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 $5f^5-5f^0$-valence ground state and delocalization of the $5f$ 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) [4] 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 [8], 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 [8] 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 [16]. 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] $H = H^0 + \Gamma$. $H^0 = \sum_{i,j,\gamma} H^0_{i,\gamma,j,\gamma} c_{i,\gamma}^{\dagger} c_{j,\gamma}$, where $i, j$ label lattice sites and $\gamma = (m, \sigma)$ mark spinorbitals $\{\phi_\gamma\}$, is the
one-electron 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 selfenergy \(\Sigma(z)\), where \(z\) is a (complex) energy. The selfenergy is constructed with the aid of an auxiliary impurity model describing the complete seven-orbital 5\(f\) 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

\[
H^\text{imp} = \sum_{kmm',\sigma\sigma'} [k^\sigma b_{kmm}^\dagger b_{km'm\sigma'}^\dagger + \sum_{m\sigma} \epsilon_f f_{m\sigma}^\dagger f_{m\sigma} + \sum_{mm'\sigma\sigma'} \xi l \cdot s + \Delta_{\text{CF}}] f_{m\sigma}^\dagger f_{m'\sigma'},
\]

where \(f_{m\sigma}^\dagger\) creates an electron in the 5\(f\) shell and \(b_{mm'}^\dagger\) creates an electron in the "bath" that consists of those host-band states that hybridize with the impurity 5\(f\) 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 5\(f\) states and the bath orbitals at energy \(\epsilon_k\).

The band Lanczos method \cite{15} 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 \(G^\text{imp}\).

Once the self-energy is known, the local Green’s function \(G(z)\) for the electrons in the solid, is used to construct an effective LDA+\(U\) potential \(V_U\), which is inserted into Kohn–Sham-like equations:

\[
-\nabla^2 + V^\text{LDA}(r) + V_U + \xi (l \cdot s) \Phi_k^\dagger(r) = \epsilon_k \Phi_k^\dagger(r).
\]

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. (3) with the self-energy \(\Sigma\) set to zero], and a new value of the 5\(f\)-shell occupation are obtained from the solution of Eq. (4). Subsequently, a new self-energy \(\Sigma(z)\) corresponding to the updated 5\(f\)-shell occupation is constructed. Finally, the next iteration is started by evaluating the new local Green’s function, Eq. (4).

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 \((U_{mm'm''m'''} = 0)\). The hybridization function \(\Delta(\epsilon)\) is then estimated as \(\Delta(\epsilon) = -\frac{1}{\pi} \text{Im} \text{Tr}[G^{-1}_{\text{LDA}}(\epsilon + i \delta)]\). The curve obtained for \(\Delta(\epsilon)\) 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 \(\epsilon^{j=5/2}_{j_z=5/2}\) and \(V^{j=5/2}_{j_z=5/2}\), and another bath state (eight orbitals) with \(\epsilon^{j=7/2}_{j_z=7/2}\) and \(V^{j=7/2}_{j_z=7/2}\). Assuming that the most important hybridization is the one occurring in the vicinity of \(E_F\), the numerical values of the bath parameters \(V^{j=5/2}_{k=5/2}, V^{j=7/2}_{k=7/2}\) are found from the relation \(20\)

\[
\sum_k |V_k^j|^2 \delta(\epsilon_k - \epsilon) = -\Delta(\epsilon)/N_f \int_{-\infty}^{E_F} dz [G(z)]_{j_11/2}.
\]
energy interval, $E_F - 0.5 \, eV \leq \epsilon \leq E_F + 0.5 \, eV$, with $N_f = 6$ for $j = 5/2$ and $N_f = 8$ for $j = 7/2$. The bath-state energies $\epsilon_{5/2,7/2}^{\pm}$ shown in Table I are adjusted to approximately reproduce the LDA $5f$-state occupations $n_f^{5/2}$ and $n_f^{7/2}$.

In Table I, $5f$-states occupations $n_f^{5/2}$ and $n_f^{7/2}$, and bath state parameters $\epsilon_{5/2,7/2}^{\pm}(eV)$, $V_{5/2,7/2}^{\pm}(eV)$ for Pu-atom in PuCoIn$_5$, PuCoGa$_5$, and $\delta$-Pu from LDA calculations.

