Fermi Surface Variation of Ce 4f-electrons in Hybridization Controlled Heavy-Fermion Systems

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Abstract

Ce 3d-4f resonant angle-resolved photoemission measurements on CeCoGe$_{1.2}$Si$_{0.8}$ and CeCoSi$_2$ have been performed to understand the Fermi surface topology as a function of hybridization strength between Ce 4f- and conduction electrons in heavy-fermion systems. We directly observe that the hole-like Ce 4f-Fermi surfaces of CeCoSi$_2$ is smaller than that of CeCoGe$_{1.2}$Si$_{0.8}$, indicating the evolution of the Ce 4f-Fermi surface with the increase of the hybridization strength. Moreover, it is suggestive that the variation of Ce 4f-Fermi surface should be ascribed to the increase of the density of state in coherent part near the Fermi level as the hybridization strength increases.

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In Ce-based metals, the Fermi surface (FS) topology of strongly correlated Ce 4f-electrons directly influences on unusual physical properties such as heavy-fermion behavior and quantum criticality [1, 2]. It is well established in many experimental and theoretical studies that localized Ce 4f-electrons, caused by the strong correlation, form the large density of states at the Fermi level ($E_F$) through the hybridization with conduction electrons: the large density of states is the so-called Kondo resonance peak and is the origin of a large effective mass of charge carriers in heavy-fermion systems [3, 4, 5, 6]. In addition, as a function of this hybridization strength, their ground state changes from magnetic to non-magnetic heavy-fermion via a quantum critical point (QCP) [7]. Recently, the variation of Ce 4f-FS through QCP has been considered as a crucial phenomenon to distinguish two contrast scenarios for the quantum criticality: One is a spin-density wave (SDW) scenario [8] where the Ce 4f-FS changes continuously through QCP as in CeRu$_2$Si$_2$ [9], CeNi$_2$Ge$_2$ [10], and CeIn$_3$ [11]. The other is a local quantum critical scenario [12] where the Ce 4f-FS changes discretely through QCP as in CeRhIn$_5$ [13], CeCu$_{0.9}$Au$_{0.1}$ [14], and YbRh$_2$Si$_2$ [15, 16]. Therefore, it is essential to understand how the FS of Ce 4f electrons microscopically forms and changes as a function of hybridization strength.

For the experimental investigation of the FS topology, there are representative two methods; one is the de Haas-van Alphen (dHvA) effect and the other the angle-resolved photoemission spectroscopy (ARPES) measurements. The dHvA measurements have shown the evidences of discrete FS variation through QCP as in CeRhIn$_5$ [13]. In ARPES measurements, FS topology can be understood together with the band dispersion which provides a fruitful information of the electronic structure [17]. In recent, by combining angle-resolved and resonance photoemission spectroscopies on CeCoGe$_{1.2}$Si$_{0.8}$, we have firstly observed the dispersive Kondo resonance peaks crossing $E_F$ in unoccupied regime, which form Ce 4f-FS though the hybridization with conduction bands [18]. This gives a good opportunity to study the Ce 4f-FS topology as a function of hybridization strength in a microscopic point of view.

In this Letter, we study Ce 4f-FS topologies by bulk-sensitive Ce 3d-4f resonant angle-resolved photoemission studies of CeCoGe$_{1.2}$Si$_{0.8}$ and CeCoSi$_2$, which are isostructural single crystals and have different hybridization strength. The results reveal that the hole-like FS of Ce 4f-electrons become small as the hybridization strength increases. This indicates that the contribution of Ce 4f-electrons to FS increases with the hybridization strength. Also, we show that such variation of Ce 4f-FS cannot be explained by a local density approximation.
(LDA) band calculations. This requires the consideration of strong correlation effects and hence suggests that the increase of Kondo resonance peak originates the FS variation in comparison with the Ce 3d-4f on-resonant angle-integrated photoemission (AIPES) spectra.

