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Electronic structure and 4 f-electron character in Ce2 PdIn8 studied by angle-resolved photoemission spectroscopy

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Abstract
The localized-to-itinerant transition of f electrons lies at the heart of heavy-fermion physics, but has only been directly observed in single-layer Ce-based materials. Here, we report a comprehensive study on the electronic structure and nature of the Ce 4f electrons in the heavy-fermion superconductor Ce2PdIn8, a typical n=2 CenMmIn3n+2m compound, using high-resolution and 4d−4f resonant photoemission spectroscopies. The electronic structure of this material has been studied over a wide temperature range, and hybridization between f and conduction electrons can be clearly observed to form a Kondo resonance near the Fermi level at low temperatures. The characteristic temperature of the localized-to-itinerant transition is around 120 K, which is much higher than its coherence temperature Tcoh~30K.

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In heavy-fermion materials, \( f \) electrons generally exhibit both itinerant and localized features as the temperature changes. According to the standard Kondo lattice model, \( f \) electrons are localized at high temperatures, while conduction electrons would screen the local moments of \( f \) electrons to form Kondo singlets upon cooling, eventually resulting in an itinerant heavy Fermi-liquid ground state [1]. On the other hand, the recent two-fluid theory suggests that part of an atom’s \( f \) electrons gives rise to the itinerant properties at low temperatures, while others account for the localization behavior at higher temperatures [2–5]. Experimentally, a detailed evolution of the localized-to-itinerant transition has also been hotly debated [6–10]. Recently, the hybridization between \( f \) and conduction electrons can be clearly observed to form a Kondo resonance near the Fermi level at low temperatures. The characteristic temperature of the localized-to-itinerant transition is around 120 K, which is much higher than its coherence temperature \( T_{coh} \sim 30 \) K.

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The localized-to-itinerant transition of \( f \) electrons lies at the heart of heavy-fermion physics, but has only been directly observed in single-layer Ce-based materials. Here, we report a comprehensive study on the electronic structure and nature of the Ce \( 4f \) electrons in the heavy-fermion superconductor Ce\(_2\)PdIn\(_8\), a typical \( n = 2 \) Ce\(_n\)M\(_{n-1}\)In\(_{3n+2}\) compound, using high-resolution and 4\(d-4f\) resonant photoemission spectroscopies. The electronic structure of this material has been studied over a wide temperature range, and hybridization between \( f \) and conduction electrons can be clearly observed to form a Kondo resonance near the Fermi level at low temperatures. The characteristic temperature of the localized-to-itinerant transition is around 120 K, which is much higher than its coherence temperature \( T_{coh} \sim 30 \) K.

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The \( \text{Ce}_2\text{PdIn}_8 \) (\( M = \text{Co}, \text{Rh}, \text{or Ir} \), with \( n = 1, 2, \infty \)) heavy-fermion compounds consist of \( n \) layers of CeIn\(_3\), stacked sequentially along the \( c \) axis with one intervening layer of \( \text{MIn}_2 \) [17]. The electronic structure of the \( n = \infty \) and 1 compounds, CeIn\(_3\) and CeMIn\(_5\), has been extensively studied by angle-resolved photoemission spectroscopy (ARPES) [10–12,18,19], which has been proved to be a powerful tool to directly observe the behavior of \( f \) electrons. For the \( n = 2 \) compounds, Ce\(_2\)CoIn\(_6\) and Ce\(_2\)RhIn\(_8\) have been investigated through off-resonant ARPES, and Ce \( 4f \) electrons were found to be predominantly localized in both compounds [15,16]. However, to date, reports on these \( n = 2 \) compounds by means of on-resonance ARPES are still needed, in which the use of the 4\(d-4f\) resonance would largely enhance the \( f \)-electron photoemission matrix element. Moreover, for another important \( n = 2 \) member, Ce\(_2\)PdIn\(_8\) with the unique paramagnetic ground state, de Haas–van Alphen (dHvA) measurements [20] and x-ray photoelectron spectroscopy (XPS) [21] both suggest a delocalized character of the Ce \( 4f \) states therein, yet a direct observation of the \( f \)-electron behavior, and particularly the itinerant-to-localized transition, in this compound is still lacking.

In this Rapid Communication, we present a systematic ARPES study on Ce\(_2\)PdIn\(_8\). Its electronic structure is comprehensively revealed and directly compared with first-principles calculations. In particular, the character of the \( f \) electrons is studied by resonant ARPES, and the localized-to-itinerant
transition is directly found to set in at a surprisingly high temperature.

