Three-dimensional bulk electronic structure of the Kondo lattice CeIn₃ revealed by photoemission

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We show the three-dimensional electronic structure of the Kondo lattice CeIn₃ using soft x-ray angle resolved photoemission spectroscopy in the paramagnetic state. For the first time, we have directly observed the three-dimensional topology of the Fermi surface of CeIn₃ by photoemission. The Fermi surface has a complicated hole pocket centred at the Γ-Z line and an elliptical electron pocket centred at the R point of the Brillouin zone. Polarization and photon-energy dependent photoemission results both indicate the nearly localized nature of the 4f electrons in CeIn₃, consistent with the theoretical prediction by means of the combination of density functional theory and single-site dynamical mean-field theory. Those results illustrate that the f electrons of CeIn₃, which is the parent material of CeMIn₅ compounds, are closer to the localized description than the layered CeMIn₅ compounds.

Heavy fermion (HF) compounds CeMIn₅ (M = Co, Rh, Ir) have attracted much attention in the last decade because of their novel properties¹–⁶. For example, the 4f electrons of CeCoIn₅ go through a transition from the localized state to the itinerant state and begin to participate in the modification of the Fermi surface (FS) at low temperatures⁷,⁸, resulting in an abnormal enhancement of the electron mass. Under certain conditions, those heavy f electrons condense into Cooper pairs, e.g., CeCoIn₅ exhibits the highest superconductivity (SC) temperature recorded in Ce-based HF compounds⁹,¹⁰. However, there are still many unresolved questions regarding this system. First, there is not an explicit definition of the crossover line from the localized f electrons to the itinerant f electrons state. Second, the SC of CeCoIn₅ cannot be explained by the BCS theory¹¹,¹². As layered compound, the structure of CeMIn₅ is comprised of alternating layers of CeIn₃ and MIn₂. The three-dimensional (3D) component CeIn₃ in CeMIn₅ contributes all the f electrons and can be viewed as adding an effective positive pressure on the CeIn₃ crystal at ambient pressure¹³,¹⁴. Further investigation of the electronic structure of CeIn₃ is of particular importance for understanding the nature of CeMIn₅. However, unlike the two-dimensional (2D) CeMIn₅ compounds⁶,⁷, the electronic structure of CeIn₃ is 3D. Consequently, the study of CeIn₃ also provides an opportunity to study the influence of the layered structure on the properties of f electrons in this system.

To investigate the properties of f electrons in CeIn₃, many experiments have been previously performed. Transport¹⁵, optical conductivity spectra¹⁶, and inelastic neutron scattering¹⁷–¹⁹ results all indicate the existence of HF at low temperature, even inside the antiferromagnetic (AFM) phase below 10 K. Quantum oscillation measurements²⁰,²¹ reveal that the HF states occupy only a small portion of the FS. Polycrystal photoemission measurements²², angular correlation of the electron-positron annihilation radiation²³, and de Haas-van Alphen (dHvA)²⁴ measurements all reveal the localized nature of f electrons at ambient pressure. Photoemission spectroscopy is a powerful tool to detect the reconstruction of the electronic structure and is often used to judge the nature of 4f electrons²⁵–²⁸. Photoemission spectroscopy can even be used to detect the SC energy gap in HF systems²⁹. However, angle-resolved photoemission spectroscopy (ARPES) studies of CeIn₃ have not been previously performed due to the difficulty of cleaving the sample and the complicated 3D electronic structure of CeIn₃.

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In this work, the electronic structure of CeIn$_3$ in the paramagnetic state is characterized using the soft x-ray ARPES technique for the first time. The 3D topology of the FS of CeIn$_3$ is observed. The FS has a complicated hole pocket centred at the $\Gamma$-Z line and an elliptical electron pocket centred at the R point of the Brillouin zone (BZ). Photoemission results indicate the nearly localized nature of the 4$f$ electrons in CeIn$_3$, consistent with the theoretical predictions of the localized assumption. These results can help us to understand the behaviours of f electrons in CeIn$_3$ and the derived CeMIn$_5$ systems.

