{\text{imp}}\) and to calculate the one-particle Green’s function \(G_{\text{imp}}(z)\) in the subspace of the \(f\) orbitals at low temperature \((k_B T = 1/500 \text{ eV})\). The self-energy \(\Sigma(z)\) is then obtained from the inverse of the Green’s-function matrix \(G_{\text{imp}}\).

Once the self-energy is known, the local Green’s function \(G(z)\) for the electrons in the solid, \(G(z)_{\gamma_1\gamma_2} = \frac{1}{V_{\text{BZ}}} \int_{\text{BZ}} \text{d}^3k \left[ \frac{1}{z + \mu - H_{\text{LDA}}(k) - \Sigma(z)} \right]_{\gamma_1\gamma_2}^{-1}, \quad \gamma_1, \gamma_2 = 1, 2, \ldots, 7, \]
is used to construct an effective LDA+\(U\) potential \(V_U\), which is inserted into Kohn–Sham-like equations:

\[
-\nabla^2 + V_{\text{LDA}}(r) + V_U + \xi (1 \cdot s) \Phi_{k}(r) = \epsilon_k \Phi_{k}(r).
\]

These equations are iteratively solved until self-consistency over the charge density is reached. In each iteration, a new Green’s function \(G_{\text{LDA}}(z)\) [which corresponds to \(G(z)\) from Eq. \(18\) with the self-energy \(\Sigma\) set to zero], and a new value of the \(5f\)-shell occupation are obtained from the solution of Eq. \(14\). Subsequently, a new self-energy \(\Sigma(z)\) corresponding to the updated \(5f\)-shell occupation is constructed. Finally, the next iteration is started by evaluating the new local Green’s function, Eq. \(14\).

In order to determine the bath parameters \(V^k\) and \(\epsilon^k\), we assume that the LDA represents the non-interacting model. We then associate the LDA Green’s function \(G_{\text{LDA}}(z)\) with the Hamiltonian of Eq. \(11\) when the coefficients of the Coulomb interaction matrix are set to zero \((U_{m'm'm''\sigma\sigma'}) = 0\). The hybridization function \(\Delta(z)\) is then estimated as \(\Delta(z) = -\frac{1}{\pi} \text{Im Tr} [G_{\text{LDA}}^{-1}(z) + \text{i} \delta]\). The curve obtained for \(\Delta(z)\) is shown in Fig. \(1\) together with the \(j = 5/2, 7/2\)-projected LDA densities of the \(f\)-states. The results also show that the hybridization matrix is, to a good approximation, diagonal in the \(\{j, j_z\}\) representation. Thus, we assume the first and fourth terms in the impurity model, Eq. \(11\), to be diagonal in \(\{j, j_z\}\), so that we only need to specify one bath state (six orbitals) with \(\epsilon^k_{j = 5/2}\) and \(V^k_{j = 5/2}\), and another bath state (eight orbitals) with \(\epsilon^k_{j = 7/2}\) and \(V^k_{j = 7/2}\). Assuming that the most important hybridization is the one occurring in the vicinity of \(E_F\), the numerical values of the bath parameters \(V^k_{5/2, 7/2}\) are found from the relation \(20\)

\[
\sum_k |V^k_j|^2 \delta(\epsilon^k_j - \epsilon) = -\Delta(\epsilon)/N_f \int_{-\infty}^{\infty} \text{d} z \left[ G(z)_{\gamma_1\gamma_2} \right], \quad \gamma_1, \gamma_2 = 1, 2, \ldots, 7.
\]
energy interval, \(E_F - 0.5 \text{ eV} \leq \epsilon \leq E_F + 0.5 \text{ eV}\), with \(N_f = 6\) for \(j = 5/2\) and \(N_j = 8\) for \(j = 7/2\). The bath-state energies \(\epsilon_{n_f}^{5/2,7/2}\) shown in Table I are adjusted to approximately reproduce the LDA 5f-state occupations \(n_f^{5/2}\) and \(n_f^{7/2}\).