Single crystalline samples, CeCoGe$_{1.2}$Si$_{0.8}$ and CeCoSi$_2$, crystallized in the orthorhombic CeNiSi$_2$-type (Cmcm) structure. They were prepared by Bridgeman and Czochralski methods, and were annealed at 900 °C for about one week. Laue pattern and X-ray diffraction analysis confirm that the samples used in this study have a good crystallization and are in single phase, respectively. Samples are categorized into non-magnetic heavy-fermions and have different hybridization strength; CeCoSi$_2$ has a larger Kondo temperature ($T_K$, an energy scale of hybridization strength between Ce 4f- and conduction electrons) rather than CeCoGe$_{1.2}$Si$_{0.8}$ ($T_K \sim 350$ K [18]). In these systems, the increase of hybridization strength is considered to be exclusively derived from the increase of chemical pressure as in CeNiGe$_{2-x}$Si$_x$ systems, where the lattice constants are reduced without the change of the Ni 3d state character near $E_F$ [19]. This provides an ideal condition to directly compare the FSs formed by hybridization between the Ce 4f- and conduction bands.

Ce 3d-4f resonant ARPES measurements have been performed at the BL23SU of SPring-8. The photon energies for on- and off-resonant ARPES are set to be 886 and 879 eV from X-ray absorption spectra; the on-resonant spectra represent the Ce 4f-electronic structure and the off-resonant spectra the electronic structure of non-4f-states [17]. Measurement temperature and total energy resolution are about 20 K and 120 meV, respectively. The clean surfaces in the (010) plane were prepared by in situ cleaving of single crystal samples under a vacuum of 2 × 10$^{-8}$ Pa. Sample cleanliness was checked by the absence of the O 1s core-level spectrum. The $E_F$ of the sample was referred to that of Au film and was calibrated by using Au 4f core-level peak.

Figures 1(a) and 1(c) are the intensity maps in the $k_x$-$k_z$ plane, which are obtained by integrating Ce 3d-4f on-resonant ARPES spectra from -0.1 to 0.1 eV, and represent Ce 4f-FSs of CeCoGe$_{1.2}$Si$_{0.8}$ and CeCoSi$_2$, respectively. Measured momentum planes, estimated with considering the inner potential ($V_0 = 15.8$ eV [20]) and the incident photon momentum ($k_{\perp\text{photon}}$) of 886 eV, are depicted by the shaded planes in Brillouin zone (BZ) in Figs. 1(b) and 1(d). We observed diamond-shaped FSs outside and obscure FSs inside in both samples. The diamond-shaped outside FSs correspond to the FS of band 28 which have the strong two-dimensional electronic structure as shown in Figs. 1(b) and 1(d). These have been
FIG. 1: (Color online). (a),(c) Ce 4f-FSs of CeCoGe$_{1.2}$Si$_{0.8}$ and CeCoSi$_2$ in the $k_z$-$k_x$ plane obtained from Ce 3$d$-4$f$ on-resonant ARPES spectra. The open circles are obtained from the minimum of second derivative of momentum distribution curves (MDCs) at $E_F$ as shown in Fig. 2(e) and 2(f), and correspond to diamond shaped Ce 4$f$-FS contours. (b),(d) The FSs of band 28 in the local-density approximation (LDA) band calculation of CeCoGe$_2$, which is a parent compound of CeCoGe$_{1.2}$Si$_{0.8}$ and CeCoSi$_2$. Shade areas depict the measured momentum planes estimated from the equation, $k_{\perp} = (2m/h^2(E_{kin}cos^2\theta + V_0))^{1/2} - k_{\perp photon}$, where $m$ is the electron mass, $E_{kin}$ the kinetic energy of the photoelectron, $V_0$ the inner potential, $k_{\perp}$ the emission angle of the photoelectron relative to the surface normal and $k_{\perp photon}$ the momentum of the incident photon perpendicular to the surface [17]. The box represents the first Brillouin zone, where $\Gamma X \approx \Gamma Z \approx 0.76$ Å$^{-1}$ and $\Gamma Y \approx 0.38$ Å$^{-1}$.