**Results**

**Fermi surface mapping.** The topology of the FS of CeIn$_3$ is presented in Fig. 1. Figure 1(a) shows the slice of the FS in the $k_z$-$k_y$ plane, observed by $h\nu$-dependent ARPES. Although the FS contours contain complicated features, we can obtain the symmetry of the electronic structure along $k_z$ direction. The slices of the FS observed by 542 eV and 595 eV photon energies correspond to the centre and boundary of the BZ, respectively. Besides, a complicated band structure $d$ centred at the $\Gamma$-Z line and an elliptical shaped pocket $a$ centred at R point are observed. To obtain a better understanding of the FS, two selected photon energies are adopted to characterize the FS contours in $k_x$-$k_y$ plane. Figure 1(b,c) are the $k_x$-$k_y$ maps at $k_z\sim0$ ($h\nu=542$ eV) and ($k_z\sim\pi$) for a photon energy of 595 eV ($h\nu=595$ eV), respectively. At the centre of the BZ in Fig. 1(b), the square-like pocket $d$ at the M point and the double-ring band $d$ centred at the $\Gamma$ point are observed. The spectral weight of $d$ is quite strong in the $\Gamma$-X direction. At the boundary of the BZ in Fig. 1(c), a square structure $d$ around the Z point and an elliptical structure $a$ centred at the R point are displayed. The topology of the FS is highly 3D in nature and agrees with the dHvA experiment and the full-potential linear augmented plane wave calculations results$^{[24]}$, which exhibit a complicated structure (denoted as $d$) centred at the $\Gamma$-Z line and an ellipsoid-like structure around the R point. Figure 1(e) shows the low energy electron diffraction (LEED) pattern of the obtained surface. A clean $1 \times 1$ pattern of the (001) surface is observed.

**Valence band structure.** An important goal in the study of a HF system is to understand the properties of f electrons. Previously, the polarized ARPES technique has been conducted to resolve the multi-orbit nature of the 3$d$ states in iron-based superconductors and has proven to be an effective method to distinguish the different orbits of 3$d$ electrons$^{[30]}$. The HF compound YbRh$_2$Si$_2$ has also been studied using different light polarizations$^{[31,32]}$. Some states in YbRh$_2$Si$_2$ are proven to possess dichroic effects, indicating that electronic states with the same symmetry can be identified by their similar response to a change of light polarization. Therefore, to
The two flat bands are observed more clearly in Fig. S1 in the SI. The origin of the non-dispersive bands could be Kondo effect or the spin-polaron effect, which both lead to the many-body resonance in the electron density of states near E_F. The suppression of non-dispersive bands located at E_F and 300 meV BE are observed in Fig. 2(c1,d1). They have much weaker intensity weight than the other conduction bands and can be observed more clearly in Fig. S1 in the SI. The origin of the non-dispersive bands could be Kondo effect or spin-polaron effect, which both lead to the many-body resonance in the electron density of states near E_F. However, the temperature dependent resistivity of CeIn3 can be described by a function ρ~−lnT beyond the coherent temperature, indicating Kondo physics takes effect. Therefore, the two non-dispersive bands correspond to the 4f^{5/2} state and its spin orbit coupling (SOC) sideband 4f^{7/2}. The two flat bands are observed more clearly, as shown in Fig. 2(c2,d2), where significant changes occur when light is changed to p-polarized light along the Γ-M and Γ-X directions, respectively. The phenomena, by using the single-site dynamical mean-field theory (DFT + DMFT), is probably the most powerful established method to study the electronic structures of strongly correlated materials. DFT + DMFT has been successfully applied in the studies of many HF systems, such as the temperature-dependent localized-itinerant transition in CeIn3, determining why the photoemission cross-section, as the suppression of non-positive spatial orientations of the electronic states with the polarization vector of the light. The phenomena, by using the single-site dynamical mean-field theory (DFT + DMFT), is probably the most powerful established method to study the electronic structures of strongly correlated materials. DFT + DMFT has been successfully applied in the studies of many HF systems, such as the temperature-dependent localized-itinerant transition in CeIn3.