<table>
<thead>
<tr>
<th>Material</th>
<th>$n_f^{5/2}$</th>
<th>$n_f^{7/2}$</th>
<th>$\epsilon_{5/2}^{\pm}$</th>
<th>$V_{5/2}^{\pm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PuCoIn$_5$</td>
<td>4.78</td>
<td>0.39</td>
<td>0.36</td>
<td>0.21</td>
</tr>
<tr>
<td>PuCoGa$_5$</td>
<td>4.38</td>
<td>0.76</td>
<td>0.25</td>
<td>0.29</td>
</tr>
<tr>
<td>$\delta$-Pu</td>
<td>4.16</td>
<td>0.85</td>
<td>0.33</td>
<td>0.27</td>
</tr>
</tbody>
</table>

In the calculations we used an in-house implementation 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$_5$, PuCoGa$_5$, and $\delta$-Pu taken from Refs. 11, 23, 24, respectively. The Slater integrals were chosen as $F_0 = 4.0 \, eV$, and $F_2 = 7.76 \, eV$, $F_1 = 5.05 \, eV$, and $F_0 = 3.07 \, eV$ 25. They correspond to commonly accepted values for Coulomb’s $U = 4.0 \, eV$ and exchange $J = 0.64 \, eV$. The SOC parameters $\xi = 0.28 \, eV$ for PuCoIn$_5$ and PuCoGa$_5$ and 0.29 eV for $\delta$-Pu were determined from LDA calculations. CF effects were found to be negligible and $\Delta$ 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 $R_{Pu} \times K_{max} = 10.54$ determined the basis set size, and the Brillouin zone (BZ) sampling was performed with 1152 $k$ points. The self-consistent procedure defined by Eqs. 4, 9 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$_5$, 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 $f$ shell and $\langle n_{bath} \rangle = 8.40$ 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 ($S_f$), orbital ($L_f$) and total ($J_f$) angular moments can be calculated as $\langle X_f^2 \rangle = X_f(X_f + 1)$, giving $S_f = 2.27$, $L_f = 3.90$, 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 PuCoGa$_5$, 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 $\langle n_{bath} \rangle = 8.70$ bath states. In a pictorial way, we can imagine that the magnetic moment of the $5f$ shell (for which we get $S_f = 2.18$, $L_f = 4.05$, $J_f = 2.43$) 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 $\delta$-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 $\langle n_{bath} \rangle = 8.79$.

The $5f$-orbital density of states (DOS) obtained from Eq. 1 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 $\delta$-Pu 18, and PuCoGa$_5$ 26 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 SmB$_6$, 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 analogous 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 PuCoGa$_5$ and $\delta$-Pu display a temperature-independent magnetic susceptibility at low temperatures 4, 29. Analogous to the intermediate-valence rare-earth compounds 30, 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], $T_{fc} = -\frac{\pi^2}{4} Z [\Delta(E_F)/N_f]$, where $[\Delta(E_F)/N_f]$ is the hybridization per orbital at $E_F$, and $Z$ is a quasiparticle weight, $Z = \langle \text{Tr}[N(E_F)(1 - \frac{\partial\Sigma(\omega)}{\partial\omega})]_{\omega=E_F} / \text{Tr}[N(E_F)] \rangle^{-1}$. We get $T_{fc} = 72 \text{ meV} \sim 850 \text{ K}$ for PuCoGa$_5$ and $T_{fc} = 63 \text{ meV} \sim 750 \text{ K}$ 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 $\gamma = \frac{\pi^2}{3} k_B^2 \text{Tr}[N(E_F)(1 - \frac{\partial\Sigma(\omega)}{\partial\omega})]_{\omega=E_F}$. For $\delta$-Pu, we get $\approx 44 \text{ mJ K}^{-2} \text{ mol}^{-1}$, in very good agreement with experimental data. For PuCoGa$_5$, we get $\approx 43 \text{ mJ K}^{-2} \text{ mol}^{-1}$ which is smaller than the experimental value of $80$–$100 \text{ mJ K}^{-2} \text{ mol}^{-1}$. For PuCoIn$_5$, the estimated $\gamma$ value of $\approx 52 \text{ mJ K}^{-2} \text{ mol}^{-1}$ is even further away from the experimental value of $\approx 180 \text{ mJ K}^{-2} \text{ mol}^{-1}$. 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 $95 \text{ mJ K}^{-2} \text{ mol}^{-1}$ is obtained. Also, note that a possible enhancement of $\gamma$ due to the electron-phonon interaction is not taken into account.

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. 5 shows also the FS for PuCoGa$_5$ (Fig. S2 of Ref. [10]). 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 $\langle v_F^2 \rangle_{\pi, \pi, \pi}$, $\langle v_F^2 \rangle_{\pm}$ 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 $H_c_2$, 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. [12] and Zhu et al. [13]. 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 $s\pm$ 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 $s\pm$ 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 $s\pm$ 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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