Electronic structure and 4f-electron character in Ce$_2$PdIn$_8$
studied by angle-resolved photoemission spectroscopy

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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$_2$In$_{3n+2}$ 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 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.

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 give rise to the itinerant properties at low temperatures, while others account for the localization behavior at higher temperatures [2–5]. Experimentally, detailed evolution of the localized-to-itinerant transition has also been hotly debated [6–10]. Recently, the hybridization between f and conduction electrons were extensively studied, and direct evidence for such localized-to-itinerant transition has been observed in the CeMIn$_3$ family (M=Co, Rh or Ir) [10–14]. However, in other Ce-based heavy-fermion compounds, temperature evolution of the localized-to-itinerant transition of the f electrons has never been reported to the best of our knowledge [15–16].

The Ce$_n$MIn$_{3n+2}$ (M=Co, Rh 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 MIn$_2$ [17]. The electronic structure of the $n=\infty$ and I 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$_6$ 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 there have been no reports on these $n=2$ compounds by means of on-resonance ARPES, in which the use of the 4d-4f resonance would largely enhance the f-electron photoemission matrix element. Moreover, for another important n=2 member, Ce$_3$PdIn$_8$ with the unique para-magnetic ground state, de Haas-van Alphen (dHvA) measurements [20] and X-ray photoelectron spectroscopy (XPS) [21] both suggest 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 Beamline 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 Ce₂PdIn₈ 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, Wang and Ernzerhof [24]. The Ce 2f electrons were removed from valence band as it was previously done in DFT calculations for Ce₃RhIn₆ [12, 16]. Spin-orbit coupling (SOC) was included as a second variational step with a basis of scalar-relativistic eigenfunctions, after the initial calculation was converged to self-consistency. The Monkhorst–Pack [25] special k-point scheme with 23 × 23 × 9 mesh was used resulting in 390 k points in the irreducible part of the Brillouin zone. The wave functions in the interstitial region were expanded using plane waves with a cutoff of (RₘₚKₘₚ) = 8, where Kₘₚ is the plane wave cut-off, and Rₘₚ is the smallest of all atomic sphere radii. Experimental lattice parameters have been used with atoms fixed in their bulk positions.

Fig. 1(a) illustrates the crystal structure of Ce₂PdIn₈ and the corresponding three-dimensional Brillouin zone (BZ). This compound forms in the tetragonal Ho₂CoIn₆-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 Ce₃In₃ layers alternating with a PdIn₂ layer along the c axis [24]. To investigate its three-dimensional electronic structure, we have performed detailed k-dependent measurements by varying the photon energy between 75 and 95 eV. As shown in Fig. 1(b), there exists weak photon-energy dependence of peak positions in the momentum distribution curves (MDCs) taken along the high symmetry Γ-M direction, indicating the quasi-two-dimensional character. An inner potential of 13 eV, comparable to that of CeIn₃, [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.

Figs. 1(c) and 1(d) compare photoemission intensity maps for the ΓXM and ZAR planes, and their detailed photoemission intensity plots along high-symmetry directions are illustrated in Figs. 1(e–j) using the same colors. The Fermi surfaces in the ΓXM plane consist of a square Fermi pocket around Γ and a racetrack pocket centered at X (both formed by the hole-like band γ), and four pockets around M resulting from the Fermi crossings of the electron-like bands α, nearly-degenerate ε/δ, and β. 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 kₚ planes. Changes in both the shape and size of the γ pocket in the ZAR plane imply a three-dimensional character of this band. The main bands in the vicinity of the Fermi level (Eₘ) have similar orbital character to those in the n=1 compound CeCoIn₅, while band splitting due to interlayer coupling makes the band structure of Ce₂PdIn₈ more complex. Overall, our experimental data show a qualitative agreement with first-principles calcu-
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 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 quasi-particle peak near $E_F$ is no longer visible at 150 K. Fig. 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 $|E_F - 100\text{ meV}|$. Here, the spectral weight has been normalized at 200K and is found to keep arising with the decreasing temperature, showing the same trend as Fig. 3(b).