**Calculations.** The comparison between the experimental band structures with the calculation results is an effective means to judge the properties of the f electrons. On the other hand, density functional theory merged with the single-site dynamical mean-field theory (DFT + DMFT) is probably the most powerful established method to study the electronic structures of strongly correlated materials. DFT + DMFT has been successfully applied in the studies of many HF systems, such as the temperature-dependent localized-itinerant transition in CeIn3.
We compare the ARPES results with the DFT + DMFT band calculations of CeIn$_3$ in Fig. 3. First, all the valence bands 1–8 in Figs 2 and 3(c,d) can be clearly duplicated in the calculation results, as are the very flat and non-dispersive f bands located at $E_F$ and the vicinity. The flat f bands appear to be constant and non-dispersive over all angles and have much weaker intensity weight than those of the other conduction bands, consistent with our experimental results in Fig. 2 and Fig. S1. This phenomenon does not agree well with the case of CeIrIn$_5$, the f states of which have strong intensity weight and form the coherent peak on $E_F$. Besides, the f states of CeIrIn$_5$ show obvious dispersions around $E_F$, induced by the strong hybridization between f states and conduction states. This indicates that the f electrons of CeIn$_3$ have different behaviours compared with those of CeIrIn$_5$, which have itinerant f states at low temperature. Second, a small renormalization of conduction band 7 on $E_F$ is displayed in both the calculation results in Fig. 3(a) and the MDCs in Fig. 3(d). This should be induced by the interaction between f states and the band 7. However, the interaction is so weak that the coherent peak does not form. In fact, if an additional pressure is added on CeIn$_3$, the interaction will be greatly enhanced. Band 7 will have obvious band bending and form the coherent peak on $E_F$ together with the hybridized f band. Through comparison of the experimental bands with the calculated results, we can conclude that the experimental band structure of CeIn$_3$ at ambient pressure and low temperature can be described by the nearly localized model.

**On-resonance photoemission.** To clarify the explicit band structures of the f electrons, Fig. 4(a) shows on-resonance photoemission intensity plot of CeIn$_3$. The dense and non-dispersive f bands emerge near $E_F$ and ~300 meV BE, enhanced by the 3d-f excitation. It is well known that the f band at $E_F$ is the tail of the Kondo resonance (KR) peak, corresponding to the Ce-4$f^{1/2}_{5/2}$ final state. The peak at 300 meV BE is the SOC sideband and corresponds to the Ce-4$f^{1/2}_{5/2}$ final state. Although the Ce-4$f^{1/2}_{5/2}$ band of CeIn$_3$ is intersected by the conduction band
at EF, it does not show any dispersion and does not open an energy gap to form the \( k \)-dependent bands \( E^+ \) and \( E^- \), as shown in Fig. 4(c). In the Periodic Anderson Model (PAM)\(^39\), if the \( f \) electrons are itinerant and have periodicity in the lattice, it should form dispersive KR peaks crossing EF in unoccupied states, as shown in the pressure-induced itinerant state for CeIn\(_3\).\(^{38}\) However, no crossing of \( f \) electron bands and no energy gap for CeIn\(_3\) are observed at ambient pressure in Fig. 4(a).

From another aspect, as shown in Fig. 4(b), except for the \( f^1 \) final states near EF, the non-dispersive structures at approximately 1.4 eV and 2 eV BE are also visible. These arise from pure charge excitations of the trivalent Ce ion (\( 4f^1 \rightarrow 4f^0 \)) and are referred to the ionization peaks\(^22\). The two \( f \) bands have been observed in the Ce-termination surface in CeRh\(_2\)Si\(_2\), which exhibits the nature of localized \( f \) electrons. Usually, if the hybridization strength is strong, then the \( f^0 \) peak is much weaker than the \( f^1 \) final state, as shown in the blue shaded area in Fig. 4(c). If the hybridization strength is weak, then the intensity of \( f^0 \) peak is strong\(^22,41\), as demonstrated by recent calculation results using the DFT+DMFT approach by H.Y.L.\(^38\). H.Y.L.\ et al. indicate that the \( 4f \) electrons of CeIn\(_3\) will undergo a localized-itinerant transition under pressure, consistent with the dHvA results\(^24\). At ambient pressure, the \( 4f \) electrons of CeIn\(_3\) are localized, and the intensity of \( f^1 \) final state is comparable with that of \( f^0 \) peak. With the crystal volume decreasing under pressure, the intensity of the \( f^1 \) final state quickly increases, and the intensity of \( f^0 \) peak nearly disappears. As the intensity of the \( f^0 \) peak is comparable with that of \( f^1 \) final state in CeIn\(_3\) in Fig. 4(b), the angle-integrated photoemission spectroscopy result is also consistent with the calculation result of CeIn\(_3\) under ambient pressure. In summary, the \( f \) electrons of CeIn\(_3\) are close to the description of the nearly localized model, similar to the angle-integrated photoemission spectroscopy results of \( f \) localized compounds CeRhIn\(_5\) and CeRh\(_2\)Si\(_2\)\(^{40,42}\).