High-quality single crystals of Ce$_2$PdIn$_8$ were synthesized by a self-flux method as described in Ref. [22]. ARPES measurements were conducted with photons from Beam-line I05 of the Diamond Light Source, which is equipped with a Scienta R4000 electron analyzer. The overall energy resolution is 15–25 meV depending on the photon energy, and the angular resolution was set to 0.3°. Samples were cleaved at 10 K and then measured between 10 and 190 K under a vacuum better than 5 × 10$^{-11}$ Torr. Electronic band-structure calculations of Ce$_2$PdIn$_8$ were performed with the all-electron general potential linearized augmented plane-wave (FL-APW) method as implemented in the WIEN2K code [23]. The exchange and correlation effects were treated using generalized gradient approximation (GGA) in the form proposed by Perdew, Burke, and Ernzerhof [24]. The Ce 2f electrons were removed from valence band as it was previously done in density functional theory (DFT) calculations for Ce$_2$RhIn$_8$ [12,16]. Spin-orbit coupling (SOC) was included as a second variational step with a basis of scalar-relativistic plane waves with a cutoff of (R$_{MT}$K$_{max}$) $= 8$, where K$_{max}$ is the plane-wave cutoff, and R$_{MT}$ is the smallest of all atomic sphere radii. Experimental lattice parameters have been used with atoms fixed in their bulk positions.

Figure 1(a) illustrates the crystal structure of Ce$_2$PdIn$_8$ and the corresponding three-dimensional Brillouin zone (BZ). This compound forms in the tetragonal Ho$_2$CoIn$_8$-type crystal structure ($P4/mmm$) with lattice parameters a = b = 4.69 Å and c = 12.185 Å, and consists of a sequence of two CeIn$_3$ layers alternating with a PdIn$_2$ layer along the c axis [26]. To investigate its three-dimensional electronic structure, we have performed detailed $k_z$-dependent measurements by varying the photon energy between 75 and 95 eV. As shown in Fig. 1(b), there exists a weak photon-energy dependence of peak positions in the momentum distribution curves (MDCs) taken along the high-symmetry $\Gamma$-M direction, indicating the quasi-two-dimensional character. An inner potential of 13 eV, comparable to that of CeIn$_3$ [19], has been obtained through the best fit to the periodic variation of the MDCs’ peak positions according to the free-electron final-state model [27], allowing us to determine the photon energies corresponding to the high-symmetry planes.

Figures 1(c) and 1(d) compare photoemission intensity maps for the $\Gamma XM$ and $ZAR$ planes, and their detailed photoemission intensity plots along high-symmetry directions are illustrated in Figs. 1(e)–1(j) using the same colors. The Fermi surfaces in the $\Gamma XM$ plane consist of a square Fermi pocket around $\Gamma$ and a racetrack pocket centered at $X$ (both formed by the holelike band $\gamma$), and four pockets around $M$ resulting from the Fermi crossings of the electronlike bands $\alpha$, nearly degenerate $\epsilon/\delta$, and $\beta$. In the $ZAR$ plane, both the shape of most Fermi pockets and the corresponding band dispersions exhibit only minor variations, confirming the quasi-two-dimensional character of these bands. Still, differences can be resolved between the Fermi-surface topologies of these two $k_z$ planes. Changes in both the shape and size of the $\gamma$ pocket in the $ZAR$ plane imply a three-dimensional character of this band. The main bands in the vicinity of the Fermi level ($E_F$) have a similar orbital character to those in the $n = 1$ compound CeCoIn$_5$, while band splitting due to...
interlayer coupling makes the band structure of \( \text{Ce}_2\text{PdIn}_8 \) more complex. Overall, our experimental data show a qualitative agreement with first-principles calculations, as displayed in Figs. 1(k) and 1(l).

In order to highlight the \( f \)-electron behavior, we chose 121-eV photons (the energy of the Ce 4\( d \)-4\( f \) transition) to realize a resonant enhancement of the Ce 4\( f \) photoionization cross section. Figures 2(b) and 2(c) show the off-resonance and on-resonance photoemission intensity plots along \( \Gamma \)-\( M \), taken with 114- and 121-eV photons, respectively, using \( s \)-polarized light. The corresponding on-resonance photoemission intensity plot taken with \( p \)-polarized light is displayed in Fig. 2(d). Here, \( p \)- and \( s \)-polarized light is defined to be from electric fields in and out of the emission plane, which is determined by the analyzer slit and the sample surface normal, as illustrated in Fig. 2(a).

As shown in Fig. 2(b), Pd 4\( d \) and Ce 5\( d \) states dominate the off-resonance spectra, consistent with the data shown in Fig. 1(e). The Ce 4\( f \) character is strongly enhanced in the on-resonance cases, as demonstrated by the flat bands in the photoemission intensity plots [Figs. 2(c) and 2(d)] and the apparent peaks in the corresponding integrated spectra [Fig. 2(e)]. The three evident features located around \( E_F \), \(-0.25 \) and \(-2.5 \) eV below \( E_F \), can be well understood by the single impurity Anderson model (SIAM) and were thus assigned as \( 4f^{5/2} \), \( 4f^{7/2} \), and \( 4f^0 \), respectively \([10,29]\). Moreover, we note that the 4\( f \) state near \( E_F \) shows a sharp peak under \( s \)-polarized light but a broad hump in \( p \)-polarized light, and the overall \( f \)-electron intensity observed with \( p \)-polarized light is weaker than with \( s \)-polarized light. Therefore, further investigations of the Ce 4\( f \) states in this compound were performed with \( s \)-polarized light.