For comparison, Fig. 3(d) and Fig. 3(e) show the normalized photoemission intensity maps taken at 5 K 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 supplementary material[23], direct comparison of MDCs taken at 5 K 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, which has never been reported in the prototypical Ce 218 heavy fermion systems before. Remarkably, the occurrence of hybridization starts from about 120 K in Ce$_2$PdIn$_8$, which is much higher than $T_{coh} \sim 30\text{ K}$ [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 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 significant enhancement to the “inside” of the hole-like bands and the “outside” of the electron-like bands. In Fig. 4(b), we indeed observe the enhancement of the f spectral weight “inside” of the hole-like $\beta$ band, which is one 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
To further quantitatively investigate the hybridization of conduction bands and $f$ electrons, we zoom in the spectral feature around $\Gamma$ in the vicinity of $E_F$ and then performed the PAM fitting, which has been proved an effective way to study the $f$ electron behaviors \cite{10, 13}. Details of the band dispersion extraction and the PAM fitting can be found in the supplementary material \cite{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 PAM picture gives a renormalized hybridization $V_c=15\pm 5$ 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$_3$ \cite{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 non-resonant 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 $T_{coh}$. These findings provide a comprehensive experimental picture of the character of $f$ electrons in Ce$_2$PdIn$_8$, complementing our understanding of $f$ electrons' itinerant-to-localized evolution in the Ce$_n$M$_m$In$_{3n+2m}$ heavy fermion family.
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[1] P. Coleman and A. H. Nevidomskyy, Journal of Low Temperature Physics 161, 182 (2010)
[2] Y. F. Yang, Z. Fisk, H.-O. Lee, J. D. Thompson, and D. Pines, Nature 454, 611 (2008)
[3] Y. F. Yang and D. Pines, Phys. Rev. Lett. 100, 096404 (2008)
[4] Y. F. Yang and D. Pines, Proc Natl Acad Sci U S A 109, E3060 (2012)
[5] Y.-t. Yang, R. Urbano, N. J. Curro, D. Pines, and E. D. Bauer, Phys. Rev. Lett. 103, 197004 (2009)
[6] H. Shishido, R. Settai, D. Aoki, S. Ikeda, H. Nakawaki, N. Nakamura, T. Iizuka, Y. Inada, K. Sugiyama, T. Takeuchi, K. Kindo, T. C. Kobayashi, Y. Haga, H. Harima, Y. Aoki, T. Namiki, H. Sato, and Y. Omuki, Journal of the Physical Society of Japan 71, 162 (2002)
[7] K. Haule, C.-H. Yee, and K. Kim, Phys. Rev. B 81, 195107 (2010)
[8] A. Koitzsch, S. V. Borisenko, D. Inosov, J. Geck, V. B. Zabolotnyy, H. Shiozawa, M. Knupfer, J. Fink, B. Büchner, E. D. Bauer, J. L. Sarrao, and R. Follath, Phys. Rev. B 77, 155128 (2008)
[9] A. Koitzsch, I. Opahle, S. Elgazzar, S. V. Borisenko, J. Geck, V. B. Zabolotnyy, D. Inosov, H. Shiozawa, M. Richter, M. Knupfer, J. Fink, B. Büchner, E. D. Bauer, J. L. Sarrao, and R. Follath, Phys. Rev. B 79, 075104 (2009)
