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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 element 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 subsystem” 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. [7,8]. 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 [14], 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 [14] 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 multi-band Hubbard Hamiltonian [10] $H = H^0 + H^{\text{int}}$, $H^0 = \sum_{i,j,\gamma} H^0_{i\gamma,j\gamma} c_{i\gamma}^\dagger c_{j\gamma}$, where $i,j$ label lattice sites and $\gamma = (lm\sigma)$ 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 $5f$ 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

$$H^{\text{imp}} = \sum_{kmm'\sigma\sigma'} [\epsilon_k f^\dagger_{m\sigma} f_{m'\sigma'} + \sum_{m'\sigma} \xi f^\dagger_{m\sigma} f_{m'\sigma'} + \sum_{m'\sigma} (|V|^2)^{\sigma'}_{\sigma} f^\dagger_{m\sigma} f_{m'\sigma'} + \text{h.c.}] + \frac{1}{2} \sum_{mm'm''m'''} U^{\text{imp}}_{mm'm''m'''} f^\dagger_{m'''} f_{m''} f^\dagger_{m'} f_{m'}$$

where $f^\dagger_{m\sigma}$ creates an electron in the $5f$ shell and $b^\dagger_{m\sigma}$ 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 $\epsilon_k^f$ 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 $V^{\text{imp}}$ describe the hybridization between the $5f$ states and the bath orbitals at energy $\epsilon_k^f$.

The band Lanczos method 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 ($k_B T = 1/500$ 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, is used to construct an effective LDA+$U$ potential $V_U$, which is inserted into Kohn–Sham-like equations:

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

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.\,[12] with the self-energy $\Sigma$ set to zero], and a new value of the $5f$-shell occupation are obtained from the solution of Eq.\,[13]. 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.\,[12].

In order to determine the bath parameters $V^f_k$ and $\epsilon^f_k$, 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 $\Delta(\epsilon) = -\frac{1}{\pi} \text{Im Tr}[G_{\text{LDA}}^{-1}(\epsilon + i\delta)]$. The curve obtained for $\Delta(\epsilon)$ is shown in Fig.\,[11] 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.\,[10], to be diagonal in (j, $j_z$), so that we only need to specify one bath state (six orbitals) with $\epsilon^{j=1}_{j_z=5/2}$ and $V^{j=1}_{j_z=5/2}$, and another bath state (eight orbitals) with $\epsilon^{j=1}_{j_z=7/2}$ and $V^{j=1}_{j_z=7/2}$. Assuming that the most important hybridization is the one occurring in the vicinity of $E_F$, the numerical values of the bath parameters $V^{j=1}_{5/2, 7/2}$ are found from the relation:\[20\]

\[
\sum_k |V^j_k|^2 \delta(\epsilon^j_k - \epsilon) = -\Delta(\epsilon)/N_f \text{ integrated over the}
\]

\[
\text{FIG. 1. (Color online) The Pu atom LDA } j = 5/2, 7/2 \text{ projected DOS, and LDA hybridization function } \Delta(\epsilon) = -\frac{1}{\pi} \text{Im Tr}[G_{\text{LDA}}^{-1}(\epsilon + i\delta)]. \text{ The inset shows the PuCoIn}_{5} \text{ crystal structure.}
\]
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 $\epsilon_1^{5/2, 7/2}$ shown in Table I are adjusted to approximately reproduce the LDA $5f$-state occupations $n_f^{5/2}$ and $n_f^{7/2}$.

<table>
<thead>
<tr>
<th>Material</th>
<th>$n_f^{5/2}$</th>
<th>$n_f^{7/2}$</th>
<th>$\epsilon_1^{5/2}$</th>
<th>$V_f^{5/2}$</th>
<th>$\epsilon_1^{7/2}$</th>
<th>$V_f^{7/2}$</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>
<td>-0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>PuCoGa$_5$</td>
<td>4.38</td>
<td>0.76</td>
<td>0.25</td>
<td>0.29</td>
<td>-0.07</td>
<td>0.34</td>
</tr>
<tr>
<td>$\delta$-Pu</td>
<td>4.16</td>
<td>0.85</td>
<td>0.33</td>
<td>0.27</td>
<td>-0.01</td>
<td>0.36</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$_5$, 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 corresponds 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 $\Delta_{CF}$ 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 $R_{Pu} \times K_{max} = 10.54$ 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$_5$, 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 $\langle X_f^2 \rangle = X_f(X_f + 1)$, $\langle S_f \rangle = S_f J_f L_f$, giving $S_f = 2.27$, $L_f = 3.90$, and $J_f = 2.09$. The individual components of the moments vanish, $\langle S_f^x \rangle = \langle L_f^x \rangle = 0$, 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. (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 $\delta$-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 $f^{n\pm 1}$. 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-
energy 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]:

$$T_{fc} = -\frac{\pi^2}{3} \frac{Z \Delta(E_F)}{N_f},$$

where $[\Delta(E_F)/N_f]$ is the hybridization per orbital at $E_F$, and $Z$ is a quasiparticle weight. $Z = \left(\text{Tr}[N(E_F)(1 - \frac{\partial^2}{\partial \omega^2})]|_{\omega = 0}\right)/\text{Tr}[N(E_F)]^{-1}$. 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 $\gamma = \frac{\pi^2 k_B^2}{3} \text{Tr}[N(E_F)(1 - \frac{\partial^2}{\partial \omega^2})]|_{\omega = 0}$. 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

![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).](image)

![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.](image)
sponding Fermi Surface (FS) for PuCoIn₅, 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 PuCoGa₅ (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 \( \langle v_x^2 \rangle / \langle v_y^2 \rangle \) of 1.54 for PuCoIn₅, and 1.55 for PuCoGa₅ are calculated in reasonable agreement with the experimental anisotropy ratio of the critical field \( H_{c2} \), 2 – 2.3 for PuCoIn₅, 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 than 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 PuCoGa₅ and PuCoIn₅ opens various possibilities for unconventional superconductivity. In PuCoIn₅ 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 PuCoGa₅ 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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