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Unified character of correlation effects in unconventional Pu-based superconductors and δ-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 δ-Pu. The $5f$ local magnetic moment is compensated by a moment formed in the surrounding cloud of conduction electrons. For PuCoGa$_5$ and δ-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 $5f$-state 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 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 δ-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.[7–9] 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 δ-Pu,[6] 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 δ-Pu (Ref. 5) and PuCoGa$_5$.[10]

Here, we report electronic structure calculations of PuCoIn$_5$, PuCoGa$_5$, and δ-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[19] $H = H^0 + H^{\text{int}}$. $H^0 = \sum_{i,j,\gamma} H^0_{i\gamma_1,j\gamma_2} c^\dagger_{i\gamma_1} c_{j\gamma_2}$, where i,j label lattice sites and $\gamma = (lm\sigma)$ mark spin-orbitals $\{\phi_\gamma\}$, is the one-particle Hamiltonian found from *ab initio* electronic structure calculations of a periodic crystal; H^{int} is the on-site Coulomb interaction[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^{int} on the electronic structure are described by a $\mathbf{k}$-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 multiorbital 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[16]

$$H_{\text{imp}} = \sum_{\substack{kmm'\\ \sigma\sigma'}} [\epsilon^k]^{\sigma\,\sigma'}_{mm'} b^\dagger_{km\sigma} b_{km'\sigma'} + \sum_{m\sigma} \epsilon_f f^\dagger_{m\sigma} f_{m\sigma}$$

$$+ \sum_{mm'\sigma\sigma'} [\xi \mathbf{l}\cdot\mathbf{s} + \Delta_{\text{CF}}]^{\sigma\,\sigma'}_{mm'} f^\dagger_{m\sigma} f_{m'\sigma'}$$

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$$+ \sum_{\substack{kmm'\\ \sigma\sigma'}} \left([V^k]^{\sigma\ \sigma'}_{mm'} f^\dagger_{m\sigma} b_{km'\sigma'} + \text{H.c.}\right)$$
$$+ \frac{1}{2} \sum_{\substack{mm'm''m'''\\ \sigma\sigma'}} U_{mm'm''m'''} f^\dagger_{m\sigma} f^\dagger_{m'\sigma'} f_{m'''\sigma'} f_{m''\sigma}, \qquad (1)$$

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 ϵ_f of the impurity level and the bath energies ϵ^k are measured from the chemical potential μ. The parameter ξ specifies the strength of the SOC, and Δ_{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 ϵ^k.

The band Lanczos method[15] is employed to find the lowest-lying eigenstates of the many-body Hamiltonian H_{imp} and to calculate the one-particle Green's function $[G_{\text{imp}}(z)]^{\sigma\ \sigma'}_{mm'}$ in the subspace of the f orbitals at low temperature ($k_{\text{B}}T = 1/500$ eV). The self-energy $[\Sigma(z)]^{\sigma\ \sigma'}_{mm'}$ 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,

$$[G(z)]_{\gamma_1\gamma_2} = \frac{1}{V_{\text{BZ}}} \int_{\text{BZ}} d^3k \, [z + \mu - H_{\text{LDA}}(\mathbf{k}) - \Sigma(z)]^{-1}_{\gamma_1\gamma_2}, \qquad (2)$$

is calculated in a single-site approximation as given in Ref. 18. Then, with the aid of the local Green's function $G(z)$, we evaluate the occupation matrix $n_{\gamma_1\gamma_2} = -\frac{1}{\pi} \operatorname{Im} \int_{-\infty}^{E_{\text{F}}} dz \, [G(z)]_{\gamma_1\gamma_2}$. The matrix $n_{\gamma_1\gamma_2}$ is used to construct an effective LDA + U potential V_U, which is inserted into Kohn-Sham-like equations:

$$[-\nabla^2 + V_{\text{LDA}}(\mathbf{r}) + V_U + \xi(\mathbf{l}\cdot\mathbf{s})]\Phi^b_{\mathbf{k}}(\mathbf{r}) = \epsilon^b_{\mathbf{k}}\Phi^b_{\mathbf{k}}(\mathbf{r}). \qquad (3)$$

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 Σ 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. (2).