**Discussion**

We have compared the ground states between CeIn\(_3\) and CeMIn\(_5\) to illustrate the different properties of the \( f \) electron. In fact, there are three possible ground states in the HF systems based on the Doniach phase diagram\(^45\) at low temperature: i) the mixed valence ground state with extremely large hybridization strength between the \( f \) electrons and the conduction electrons and \( 0 < n_f < 1 \), where \( n_f \) represents the occupation number of \( f \) electrons;
ii) the magnetic ground state with weak hybridization strength and $n_f \approx 1$; iii) Non-Fermi liquid (sometimes SC) ground state with strong spin fluctuations, located between the two states discussed above.

CeCoIn$_3$ and CeIrIn$_5$ become superconducting at low temperature, implying that they are located in the SC region in the Doniach phase diagram and that they have relatively strong hybridization strength. In contrast, CeIn$_3$ has the antiferromagnetic ground state with much weaker hybridization strength. Although CeRhIn$_5$ is also an antiferromagnetic compound below 3.8 K, the CeIn$_3$ units in it can be viewed as adding a pressure of approximate 1.4 GPa to the CeIn$_3$ compound at atmospheric pressure$^{14}$. For CeIn$_3$, the hybridization strength is enhanced under pressure$^{16,24}$. This indicates that CeRhIn$_5$ has a larger hybridization strength than that of CeIn$_3$. These results agree well with our ARPES results of CeIn$_3$, regarding that the 4$f$ electrons of CeIn$_3$ are a nearly localized type.

Now the DFT+DMFT calculation results, our ARPES results, angular correlation of the electron-positron annihilation radiation$^{23}$ and dHvA$^{24}$ results all support the view that the 4$f$ electrons of CeIn$_3$, at ambient pressure are nearly localized. However, the optical conductivity results$^{16}$, transport$^{15}$ and inelastic neutron scattering$^{17,19}$ measurements hold the opposite view. Why are the conclusions of different references on CeIn$_3$ totally different? First, from our DFT+DMFT calculations and experimental results in Fig. 3, the interaction between band $7$ and $f$ band really exists, although the intensity of the interaction strength is too small to form the coherent peak, implying that most of the $f$ electrons are localized and a small portion of the $f$ electrons tend to be itinerant, but incompletely. Second, refs 20 and 21 prove that the hybridized $f$ holes exist at low temperature in CeIn$_3$. However, the $f$ holes just occupy a small portion of the FS and are not along the high symmetry directions in BZ. Such a small proportion may make some techniques hard to detect them. However, this situation will change under pressure. More $f$ electrons begin to participate in the modification of the FS and the collective behaviors of $f$ electrons make the system itinerant and heavy under pressure$^{33}$. Based on the above discussions, we propose that most of the $f$ electrons of CeIn$_3$ stay localized at ambient pressure and the situation can be changed by means of adding additional pressure.

In summary, the electronic structure of CeIn$_3$ in the paramagnetic state was characterized using the soft x-ray ARPES technique. 3D FS of CeIn$_3$ was revealed. The FS has a complicated hole pocket and an elliptical electron pocket centred at the $\Gamma$-Z line and an elliptical electron pocket $a$ centred at the R point of the BZ. The photoemission results and the calculated results all indicate a nearly localized nature of the 4$f$ electrons in CeIn$_3$ at ambient pressure.