**TABLE I.** 5f-states occupations \(n_f^{5/2}\) and \(n_f^{7/2}\), and bath state parameters \(\epsilon_{n_f}^{5/2,7/2}\) and \(V_{n_f}^{5/2,7/2}\) for Pu-atom in PuCoIn, PuCoGa5, and δ-Pu from LDA calculations.

<table>
<thead>
<tr>
<th>Material</th>
<th>(n_f^{5/2})</th>
<th>(n_f^{7/2})</th>
<th>(\epsilon_{n_f}^{5/2})</th>
<th>(V_{n_f}^{5/2})</th>
<th>(\epsilon_{n_f}^{7/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PuCoIn</td>
<td>4.78</td>
<td>0.39</td>
<td>0.36</td>
<td>0.21</td>
<td>-0.25</td>
</tr>
<tr>
<td>PuCoGa5</td>
<td>4.38</td>
<td>0.76</td>
<td>0.25</td>
<td>0.29</td>
<td>-0.07</td>
</tr>
<tr>
<td>δ-Pu</td>
<td>4.16</td>
<td>0.85</td>
<td>0.33</td>
<td>0.37</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

In the calculations we used an in-house implementation \[21, 22\] of the FP-LAPW method that includes both scalar-relativistic and spin-orbit coupling effects. The calculations were carried out assuming a paramagnetic state with crystal structure parameters for PuCoIn, PuCoGa5, and δ-Pu taken from Refs. \[11, 23, 24\], respectively. The Slater integrals were chosen as \(F_0 = 4.0 \text{ eV}\), and \(F_2 = 7.76 \text{ eV}, F_4 = 5.05 \text{ eV}\), and \(F_6 = 3.07 \text{ eV}\) \[22\]. This corresponds to commonly accepted values for Coulomb’s \(U = 4.0 \text{ eV}\) and exchange \(J = 0.64 \text{ eV}\). The SOC parameters \(\xi = 0.28 \text{ eV}\) for PuCoIn and PuCoGa5 and 0.29 eV for δ-Pu were determined from LDA calculations. CF effects were found to be negligible and \(\Delta_{\text{CF}}\) was set to zero. For the double-counting term entering the definition of the LDA+U potential, \(V_U\), we have adopted the fully-localized (or atomic-like) limit (FLL) \(V_{dc} = U(n_f - 1/2) - J(n_f - 1)/2\). Furthermore, we set the radii of the atomic spheres to 3.1 a.u. (Pu), 2.3 a.u. (Co), 2.3 a.u. (Ga), and 2.5 a.u. (In). The parameter \(R_{Pu} \times K_{\text{max}} = 10.54\) determined the basis set size, and the Brillouin zone (BZ) sampling was performed with 1152 k points. The self-consistent procedure defined by Eqs. \[1, 3\] was repeated until the convergence of the 5f-manifold occupation \(n_f\) was better than 0.01.

We are now ready to discuss the solution of Eq. (1). For PuCoIn, the ground state of the cluster formed by the 5f shell and the bath is given by a superposition of a magnetic sextet (23%) and a non-magnetic singlet (77%), with occupation numbers \(\langle n_f \rangle = 5.40\) in the shell and \(\langle n_{\text{bath}} \rangle = 8.40\) in the bath states. This ground state is not a singlet and carries a non-zero magnetic moment. For the 5f shell alone, the expectation values of the spin \(\langle S_f \rangle\), orbital \(\langle L_f \rangle\) and total \(\langle J_f \rangle\) angular momenta, respectively, can be calculated as \(\langle S^2 \rangle = X_f(X_f + 1)\), \(\langle L^2 \rangle = X_f\), \(\langle J^2 \rangle = 3.90\), and \(J_f = 2.09\). The individual components of the moments vanish, \(\langle S_f^2 \rangle = \langle L_f^2 \rangle = 0\), unless the symmetry is broken by an external magnetic field.