In order to determine the bath parameters V^k and ϵ^k, we assume that the LDA represents the noninteracting 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 $\Delta(\epsilon) = -\frac{1}{\pi} \operatorname{Im} \operatorname{Tr}[G^{-1}_{\text{LDA}}(\epsilon + i\delta)]$. 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. (1), to be diagonal in $\{j, j_z\}$, so that we only need to specify one bath state (six orbitals) with $\epsilon^{k=1}_{j=5/2}$ and $V^{k=1}_{j=5/2}$ and another bath state (eight orbitals) with $\epsilon^{k=1}_{j=7/2}$ and $V^{k=1}_{j=7/2}$. Assuming that the most important hybridization is the one occurring in the vicinity of E_F, the numerical values of the bath parameters $V^{k=1}_{5/2,7/2}$ are found from the relation[20] $\sum_k |V^k_j|^2 \delta(\epsilon^k_j - \epsilon) = -\Delta(\epsilon)/N_f$ integrated over the energy interval $E_F - 0.5 \text{ eV} \leqslant \epsilon \leqslant E_F + 0.5$ eV, with $N_f = 6$ for $j = 5/2$ and $N_f = 8$ for $j = 7/2$. The bath-state energies $\epsilon^{k=1}_{5/2,7/2}$ shown in Table I are adjusted to approximately reproduce the LDA $5f$-state occupations $n^{5/2}_f$ and $n^{7/2}_f$.

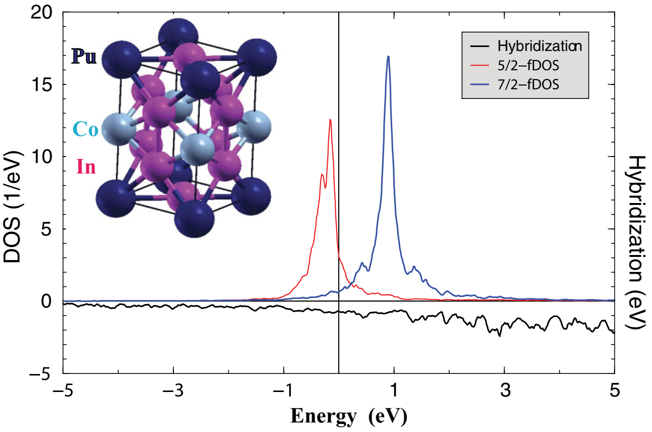

FIG. 1. (Color online) The Pu atom LDA $j = 5/2, 7/2$ projected DOS and LDA hybridization function $\Delta(\epsilon) = -\frac{1}{\pi} \operatorname{Im} \operatorname{Tr}[G^{-1}(\epsilon + i\delta)]$. The inset shows the PuCoIn$_5$ crystal structure.

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 δ-Pu taken from Refs. 11,23, and 24, respectively. The Slater integrals were chosen as $F_0 = 4.0$ eV and $F_2 = 7.76$ eV, $F_4 = 5.05$ eV, and $F_6 = 3.07$ 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 δ-Pu were determined from LDA calculations. CF effects were found to be negligible, and Δ_{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) $V_{\text{dc}} = U(n_f - 1/2) - J(n_f - 1)/2$. 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 $R_{\text{Pu}} \times K_{\text{max}} = 10.54$ 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$_5$, the ground state of the cluster formed by

TABLE I. $5f$-state occupations $n^{5/2}_f$ and $n^{7/2}_f$ and bath-state parameters $\epsilon^1_{5/2,7/2}$ (eV) and $V^1_{5/2,7/2}$ (eV) for Pu atoms in PuCoIn$_5$, PuCoGa$_5$, and δ-Pu from LDA calculations.

Material	$n^{5/2}_f$	$n^{7/2}_f$	$\epsilon^1_{5/2}$	$V^1_{5/2}$	$\epsilon^1_{7/2}$	$V^1_{7/2}$
PuCoIn$_5$	4.78	0.39	0.36	0.21	−0.25	0.25
PuCoGa$_5$	4.38	0.76	0.25	0.29	−0.07	0.34
δ-Pu	4.16	0.85	0.33	0.27	−0.01	0.36

the $5f$ shell and the bath is given by a superposition of a magnetic sextet (23%) and a nonmagnetic singlet (77%), with occupation numbers $\langle n_f \rangle = 5.40$ in the f shell and $\langle n_{\text{bath}} \rangle = 8.40$ in the bath states. This ground state is not a singlet and carries a nonzero 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 $\langle \hat{X}_f^2 \rangle = X_f(X_f + 1)$ $(X_f = S_f, L_f, J_f)$, giving $S_f = 2.27$, $L_f = 3.90$, and $J_f = 2.09$. The individual components of the moments vanish, $\langle \hat{S}_f^z \rangle = \langle \hat{L}_f^z \rangle = 0$, 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 nonmagnetic 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 $S_f = 2.18$, $L_f = 4.05$, $J_f = 2.43$) 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 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 ($f^6 \to f^5$ transition, lying closer to E_F) are better resolved than for the f^5 part of the spectrum ($f^5 \to f^4$ transition).

