Electronic Structure and Correlation Effects in PuCoIn$_5$ as compared to PuCoGa$_5$

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Since their discovery nearly a decade ago, plutonium-based superconductors have attracted considerable interest, which is now heightened by the latest discovery of superconductivity in PuCoIn$_5$. In the framework of density functional theory (DFT) within the generalized gradient approximation (GGA) together with dynamical mean-field theory (DMFT), we present a comparative study of the electronic structure of PuCoIn$_5$ with the related material, PuCoGa$_5$. Overall, a similar GGA-based electronic structure, including the density of states, energy dispersion, and Fermi surface topology, was found for both compounds. The GGA Pu 5$f$ band was narrower in PuCoIn$_5$ than in PuCoGa$_5$, resulting in an effective reduction of Kondo screening in the former system, as also shown by DMFT calculations. This phenomenon is due to the expanded lattice for PuCoIn$_5$.

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Introduction. Plutonium-based materials have been studied for many years due to their importance in nuclear energy applications. Scientifically, these materials exhibit highly complex properties. Pu metal shows a significant volume expansion and anomalous magnetic properties [1]. These intriguing phenomena originate from the special location of Pu in the periodic table, which is at the boundary between the light actinides and heavy elements [2]. More recently, PuCoGa$_5$ [2] and PuRhGa$_5$ [3] were found to be unconventional superconductors [4–6]. Their respective transition temperatures of 18.5 K [2] and 8.7 K [3] are remarkably higher than in Ce-based heavy fermion compounds [7]. These discoveries have stimulated further interest in actinide compounds. It is now well accepted that these interesting phenomena in both Pu elemental solids and compounds arise from the strong electronic correlation in the 5$f$ electrons [8–14]. More recently, superconductivity has been discovered in PuCoIn$_5$ [15]. This new Pu compound shows superconductivity with a relatively lower transition temperature $T_N = 2.4$ K and preliminary measurements suggest it is magnetic at $T_N = 15$ K. The dramatic 28% volume expansion relative to PuCoGa$_5$ permits the exploration of competing Kondo-type coupling and RKKY-type superexchange interactions and their possible role for superconductivity as has been done in Ce-based compounds under pressure [16, 17]

Understanding the nature of 5$f$ electrons is central to understanding the electronic properties of the Pu-115s [18–22]. In this Letter, we present a comparative study of the electronic structure of PuCoIn$_5$ and PuCoGa$_5$. We show theoretically that the bare (GGA) 5$f$ band is narrower in PuCoIn$_5$ than in PuCoGa$_5$. Although they have the same number of Fermi surface sheets and similar band-center locations, the details of their Fermi surface topology are slightly different. In addition, the LDA+DMFT calculations show a reduction of Kondo screening in PuCoIn$_5$ relative to PuCoGa$_5$, which is related to the narrowing of the bare 5$f$ band. This reduction tips the competition between the Kondo coupling and the RKKY interaction towards magnetism in PuCoIn$_5$.

Methodology. We perform electronic structure calculations of PuCoIn$_5$ and PuCoGa$_5$ within the framework of density functional theory (DFT) in the generalized gradient approximation (GGA) [23]. Our calculations were carried out by using two relativistic band-structure methods — the full-potential linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN2k code [24], and the full-potential linear muffin-tin orbital (FP-LMTO) method as implemented in the RSPt code [25]. To address the 5$f$-electron correlation, we have used the GGA+U and the GGA+DMFT [26] approximations, which are implemented in the WIEN2k code [27]. For the DMFT impurity solver, we used the vertex-corrected one-crossing approximation (OCA) [28], which is reasonable for the description of more localized correlated electron systems.

LDA bandstructure and Fermi surface topology. PuCoIn$_5$ and PuCoGa$_5$ have a tetragonal HoCoGa$_5$ crystal structure ($P4/mmm$ space group) with one internal In or Ga z coordinate. We have calculated the volume dependence of the GGA-based total energy with the In and Ga z coordinates...
fixed at their experimental value of $z$(In)=0.306 [15] and $z$(Ga)=0.312 [2], respectively. As shown in Fig. 1, we find the theoretical equilibrium volumes to be 1052.7 a.u.$^3$ for PuCoIn$_5$ and 811.8 a.u.$^3$ for PuCoGa$_5$, which compare reasonably well with the experimental values of 1050.5 a.u.$^3$ for PuCoIn$_5$ and 820.2 a.u.$^3$ for PuCoGa$_5$. The good agreement at the GGA level indicates that the bonding between the transition metal and ligand atoms is the dominant factor determining the equilibrium volume of these Pu-115s, with the effect of the Pu 5f electron correlation secondary in this regard, which is in striking contrast to the situation for elemental Pu [8]. Hereafter all calculations are performed at the experimentally determined lattice constants [15].