In the case of PuCoGa5, on the other hand, the hybridized ground state of the impurity is a non-magnetic singlet with all angular moments of the 5f-bath cluster equal to zero \((S = L = J = 0)\). It consists of \(\langle n_f \rangle = 5.30\) f states and \(\langle n_{\text{bath}} \rangle = 8.70\) bath states. In a pictorial way, we can imagine that the magnetic moment of the 5f shell (for which we get \(S_f = 2\), \(L_f = 4.05\), \(J_f = 2.43\)) is completely compensated by the moment carried by the electrons in the conduction band. As the value of the 5f magnetic moment fluctuates in time, because of the intermediate-valence electronic configuration, this compensation must be understood as dynamical in nature. The same situation is realized in δ-Pu (\(S_f = 2.11\), \(L_f = 4.21\), \(J_f = 2.62\)), whose ground state is found to be a nonmagnetic singlet with \(\langle n_f \rangle = 5.21\) and \(\langle n_{\text{bath}} \rangle = 8.79\).

The 5f-orbital density of states (DOS) obtained from Eq. (2) for the three investigated compounds is shown in Fig. 2. Below the Fermi energy \(E_F\) the DOS exhibits the three-peak structure typical for Pu and for a number of its compounds, and its shape is in good agreement with experimental photoemission spectra. It can be noticed that the multiplets for the atomic \(f^6\) configuration \((f^6 \rightarrow f^5\) transition, lying closer to \(E_F\)) are better resolved than for the \(f^5\) part of the spectrum \((f^5 \rightarrow f^4\) transition).

Comparison with previous LDA+Hubbard-I (HIA) calculation for δ-Pu \[18\] and PuCoGa5 \[20\] shows that the three-peak manifold lying above 2 eV binding energy has a slight upright shift towards \(E_F\). At binding energies around 4 eV, the LDA+HIA peaks are substantially modified, and in the LDA+ED calculations they are spread over a \(\sim 3\) eV energy interval. These changes in the DOS are induced by the hybridization and suggest partial delocalization of the \(f^5\) multiplet. This is a situation suggested first by Hanzawa \[27\] in intermediate-valence rare-earth compounds such as SmS or SmB6, where fluctuations occur between two atomic-like \(4f\) configurations. Here, the 5f states remain localized for the \(f^6\) configuration but become itinerant for the \(f^5\) one.

As the many-body resonances lying closer to the Fermi energy are produced by \(f^6 \rightarrow f^5\) multiplet transitions, they are in a way analogs to the Racah peaks, specific transitions between Racah multiplets \[28\] of \(f^n\) and \(f^{n+1}\). On the other hand, these structures determine the metallic character of the investigated materials that can therefore be considered as a realization of a Racah metal, situated between the two limiting cases represented by fully localized intermediate-valence rare-earth compounds and metallic systems (e.g., nickel) with a non-integer number of \(d\) electrons.

Both PuCoGa5 and δ-Pu display a temperature-independent magnetic susceptibility at low temperatures \[4, 29\]. Analogous to the intermediate-valence rare-earth compounds \[50\], the magnetic susceptibil-
FIG. 2. (Color online) f-electron density of states (DOS, $j = 5/2, 7/2$ projected) for the Pu atom in PuCoIn$_5$ (a), PuCoGa$_5$ (b) and $\delta$-Pu (c).

ity is anticipated to behave as $\chi \sim 1/(T + T_{fc})$, where the temperature $T_{fc}$ describes fluctuations between the $5f$ and conduction band electron states. $T_{fc}$ corresponds indeed to the broadening of the quasiparticle resonance near $E_F$ due to valence fluctuations [31]. As the ground state of the impurity is a singlet, we estimate $T_{fc}$ using a renormalized perturbation theory of the Anderson model [16]; $T_{fc} = -\pi^2k_B^2\Delta(E_F)/4|\Delta(E_F)/N_f|^2$, where $|\Delta(E_F)/N_f|$ is the hybridization per orbital at $E_F$, and $Z$ is a quasiparticle weight, $Z = (\text{Tr}[N(E_F)(1 - \delta \Sigma(\omega)/\partial \omega)]_{\omega = 0})/\text{Tr}[N(E_F)]$. We get $T_{fc} = 72$ meV ($\sim 850$ K) for PuCoGa$_5$ and $T_{fc} = 63$ meV ($\sim 750$ K) for $\delta$-Pu. Since $T_{fc}$ is high, $\chi$ remains constant for $T \ll T_{fc}$, as observed experimentally for PuCoGa$_5$ and $\delta$-Pu. The situation is different in the case of PuCoIn$_5$ where the ground state of the impurity is not a pure singlet due to weaker hybridization. Consequently, the temperature dependence of $\chi$ is expected to be more pronounced.