Comparison with previous LDA + Hubbard-I approximation (HIA) calculations for δ-Pu (Ref. 18) and PuCoGa_5 (Ref. 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 an ~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 $f^6 \to f^5$ multiplet transitions, they are in a way analogs to the Racah peaks, specific transitions between Racah multiplets[28] of f^n and $f^{n\pm1}$. 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., nickel) with a noninteger number of d electrons.

Both PuCoGa_5 and δ-Pu display a temperature-independent magnetic susceptibility at low temperatures.[6,29] Analogous to the intermediate-valence rare-earth compounds,[30] the magnetic susceptibility 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 renor-

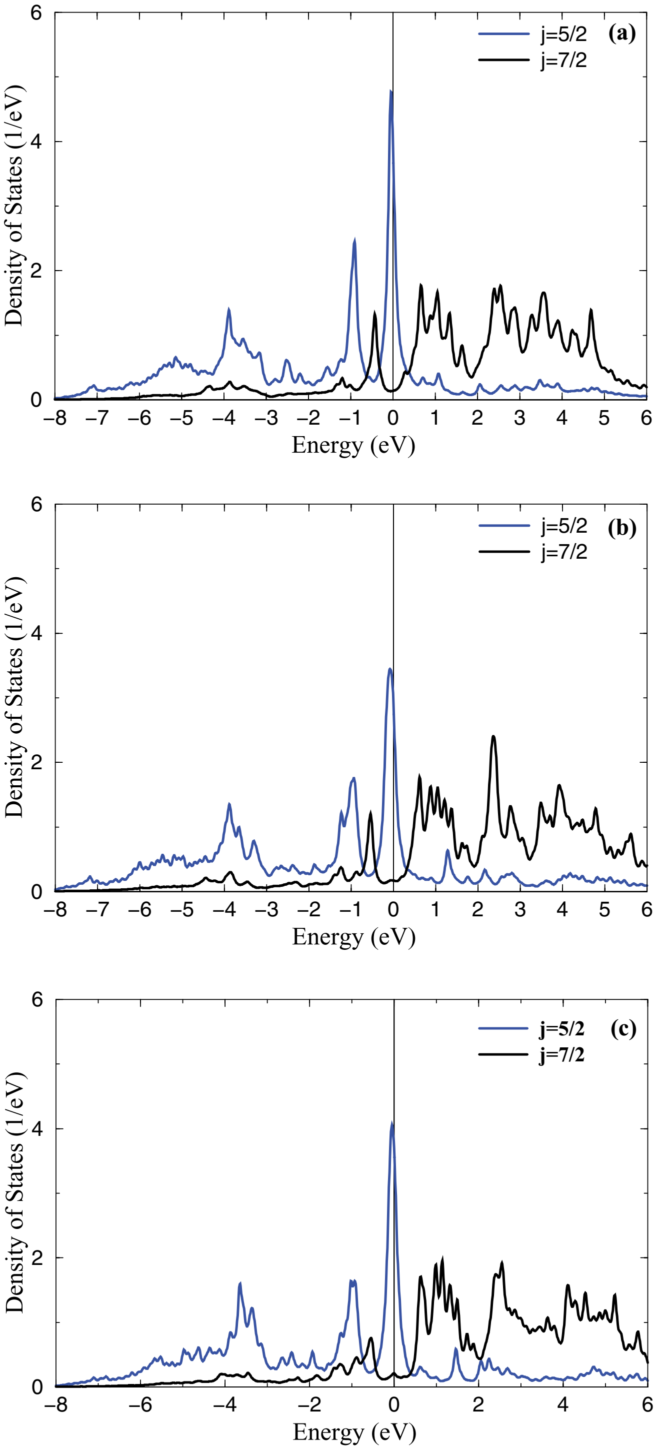

FIG. 2. (Color online) f-electron density of states ($j = 5/2, 7/2$ projected) for the Pu atom in (a) PuCoIn_5, (b) PuCoGa_5, and (c) δ-Pu.

malized 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, $Z = \{\mathrm{Tr}[N(E_F)(1 - \frac{d\Sigma(\epsilon)}{d\epsilon})|_{\epsilon=E_F}]/\,\mathrm{Tr}[N(E_F)]\}^{-1}$. We get $T_{fc} =$ 72 meV (~850 K) for $\mathrm{PuCoGa_5}$ and $T_{fc} = 63$ meV (~750 K) for δ-Pu. Since T_{fc} is high, χ remains constant for $T \ll T_{fc}$, as observed experimentally for $\mathrm{PuCoGa_5}$ and δ-Pu. The situation is different in the case of $\mathrm{PuCoIn_5}$, where the ground state of the impurity is not a pure singlet due to weaker hybridization. Consequently, the temperature dependence of χ is expected to be more pronounced.