also observed in Ce 4$d$-4$f$ resonant ARPES measurements on CeCoGe$_{1.2}$Si$_{0.8}$ [18]. On the other hand, we can ascribe the inside FSs to those of band 26 and 27 which show weak two-dimensionality in LDA calculation (not shown here), even though they are too obscure to compare FSs between CeCoGe$_{1.2}$Si$_{0.8}$ and CeCoSi$_2$. This shows that LDA calculation roughly explain the overall FS topology of both CeCoGe$_{1.2}$Si$_{0.8}$ and CeCoSi$_2$ as in many heavy-fermion systems [21, 22]. However, for a detailed electronic structure, it is found that the size of the outside FSs between two samples is different in ARPES while it is almost the same in LDA calculation as shown Figs. 1(b), 1(d), and 3(b). In order to understand
FIG. 2: (Color online). Intensity plots of Ce 3d-4f off- and on-resonant ARPES spectra represent the band dispersion of conduction and f-electrons, respectively, along the indicated the dashed-line shown in Figs. 1(a) and 1(c) [(a),(b) for CeCoGe$_{1.2}$Si$_{0.8}$; (c),(d) for CeCoSi$_2$]. The dashed lines are a guide to the eye for conduction bands. MDCs at $E_F$ of on-resonance and their second derivatives are shown for (e) CeCoGe$_{1.2}$Si$_{0.8}$ and (f) CeCoSi$_2$. The extreme values of the second derivative stand for $k_F$s.

the origin of this detailed Ce 4f-FS variation, we here focus on the outside FSs which are diamond-shaped and distinct.

Figures 2(a) and 2(b) [2(c) and 2(d)] are intensity plots of the off- and on-resonant ARPES spectra of CeCoGe$_{1.2}$Si$_{0.8}$ [CeCoSi$_2$] along a dashed line assigned in Fig. 1(a) and 1(c), respectively: remind that the off-spectra represent the band dispersion of conduction electrons and the on-spectra that of Ce 4f-electrons. In Ce 3d-4f off-resonant ARPES spectra, we observe the nearly flat band around -1.2 eV and the steep band near $E_F$ even though feature is not clear. The former corresponds to mainly Co 3d band as shown in angle-integrated photoemission (ARPES) of CeCoGe$_2$ and band calculation [23, 24]. The latter is the band composing the outside diamond-shaped FS in agreement with Ce 4d-4f off-resonant ARPES results of CeCoGe$_{1.2}$Si$_{0.8}$ [18]. In Ce 3d-4f on-resonant ARPES spectra, the large enhancement of the spectral weight of Ce 4f-bands near $E_F$ are clearly observed where the conduction bands cross $E_F$. Such electronic structure comes from hybridization
FIG. 3: (Color online). (a) Comparison of Ce 4f-Fermi surfaces between CeCoGe$_{1.2}$Si$_{0.8}$ (open circles) and CeCoSi$_2$ (solid circles). Raw FS-contours in Figs. 1(a) and 1(c) were a little rotated to match the k-axis. Dashed- and solid-lines are guides for eyes. (b) In LDA calculation, the FS contours of band 28 on the measured k-planes in ARPES (see Figs. 1(b) and 1(d)) are almost same for CeCoGe$_{1.2}$Si$_{0.8}$ and CeCoSi$_2$.

between a renormalized Ce 4f-band just above $E_F$ and conduction bands as in a periodic Anderson model (PAM) [18]. Figures 2(e) and 2(f) show the momentum distribution curves (MDCs) at $E_F$ and the second derivative of them. We observe that the width of the peak in CeCoGe$_{1.2}$Si$_{0.8}$ is larger than that in CeCoSi$_2$ and seems to be not single peak at a glance. The second derivative of MDC shows the double peak at $k_{x(z)} \sim \pm 0.15$ Å$^{-1}$ in CeCoGe$_{1.2}$Si$_{0.8}$, while single peak at $k_{x(z)} \sim 0$ Å$^{-1}$ in CeCoSi$_2$. The peak positions are regarded to be the point where a band dispersion crosses $E_F$, namely, the Fermi vector ($k_F$) [25]. Despite some ambiguity, in comparison between the FS topologies [Figs. 1(a) and 1(c)], we recognize that the one $k_F$ of CeCoSi$_2$ can be ascribed to the superposition of the two $k_F$s of CeCoGe$_{1.2}$Si$_{0.8}$.

