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

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(Dated: January 17, 2013)

Electronic structure calculations combining the local-density approximation with an exact diagonalization of the Anderson impurity model show an intermediate $5f^6-5f^6$-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$_5$.

PACS numbers: 74.70.Tx, 74.45.+c, 74.20.Mn, 74.20.Pq

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. [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 [9] 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 [3], 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 [12,13], 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 [3] 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 [19] $H = H^0 + H^{\text{int}}$. $H^0 = \sum_{i,j,\gamma} H_{ij}^{\gamma} c_i^\dagger \gamma c_j \gamma$, where $i,j$ label lattice sites and $\gamma = (l m \sigma)$ 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\cite{19} 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\cite{10}:

$$H_{\text{imp}} = \sum_{km\sigma'} \left[ e_f^{k\sigma'} b^\dagger_{km\sigma'} b_{km\sigma'} + \sum_{m\sigma} \xi \sigma \sigma' f^\dagger_{m\sigma} f_{m\sigma} ight]$$

$$+ \sum_{mm'\sigma\sigma'} \left[ \xi \mathbf{1} \cdot \mathbf{s} + \Delta_{\text{CF}} \right] b_{mm'\sigma} f_{m'\sigma'}$$

$$+ \sum_{km\sigma'} \left[ V^k \right] \sigma \sigma' f^\dagger_{m\sigma} b_{km'\sigma'} + \text{h.c.} \right]$$

$$+ \frac{1}{2} \sum_{mm'm''m'''} \left[ U_{mm'm''m'''} f^\dagger_{m''m'} f_{m''m'} + \text{h.c.} \right]$$

where $f^\dagger_{m\sigma}$ creates an electron in the $5f$ shell and $b^\dagger_{mn\sigma}$ creates an electron in the “bath” that consists of those host-band states that hybridize with the impurity $5f$ shell. The energy position $\xi_f$ of the impurity level, and the bath energies $\xi$ 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 $\xi^k$.

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 $[G^{\text{imp}}(z)]_{\pi\pi'}$ in the subspace of the $f$ orbitals at low temperature ($k_B T = 1/500$ eV). The self-energy $[\Sigma(z)]_{\pi\pi'}$ 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:

$$-\nabla^2 + V_{\text{LDA}}(r) + V_U + \xi (\mathbf{1} \cdot \mathbf{s}) \Phi^\dagger_k(r) = \epsilon_k \Phi_k(r).$$

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. (2) with the self-energy $\Sigma$ set to zero], and a new value of the $5f$-shell occupation are obtained from the solution of Eq. (3). 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. (4).

In order to determine the bath parameters $V^k$ and $\xi^k$, 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. (1) 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. 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. (1), to be diagonal in $\{j, j_z\}$, so that we only need to specify one bath state (six orbitals) with $\epsilon^k = \epsilon_{3j = 5/2}$ and $V^k = \epsilon_{3j = 5/2}$, and another bath state (eight orbitals) with $\epsilon^k = \epsilon_{3j = 7/2}$ and $V^k = \epsilon_{3j = 7/2}$. Assuming that the most important hybridization is the one occurring in the vicinity of $E_F$, the numerical values of the bath parameters $V^k$ are found from the relation\cite{20}:

$$\sum_{k} \left| V^k \right|^2 \delta(\epsilon^k - \epsilon) = -\Delta(\epsilon)/N_f$$

integrated over the
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 \( N_f = 8 \) for \( j = 7/2 \). The bath-state energies \( \epsilon_{5/2,7/2} \) shown in Table I are adjusted to approximately reproduce the LDA 5f-state occupations \( n_{5/2} \) and \( n_{7/2} \).

<table>
<thead>
<tr>
<th>Material</th>
<th>( n_{5/2} )</th>
<th>( n_{7/2} )</th>
<th>( \epsilon_{5/2} )</th>
<th>( V_{5/2} )</th>
<th>( \epsilon_{7/2} )</th>
<th>( V_{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 \( F_0 = 4.0 \text{ eV} \), and \( F_2 = 7.76 \text{ eV} \), \( F_3 = 5.05 \text{ eV} \), and \( F_6 = 3.07 \text{ eV} \) \([22]\). They correspond 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_5 and PuCoGa_5 and 0.29 eV for \( \delta \)-Pu were determined from LDA calculations. CF effects were found to be negligible and \( \Delta_{\text{CF}} \) was set to zero. For the double-counting term entering the definition of the LDA+U potential, \( V_{U_{\text{FLL}}} \), we have adopted the fully-localized (or atomic-like) limit (FLL) \( V_{\text{dc}} = U(n_f - 1/2) - J(n_f - 1)/2 \). 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. \([4, 9]\) 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 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 moments can be calculated as \( \langle X_f^2 \rangle = X_f(X_f + 1), \langle X_f = S_f, L_f, J_f \rangle \), 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 \( \langle S = L = J = 0 \rangle \). 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 \( S_f = 2.18 \), \( L_f = 4.05 \), \( J_f = 2.43 \)) 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 \( \langle n_{\text{bath}} \rangle = 8.79 \).

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 \([18]\), and PuCoGa_5 \([20]\) shows that the three-peak manifold lying above \( 2 \text{ eV} \) binding energy has a slight upright shift towards \( E_F \). At binding energies around \( 4 \text{ eV} \), the LDA+HIA peaks are substantially modified, and in the LDA+ED calculations they are spread over a \( \sim 3 \text{ eV} \) 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 way analogs to the Racah peaks, specific transitions between Racah multiplets \([28]\) of \( f^n \) and \( f^{n\pm1} \). 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 \((e.g., \text{nickel})\) with a non-integer number of \( d \) electrons.

Both PuCoGa_5 and \( \delta \)-Pu display a temperature-independent magnetic susceptibility at low temperatures \([3, 29]\). Analogous to the intermediate-valence rare-earth compounds \([30]\), the magnetic susceptibil-
The electronic specific-heat coefficient can be estimated as \[ \gamma = \frac{\pi^2}{3 k_B^2} \text{Tr}[N(E_F)(1 - \frac{\partial^2}{\partial \omega^2})](\omega=0) \]. 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 mJ K\(^{-2}\) 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 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. 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).

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 5$f^5$-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 $v_{\pi}^2/(v_{\pi}^2)$ of 1.54 for PuCoIn$_5$, and 1.55 for PuCoGa$_5$ are calculated in reasonable agreement with the experimental anisotropy of the critical field $H_{c2}$, 2.0 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 $s\pm$ 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 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 $s\pm$ gap symmetry 32.

The presence of a 5$f$ 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 11,33. 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.

We are grateful to D. Daghero and L. Havela for helpful comments and discussion. We acknowledge financial support from Czech Republic Grants No. GACR P204/10/0330 and No. GAAV IIA100100912 and from DFG Grant No. 436 TSE 113/53/0-1.

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