The electronic specific-heat coefficient can be estimated as $\gamma = \frac{\pi^2}{3} k_B^2\, \mathrm{Tr}[N(E_F)(1 - \frac{d\Sigma(\omega)}{d\omega})|_{\omega=0}]$. For δ-Pu, we get ≈ 44 mJ $\mathrm{K^{-2}}$ $\mathrm{mol^{-1}}$, in very good agreement with experimental data. For $\mathrm{PuCoGa_5}$, we get ≈ 43 mJ $\mathrm{K^{-2}}$ $\mathrm{mol^{-1}}$, which is smaller than the experimental value of 80–100 mJ $\mathrm{K^{-2}}$ $\mathrm{mol^{-1}}$. For $\mathrm{PuCoIn_5}$, the estimated γ value of ≈ 52 mJ $\mathrm{K^{-2}}$ $\mathrm{mol^{-1}}$ is even further away from the experimental value of ≈ 180 mJ $\mathrm{K^{-2}}$ $\mathrm{mol^{-1}}$. In this case, it is difficult to obtain an accurate value for γ due to the sharp DOS peak in the vicinity of E_F (see Fig. 2). When taken right at the DOS peak position, the γ value of 95 mJ $\mathrm{K^{-2}}$ $\mathrm{mol^{-1}}$ is obtained. Also, note that a possible enhancement of γ due to the electron-phonon interaction is not taken into account.

Figure 3 shows the band structure and the corresponding Fermi surface (FS) for $\mathrm{PuCoIn_5}$, calculated from the solutions of Eq. (3), which represents an extended LDA + U static-mean-field band structure with the $5f$-state occupation matrix obtained from the local impurity Green's function equation (2). For comparison, Fig. 3 shows also the FS for $\mathrm{PuCoGa_5}$ (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 fat bands. 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 ratios $\langle v_{x,y}^2\rangle^{\frac{1}{2}}/\langle v_z^2\rangle^{\frac{1}{2}}$ of 1.54 for $\mathrm{PuCoIn_5}$ and 1.55 for $\mathrm{PuCoGa_5}$ are calculated in reasonable agreement with the experimental anisotropy ratio of the critical field H_{c2}, which is 2–2.3 for $\mathrm{PuCoIn_5}$, and indicate a two-dimensional character of the electronic structure.

DFT electronic structure calculations for Pu-based 115 materials 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]

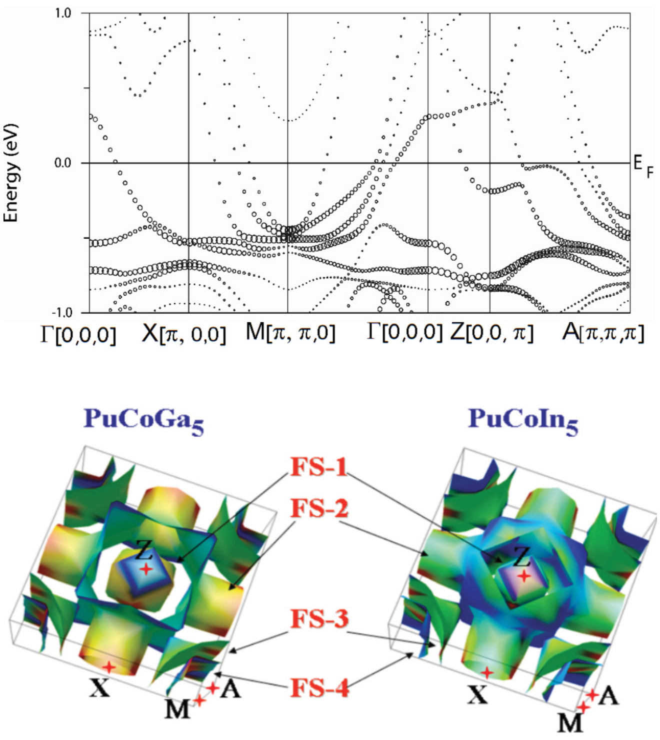

FIG. 3. (Color online) (top) The band structure with f-weight fat bands for $\mathrm{PuCoIn_5}$ and (bottom) the Fermi surface of $\mathrm{PuCoGa_5}$ and $\mathrm{PuCoIn_5}$ obtained from LDA + ED calculations. The shade of color encodes the size of the energy gradient.

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 $\mathrm{PuCoGa_5}$ and $\mathrm{PuCoIn_5}$ opens various possibilities for unconventional superconductivity. In $\mathrm{PuCoIn_5}$ 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 $\mathrm{PuCoGa_5}$ 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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