Next, we performed temperature-dependent ARPES measurements on this compound to investigate the evolution of the itinerant/localized nature of the \( f \) electrons with temperature. At 5 K, a flat \( f \)-electron feature near \( E_F \) can be clearly observed in the intensity plot, as demonstrated in Fig. 3(a). At this temperature, large \( f \) spectral weight can be clearly observed near \( E_F \), suggesting a rather itinerant nature of the \( f \) electrons. Upon increasing the temperature, the spectral weight of the \( f \) states gradually diminishes while that of the \( \beta \) band is still preserved even to a rather high temperature (180 K). This temperature dependence is also clearly visible.
when directly comparing the EDCs at $\Gamma$ taken at different temperatures [Fig. 3(b)]. We observe a suppression of the $f$ spectral weight upon increasing temperature, and the sharp $f$-electron quasiparticle peak near $E_F$ is no longer visible at 150 K. Figure 3(c) presents the temperature dependence of $f$-electron spectral weight in the vicinity of $\Gamma$ in Ce$_2$PdIn$_8$, which is obtained by integrating the EDCs over $[E_F - 100 \text{meV}, E_F + 10 \text{meV}]$. Here, the spectral weight has been normalized at 200 K and is found to keep rising with the decreasing temperature, showing the same trend as Fig. 3(b).

For comparison, Figs. 3(d) and 3(e) show the normalized photoemission intensity maps taken at 5 and 190 K, respectively. In the 5-K Fermi-surface map, the normalized intensity around the Brillouin zone center is strongly enhanced, originating from the itinerant $f$ states. In contrast, the $f$ electron spectral weight around the same momentum is greatly suppressed for the map contour taken at 190 K. Note that we have presented both maps using the same color scale, so the much higher spectral weight around the zone center at 5 K should not be artificial. Moreover, as shown in the Supplemental Material [28], a direct comparison of MDCs taken at 5 and 190 K can further confirm the spreading out of the $f$-band spectral weight from the zone center to somewhere with the increasing temperature. All the above data explicitly show the characteristic localized-to-itinerant crossover of $f$ electrons. Remarkably, the occurrence of hybridization starts from about 120 K in Ce$_2$PdIn$_8$, which is much higher than $T_{\text{coh}} \approx 30 \text{ K}$ [22,30–32].

In Fig. 4 we present the zoomed-in photoemission intensity plot near $E_F$ to concentrate on the $f$-electron character and quasiparticle bands. Compared with spectra taken at high temperatures, when the $\beta$ band shows linear dispersion, evident bending of this band around $E_F$ can be observed at the low temperature [Fig. 4(a)]. This is a direct evidence of the hybridization between the $f$ and conduction electrons. According to the standard view on the heavy-fermion ground state based on the periodic Anderson model (PAM), the hybridization between the $f$ and conduction electrons would create two separate bands with band bending near $E_F$. Meanwhile, the $f$ spectral weight should be redistributed, with a significant enhancement to the “inside” of the holelike bands and the “outside” of the electronlike bands. In Fig. 4(b), we indeed observe the enhancement of the $f$ spectral weight “inside” of the holelike $\beta$ band, which is more evidence for the hybridization between the $f$ and conduction electrons in Ce$_2$PdIn$_8$. Such behavior is similar to that observed in the heavy-fermion compound CeIrIn$_5$ [14].

To further quantitatively investigate the hybridization of conduction bands and $f$ electrons, we zoomed in on the spectral feature around $\Gamma$ in the vicinity of $E_F$ and then performed the PAM fitting, which has been proved to be an effective way to study the $f$-electron behaviors [10,13]. Details of the band dispersion extraction and the PAM fitting can be found in the Supplemental Material [28]. Here, the resolution-convoluted Fermi-Dirac distribution has been divided in order to probe the band structure slightly above $E_F$, as shown in Fig. 5(a).

Quantitatively, a fit to the PAM picture gives a renormalized hybridization $V_2 = 15 \pm 5 \text{ meV}$ for both conduction bands, which implies the substantial hybridization strength between $f$ electrons and conduction $d$ bands. Moreover, as shown in Fig. 5(b), a heavy quasiparticle band is induced with an energy dispersion of around 6 meV, which is larger than that in CeIn$_3$ [18,33], indicating a stronger hybridization in CeIn$_3$.

To summarize, we have characterized the electronic structure and $f$-electron behavior of Ce$_2$PdIn$_8$ using high-resolution resonant and nonresonant ARPES. Besides presenting the low-lying electronic structure of this material, we have shown how localized $f$ electrons in Ce$_2$PdIn$_8$ become partially itinerant and evolve into the heavy-fermion state from a much higher temperature than the coherence temperature $T_{\text{coh}}$. These findings provide a comprehensive experimental picture of the character of $f$ electrons in Ce$_2$PdIn$_8$, complementing our understanding of the $f$ electrons’ itinerant-to-localized evolution in the Ce$_nM_{m}$In$_{3n+2m}$ heavy-fermion family.

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