Fig. 2 shows the GGA total and partial density of states (DOS). The two compounds exhibit somewhat similar features in the DOS. The strong spin-orbit coupling of Pu causes the 5f states to be split into two manifolds or subshells, corresponding to a total angular momentum of $j = 5/2$ and $j = 7/2$. The partial DOS for Pu 5f orbitals shows that the Pu 5f$_{5/2}$ states are the largest contribution at the Fermi energy, whereas the Co 3d and Ga 4p or In 5p orbitals have very small contributions. Furthermore, the narrow peak corresponding to Pu 5f$_{7/2}$ is located slightly below the Fermi energy. Both the f$_{5/2}$ and f$_{7/2}$ peaks are narrower and exhibit less structure in PuCoIn$_5$ than in PuCoGa$_5$, indicating a weakened hybridization in the former system. This is related to the larger lattice constant of PuCoIn$_5$, since the PuCoGa$_5$ unit-cell volume is 22% smaller than that of PuCoIn$_5$.

In Fig. 3, we show the band dispersion as a function of wave vector along high-symmetry lines. The Pu 5f band character is indicated by the relative width of each line. The overall structure in the two compounds is fairly similar, and, as expected from the DOS results, the bands in the vicinity of the Fermi energy consist mainly of Pu 5f states. How these bands cut the Fermi energy determines the Fermi-surface topology. In total, there are four bands that cut the Fermi energy, which gives rise to four Fermi-surface sheets, as shown in Fig. 4. Among these four sheets, two of them are of hole character derived from the two lower bands cutting the Fermi energy and two of them of electron character derived from the two upper bands cutting the Fermi energy. Two hole pockets are centered at the $\Gamma$ point in the zone center, while two electron pockets are centered at the $M$ point in the zone corners. At this level, the electronic structure of the Pu-115’s bears some resemblance to the recently discovered Fe-based superconduc-
Pu 5f occupancy and correlations effects. Our GGA calculations for the Sommerfeld coefficients were found to be $\gamma_{\text{GGA}} = 18$ mJ/mol·K$^2$ for PuCoIn$_5$ and $\gamma_{\text{GGA}} = 21$ mJ/mol·K$^2$ for PuCoGa$_5$. These values are smaller by a factor of about 10 and 4 to 5, respectively, than the experimental specific coefficients, which are estimated to be 200 mJ/mol·K$^2$ [15] for PuCoIn$_5$ and 80 to 116 mJ/mol·K$^2$ [4, 30, 31] for PuCoGa$_5$. Although the renormalization effect is not so strong as in Ce-based compounds [17, 32], the electronic correlations are important. To understand how it affects the magnetism and superconductivity in the Pu-115s, it would be valuable to have some insight into the Pu 5f valence of these compounds. For this purpose, we have performed GGA+U calculations by using two different methods for double counting corrections: the self-interaction correction (SIC) approximation [33] and the around-mean field (AMF) method [34]. In the calculations, we have taken an identical value of the muffin tin radius $R_{\text{MT}} = 3.28$ a.u. for both compounds. The Pu 5f occupation

for several values of $U$ is listed in Table I. As can be seen, only relative occupations between compounds are meaningful, since the occupation depends on the basis sets used as well as on the double-counting correction method, and is systematically larger with the AMF method than with the SIC approximation. However, regardless of which scheme was used, the Pu 5f occupation was found to be a little larger in PuCoIn$_5$ than in PuCoGa$_5$. The Fermi surface was qualitatively unchanged from that presented in Fig. 4 with the addition of $U$. Overall the Pu 5f valence was near 5, in agreement with a previous estimate based on the DFT+DMFT method [13, 14]. This number of Pu 5f electrons suggests a trivalent Pu ion (Pu$^{3+}$), which is consistent with experiment [2]. In addition, the magnetic susceptibility in PuCoGa$_5$ exhibits a Curie-like behavior [2, 35] before it enters the superconducting state, suggesting that the system is in close proximity to the magnetic instability. For PuCoIn$_5$, a magnetic state is observed at 15 K [15].