For a detailed study of Ce 4f-FSs, we plot the superimposed FS contours of CeCoGe$_{1.2}$Si$_{0.8}$ and CeCoSi$_2$ as shown in figure 3(a). It is clearly observed that the hole-like Ce 4f-FS of CeCoGe$_{1.2}$Si$_{0.8}$ is larger than that of CeCoSi$_2$. This reveals that the hole-like Ce 4f-FS shrinks with increasing the hybridization strength. On the other hand, in LDA band calculation the size of FSs of both samples is almost same; specifically, the FS of CeCoGe$_2$ is a little smaller than that of CeCoSi$_2$, exhibiting an opposite tendency to the results of ARPES. This indicates that the LDA band calculation is not sufficient to explain the FS variation in the different hybridization strength, even though it well reproduce the overall FS shape [21, 26]; this is another evidence why LDA calculation is usually considered not to properly treat the strong correlation effects of Ce 4f-electrons. In heavy-fermion systems, the
FIG. 4: (Color online). (a) Ce 3d-4f on-resonant AIPES spectra of CeCoGe$_{1.2}$Si$_{0.8}$ and CeCoSi$_2$. Schematics show that the hole-like Ce 4f-FS shrinks as the hybridization of the system increases (from (b) to (c)).

hybridization of the strongly correlated Ce 4f-electrons with conduction electrons causes the separation of the spectral weight of Ce 4f-electrons into the coherent peak (Ce 4f$^1$) around $E_F$ and the incoherent peak (Ce 4f$^0$) around -2 eV [5, 6].

Figure 4(a) shows Ce 3d-4f on-resonant AIPES spectra of CeCoGe$_{1.2}$Si$_{0.8}$ and CeCoSi$_2$ [27]. The spectra are normalized to the area of the valence band from -7 to 1 eV after the nominal Shirley correction which is commonly used to subtract secondary background weights [17, 23]. It is observed that, when the system changes from CeCoGe$_{1.2}$Si$_{0.8}$ to CeCoSi$_2$, the $f^0$ spectral weight decreases and the $f^1$ spectral weight increases. This indicates that the spectral weight of $f^0$ peak around -2 eV is transferred to the weight of $f^1$ peak near $E_F$ with increasing the hybridization strength; it should be noted that the total number of Ce 4f-electron is almost constant in occupied states, and hence there are only complementary variation between the Ce 4f$^0$ and 4f$^1$ peaks [5]. Such behaviors have been also observed in other many photoemission experiments [4, 5, 19, 23] and theoretical studies based on the impurity Anderson model [5, 6]. Taking it into account that both the Ce 4f spectral weight transfer and FS variation have originated from the strong correlation effects, it is suggestive that the Ce 4f-number at $E_F$ increases with the hybridization strength through the spectral weight transfer and eventually the size of Ce 4f-FS changes.
as depicted in Fig. 4(b) and 4(c). Moreover, this enables us to recognize an important thing that, while in normal metals the size of FS can not be changed by the variation of the hybridization strength without the phase transition [28], in the strongly correlated \(f\)-electrons system the FS size can be done with complementary variation between the coherent state near \(E_F\) and the incoherent state in occupied states [29]. For future work, the FS topologies of conduction electrons (non-Ce \(4f\)-states) should be investigated to comprehensively understand the whole electronic structure. It is also meaningful that the Ce \(4f\)-FS variation are reproduced by theoretical approach such a dynamical mean-field theory combining LDA (LDA+DMFT) [26]. We believe that our results provide an important experimental evidence to exactly describe the strongly correlated \(f\)-electrons.

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