The electronic specific-heat coefficient can be estimated as $\gamma = \frac{\pi^2k_B^2}{3}\text{Tr}[N(E_F)(1 - \delta \Sigma(\omega)/\partial \omega)]_{\omega = 0}$. For $\delta$-Pu, we get $\approx 44$ mJ K$^{-2}$ mol$^{-1}$, in very good agreement with experimental data. For PuCoGa$_5$, we get $\approx 43$ mJ K$^{-2}$ mol$^{-1}$ which is smaller than the experimental value of 80–100 mJ K$^{-2}$ mol$^{-1}$. For PuCoIn$_5$, the estimated $\gamma$ value of $\approx 52$ mJ K$^{-2}$ mol$^{-1}$ is even further away from the experimental value of $\approx 180$ mJ K$^{-2}$ mol$^{-1}$. In this case, it is difficult to obtain an accurate value for $\gamma$ due to the sharp DOS peak in the vicinity of $E_F$ (see Fig. 2). When taken right at the DOS peak position, the $\gamma$ value of 95 mJ K$^{-2}$ mol$^{-1}$ is obtained. Also, note that a possible enhancement of $\gamma$ due to the electron-phonon interaction is not taken into account.

FIG. 3. (Color online) (Top) The band structure with $f$-weight fatbands for PuCoIn$_5$, and (bottom) the Fermi surface of PuCoGa$_5$ and PuCoIn$_5$ obtained from LDA+ED calculations. The shade of colors encodes the size of the energy gradient.

Figure 3 shows the band structure and the corre-
sponding Fermi Surface (FS) for PuCoIn$_5$, calculated from the solutions of Eq. 3, which represents an extended LDA+U static-mean-field band structure with the 5f-states occupation matrix obtained from the local impurity Greens function Eq. 2. For comparison, Fig. 3 shows also the FS for PuCoGa$_5$ (Fig. S2 of Ref. [12]). Close similarities in the band structure of the two compounds are immediately apparent. Both are compensated multiband metals, as the Fe-based superconductors, and for both materials the f bands move away from the Fermi level when the Coulomb-U is included, as can be seen by examining the f-weighted fatbands. The Fermi surfaces are composed by four sheets (1–4), one that is hole-like (FS-1) and three that are electron-like (FS-2,3,4). The Fermi velocities ratio $(v^2_x)^{1/2}/(v^2_y)^{1/2}$ of 1.54 for PuCoIn$_5$, and 1.55 for PuCoGa$_5$ are calculated in reasonable agreement with the experimental anisotropy ratio of the critical field $H_{c2}$, 2–2.3 for PuCoIn$_5$, and indicate a two-dimensional character of the electronic structure.

DFT electronic structure calculations for Pu-based 115 material have recently been reported by Ronning et al. [13] and Zhu et al. [12]. Their analysis of the DFT band structure and FS (see, e.g., Figs. 3 and 4 of Ref. [12]) indicated two possible superconducting gap symmetries, the so-called s± and $d_{x^2−y^2}$, which correspond to a pairing potential peaked at the $(\pi, \pi, 0)$ reciprocal lattice position. The conclusion was drawn that for Pu-based “115” superconductors, the s± order parameter is more likely that the $d_{x^2−y^2}$ one. This is in contradiction with point-contact spectroscopy results [10] showing a zero-bias conductance anomaly that is not expected for s± gap symmetry [32].

The presence of a 5f local moment dynamically compensated by the surrounding conduction electrons together with the f$^5$-f$^6$ intermediate-valence ground state in PuCoGa$_5$ and PuCoIn$_5$ opens various possibilities for unconventional superconductivity. In PuCoIn$_5$ the Pu f-shell local moment is not fully compensated and superconductivity could be related to an antiferromagnetic quantum critical point [11, 53]. On the other hand, in PuCoGa$_5$ the ground state is a singlet and it seems more plausible that superconductivity results from a valence instability, as in heavy-fermion superconductors [34].

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