Methods

High-quality single crystals of CeIn$_3$ were grown using the self-flux method$^{44}$. The fresh and smooth surfaces were obtained by performing cycles of Ar$^+$-ion sputtering and annealing with a base pressure better than $3 \times 10^{-10}$ mbar after the surfaces are polished in the atmosphere. The polarization and photon-energy dependent soft x-ray ARPES experiments were performed at the ADDRESS station of the Swiss Light Source facility. The soft x-ray ARPES spectra were obtained using a PHOIBOS-150 photoelectron analyser$^{45}$. The combined energy resolution is 90 meV or better, and the angle resolution is 0.1°. The base pressure of the ultra-high vacuum system was below $5 \times 10^{-11}$ mbar during the entire measurement. The samples were kept at $T = 13$ K in the ARPES measurements. Unless a particular explanation is given, all the data are taken using $s$-polarized light.

The calculation method is the density functional theory merged with the single-site dynamical mean-field theory (DFT+DMFT) that combines the first-principles aspect of DFT with the non-perturbative many-body treatment of local interaction effects in DMFT. The method used in this paper is introduced in detail in the literature$^{48}$. All of the calculations were conducted at the inverse temperature $\beta = 1000$ ($T = 11.6$ K), which is comparable with the experimental temperature. Here we adopted $U = 6.2$ eV and $J = 0.7$ eV, where $U$ is the Coulomb interaction strength and $J$ the Hund’s exchange parameter.

References

1. P. Aynajian et al. Visualizing heavy fermions emerging in a quantum critical Kondo lattice. Nature 486, 201–206 (2012).
2. M. P. Allan et al. Imaging Cooper pairing of heavy fermions in CeCoIn$_5$. Nat. Phys. 9, 468–473 (2013).
3. B. B. Zhou et al. Visualizing nodal heavy fermion superconductivity in CeCoIn$_5$. Nat. Phys. 9, 474–479 (2013).
4. H. C. Choi, B. I. Min, J. H. Shim, K. Haule & G. Kotliar. Temperature-dependent Fermi surface evolution in heavy fermion CeIrIn$_5$. Phys. Rev. Lett. 108, 016402 (2012).
5. J. H. Shim, K. Haule & G. Kotliar. Modeling the localized-to-itinerant electronic transition in the heavy fermion system CeIn$_3$. Science 318, 1615–1617 (2007).
6. L. Jiao et al. Fermi surface reconstruction and multiple quantum phase transitions in the antiferromagnet CeRhIn$_5$. Nat. Phys. 7, 220–223 (2011).
7. B. B. Zhou et al. Band-dependent emergence of heavy quasiparticles in CeCoIn$_5$. Phys. Rev. B. 88, 035124 (2013).
8. A. Kottsch et al. Hybridization effects in CeIn$_3$, observed by angle-resolved photoemission. Phys. Rev. B. 77, 155128 (2008).
9. A. Akbari, P. Thalmeier & I. Eremin. Quasiparticle interference in the heavy-fermion superconductor CeCoIn$_5$. Phys. Rev. B. 84 (2011).
10. H. Kim et al. Nodal to nodeless superconducting energy-gap structure change concomitant with fermi-surface reconstruction in the heavy-fermion compound CeCoIn$_5$. Phys. Rev. Lett. 114, 027003 (2015).
11. O. Strockert et al. Magnetically driven superconductivity in CeCu$_3$Sn$_3$. J. Phys. Soc. Jpn. 79, 119–124 (2010).
12. K. Izawa et al. Angular position of nodes in the superconducting gap of quasi-2D heavy-fermion superconductor CeCoIn$_5$. Phys. Rev. Lett. 87, 057002 (2001).
13. H. Hegger et al. Pressure-induced superconductivity in quasi-2D CeRhIn$_5$. Phys. Rev. Lett. 84, 4986 (2000).
14. G. Oomi, T. Kagayama & J. Sakurai. High pressure studies of the concentrated Kondo compounds Ce (In$_{0.5}$Sn$_{0.5}$). J. Mater. Process. Tech. 85, 220–223 (1999).
15. N. Berry, E. M. Bittar, C. Capan, P. G. Pagliuso & Z. Fisk. Magnetic, thermal, and transport properties of Cd-doped CeIn$_3$. Phys. Rev. B. 81, 174413 (2010).
16. T. Iizuka, T. Mizuno, B. Han Min, Y. Seung Kwon & S.-i. Kimura. Existence of Heavy Fermions in the Antiferromagnetic Phase of CeIn$_3$. J. Phys. Soc. Jpn. 81, 043703 (2012).
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