[10] Q. Y. Chen, D. F. Xu, X. H. Niu, J. Jiang, R. Peng, H. C. Xu, C. H. P. Wen, Z. F. Ding, K. Huang, L. Shu, Y. J. Zhang, H. Lee, V. N. Strocov, M. Shi, F. Bisti, T. Schmitt, Y. B. Huang, P. Dudin, X. C. Lai, S. Kirchner, H. Q. Yuan, and D. L. Feng, Phys. Rev. B 96, 045107 (2017)
[11] S.-i. Fujimori, T. Okane, J. Okamoto, K. Mamiya, Y. Muramatsu, A. Fujimori, H. Harima, D. Aoki, S. Ikeda, H. Shishido, Y. Tokiwa, Y. Haga, and Y. Ōnuki, Phys. Rev. B 67, 144507 (2003)
[12] S.-i. Fujimori, A. Fujimori, K. Shimada, T. Narimura, K. Kobayashi, H. Namatame, M. Taniguchi, H. Harima, H. Shishido, S. Ikeda, D. Aoki, Y. Tokiwa, Y. Haga, and Y. Ōnuki, Phys. Rev. B 73, 224517 (2006)
[13] Q. Y. Chen, D. F. Xu, X. H. Niu, R. Peng, H. C. Xu, C. H. P. Wen, X. Liu, L. Shu, S. Y. Tan, X. C. Lai, Y. J. Zhang, H. Lee, V. N. Strocov, F. Bisti, P. Dudin, J.-X. Zhu, H. Q. Yuan, S. Kirchner, and D. L. Feng, Phys. Rev. Lett. 120, 066403 (2018)
[14] Q. Y. Chen, C. H. P. Wen, Q. Yao, K. Huang, Z. F. Ding, L. Shu, X. H. Niu, Y. Zhang, X. C. Lai, Y. B. Huang, G. B. Zhang, S. Kirchner, and D. L. Feng, Phys. Rev. B 97, 075149 (2018)
[15] S. Raj, Y. Iida, S. Souma, T. Sato, T. Takahashi, H. Ding, S. Ohara, T. Hayakawa, G. F. Chen, I. Sakamoto, and H. Harima, Phys. Rev. B 71, 224516 (2005)
[16] R. Jiang, D. Mou, C. Liu, X. Zhao, Y. Yao, H. Ryu, C. Petrovic, K.-M. Ho, and A. Kaminski, Phys. Rev. B 91, 165101 (2015)
[17] W. Bao, P. G. Pagluso, J. L. Sarrao, J. D. Thompson, Z. Fisk, and J. W. Lynn, Phys. Rev. B 64, 020401 (2001)
[18] Y. Zhang, W. Feng, X. Lou, T. Yu, X. Zhu, S. Tan, B. Yuan, Y. Liu, H. Lu, D. Xie, Q. Liu, W. Zhang, X. Luo, Y. Huang, L. Luo, Z. Zhang, X. Lai, and Q. Chen, Phys. Rev. B 97, 045128 (2018)
[19] Y. Zhang, H. Lu, X. Zhi, S. Tan, Q. Liu, Q. Chen, W. Feng, D. Xie, L. Luo, Y. Liu, H. Song, Z. Zhang, and X. Lai, Scientific Reports 6, 33613 (2016)
[20] K. Götzke, J. Klotz, D. Gnida, H. Harima, D. Aoki, A. Demuer, S. Elgazzar, J. Wosnitza, D. Kaczorowski, and I. Sheikin, Phys. Rev. B 92, 115141 (2015)
[21] M. Wierwiński, A. Szajek, A. Ślebarski, and D. Kaczorowski, Journal of Alloys and Compounds 647, 605 (2015)
[22] D. Kaczorowski, A. P. Pikul, D. Gnida, and V. H. Tran, Phys Rev Lett 103, 027003 (2009)
[23] P. K. S. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, Technische Universität Wien, Wien, 28 (2001)
[24] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)
[25] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976)
[26] A. Tursina, S. Nesterenko, Y. Seropegin, H. Noël, and D. Kaczorowski, Journal of Solid State Chemistry 404, 287 (2010)
[27] S. Hübner, Photoelectron Spectroscopy (Springer, New York, 2003) pp. 39–60.
[28] See Supplemental Material for detailed band dispersion analyses.
[29] O. Gunnarsson and K. Schönhammer, Phys. Rev. B 28, 4315 (1983)
[30] D. Kaczorowski, A. P. Pikul, D. Gnida, and V. H. Tran, Phys Rev Lett. 104, 059702 (2010)
[31] D. Kaczorowski, A. Pikul, B. Belan, L. Sojka, and Y. Kalychak, Physica B: Condensed Matter 404, 2975 (2009)
[32] D. Kaczorowski, D. Gnida, A. Pikul, and V. Tran, Solid State Communications 150, 411 (2010)
[33] S. Fujimori, Journal of Physics: Condensed Matter 28, 153002 (2016)