FIG. 4. (Color) Calculated Fermi surface of PM PuCoIn$_5$ (a) and PuCoGa$_5$ (b).

TABLE I. The Pu 5f occupations, which are obtained in the GGA+U approximation for both SIC and AMF methods for double counting corrections.

<table>
<thead>
<tr>
<th>Compound</th>
<th>U (eV)</th>
<th>$n_{5f}$/SIC</th>
<th>$n_{5f}$/AMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>PuCoIn$_5$</td>
<td>0.0</td>
<td>5.15</td>
<td>5.17</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>5.28</td>
<td>5.23</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>5.40</td>
<td>5.40</td>
</tr>
<tr>
<td>PuCoGa$_5$</td>
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<td>5.09</td>
<td>5.05</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>5.05</td>
<td>5.05</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>5.22</td>
<td>5.22</td>
</tr>
</tbody>
</table>

FIG. 5. (Color) Pu 5f DOS in the PM PuCoIn$_5$ and PuCoGa$_5$ from the GGA+DMFT calculations. (a): zoom-out view; (b) zoom-in view. The temperature is taken as 20 K. The data represented by blue line is for a conjectured PuCoIn$_5$ with volume reduced by 20%.
petition between the Kondo coupling and the magnetic exchange interactions. To have a qualitative understanding of the Kondo exchange coupling in these systems, we performed GGA+DMFT calculations. We used $U = 4$ eV for the Hartree component of the screened Coulomb interaction, which is consistent with previous work on elemental Pu [8–11]. Fig. 5 shows the Pu $5f$ partial DOS. It exhibits a three-peak structure. The two broad peaks below and above the Fermi energy correspond to the $j = 5/2$ and $j = 7/2$ subshells, respectively. The energy difference between these two peak is due mainly to the Hubbard $U$ and the spin-orbit coupling splittings. The central peak, which is very close to the Fermi energy, is a Kondo resonance state, which is a hallmark of quantum many-body effects. The Kondo resonance state, which constitutes a strongly renormalized quasiparticle band, is a generic feature that applies to both Pu-115 compounds. We have found a narrower quasiparticle bandwidth for PuCoIn$_5$ than for PuCoGa$_5$, which is consistent with the relative bare (GGA) Pu $5f$ bandwidths. We suspect that the expansion of the lattice plays a major role in the reduction of the Kondo screening. We have checked this by showing a broadening of the quasiparticle band when the unit-cell volume of PuCoIn$_5$ is reduced by 20% (c.f. the blue line in Fig. 5). By comparing the renormalized bandwidth with the bare one, a crude estimate of the renormalization would be about two orders of magnitude. This is reasonable, since the impurity solver is based on the non-crossing type of approximation that underestimates the Kondo screening [26]. Nonetheless, the overall trend of the Pu $5f$ electron properties that we have found for these compounds are expected to be robust, since they have persisted at every level of our calculations.

Concluding remarks. We have performed GGA band-structure calculations for PuCoIn$_5$ and PuCoGa$_5$. A similar electronic structure was found for both compounds. The bare Pu $5f$ band width in PuCoIn$_5$ was narrower due to the expanded lattice in PuCoIn$_5$ relative to PuCoGa$_5$, and caused a consequent reduction of the Kondo coupling. When put in the context of the Doniach phase diagram [36, 37], our calculations suggest that PuCoIn$_5$ is on the side of the weak hybridization limit, while PuCoGa$_5$ is more in the strong hybridization limit. We anticipate that a hypothetical PuCoTl$_5$ compound would have a magnetic state down to zero temperature. To experimentally uncover the localization-delocalization transition of Pu $5f$ electrons, PuCo(Ga,In)$_5$ alloys would be natural candidates. This study supports the notion that an expansion in lattice constant can indeed drive a transition into a localized state of Pu $5f$ electrons accompanied by magnetism. However, the role of spin, orbital, and/or valence fluctuations for the observation of superconductivity in Pu-based compounds remains to be determined [38, 39].

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