Soft x-ray angle-resolved and resonance photoemission study of CeCu$_2$Ge$_2$ and LaCu$_2$Ge$_2$

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Abstract. We have performed bulk-sensitive soft x-ray angle-resolved photoemission spectroscopy for CeCu$_2$Ge$_2$ isostructural to a heavy fermion superconductor CeCu$_2$Si$_2$, indicating the localized 4f character in ambient pressure. Resonance enhancement is seen at the La 3d$_{5/2}$-edge for LaCu$_2$Ge$_2$ in both angle-resolved and integrated photoemission although the magnitude of enhancement is less than that in the Ce 3d$_{5/2}$-edge resonance photoemission for CeCu$_2$Ge$_2$, which indicates that the rare-earth 5d contributions can also be enhanced in addition to the 4f contributions at the resonance conditions.

1. Introduction

Since the discovery of superconductivity in a heavy fermion system CeCu$_2$Si$_2$ [1], many Ce-based strongly correlated materials have been surveyed to find "heavy-fermion" superconductors in order to better understand these unconventional superconductivity [2]. CeCu$_2$Ge$_2$ is isostructural to CeCu$_2$Si$_2$ with the tetragonal ThCr$_2$Si$_2$ crystal structure and shows superconductivity under high pressure of $\sim 10$ GPa [3, 4]. An antiferromagnetic order is seen below $\sim 4$ K in ambient pressure while the Sommerfeld coefficient $\gamma$ has been reported as about 100 mJ/(mol K$^2$) in the antiferromagnetic phase which is much larger than that for conventional metals [5]. The former suggests a localized character of the Ce 4f electrons in CeCu$_2$Ge$_2$ in ambient pressure whereas the heavy fermion behavior originating from the hybridization between the 4f orbitals and the valence bands crossing the Fermi level ($E_F$) is expected from the latter. Although the electronic structure and Fermi surface topology are very important for discussing the itinerant or localized 4f nature in the system, quantum oscillation measurements have not been successful to date for CeCu$_2$Ge$_2$.

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Soft x-ray angle-resolved photoemission spectroscopy (ARPES) at $h\nu > 500$ eV has an advantage in probing the three-dimensional bulk electronic structure of strongly correlated electron systems as well as their Fermi surface topology, suppressing their surface contributions highly deviated from the bulk ones [6, 7, 8, 9]. In this paper we report the electronic structure of CeCu$_2$Ge$_2$ probed by the soft x-ray ARPES and the resonance photoemission study near the $3d_{5/2}$ edges for LaCu$_2$Ge$_2$ ($h\nu \sim 830$ eV) and CeCu$_2$Ge$_2$ ($h\nu \sim 880$ eV).

2. Experimental

Single crystalline LaCu$_2$Ge$_2$ and CeCu$_2$Ge$_2$ were prepared by a flux method. Soft x-ray ARPES and resonance photoemission spectroscopy as well as x-ray absorption spectroscopy (XAS) were performed at twin-helical undulator beamlines BL23SU [10] and BL25SU [11] in SPring-8. A Scienta SES200 analyzer covering more than a whole Brillouin zone along the direction of the slit was used. The energy resolution was set to 120 – 200 meV. The angular resolution was ±0.1° (±0.15°) and ±0.15° for the perpendicular and parallel directions to the analyzer slit at BL25SU (BL23SU), respectively. The clean surface was obtained by cleaving in situ providing a (001) plane at the measuring temperature of 20 K in the base pressure of $\sim 1 \times 10^{-8}$ Pa. It is known that compounds with the ThCr$_2$Si$_2$ crystal structure can be reproducibly cleaved by a commonly used a “lever-a-post” method [7, 8, 9]. Neither O nor C 1s photoelectron signal was detected, which suggests the cleanliness of the cleaved surface.

![Figure 1. Brillouin zone of the body-centred tetragonal crystal CeCu$_2$Ge$_2$.](image)

We performed $h\nu$-dependent soft x-ray ARPES with an energy step of 5 eV to obtain the excitation energy $h\nu$ covering the $Z[(0,0,2c/a), (2c/a,0,0)]$ etc. in a reciprocal space where $a$ and $c$ stand for the lattice constants]-X[(a/a,a/2c), (a/a,a/0), etc.] and $\Gamma(0,0,0)$-X directions in the Brillouin zone, finding that $h\nu = 675$ eV is one of the corresponding photon energies to observe the electronic structure along both directions [It should be noted that the Z and $\Gamma$ points are placed on the same $k_z$ (momentum perpendicular to the cleaved (001) surface) plane in the body-centred tetragonal crystal structure as shown in Fig.1]. The XAS spectra were measured by the total electron yield mode with the energy resolution of better than 150 meV.

3. Soft x-ray ARPES for CeCu$_2$Ge$_2$

The results of the soft x-ray ARPES for CeCu$_2$Ge$_2$ are shown in Figs.2(a-d), revealing that an electron-like band crosses $E_F$ around the Z point and again crosses to the occupied side on going to the X point. There is another band which crosses $E_F$ nearer the X point than that for the above band as shown in Figs.2(a) and (c). In total, there are three Fermi wave vectors ($k_F$s) between the Z and X points as indicated by the arrows in Fig.2(c), which shows the second order differential image reflecting the band dispersions from $E_F$ to the binding energy of $\sim 3$
Figure 2. (a) Soft x-ray angle-resolved photoemission spectra (energy distribution curves, EDCs) of CeCu$_2$Ge$_2$ at 20 K and $h\nu = 675$ eV along the Z-X direction. The spectra at the Fermi wave vector $k_F$ (high-symmetry points Z and X) shown by bold solid (dashed) lines whereas the dotted curves representing the band dispersions near $E_F$ are guides to the eye. (b) Same as (a) but along the Γ-X direction. (c, d) Second order differential images along the Z-X and Γ-X directions representing the band dispersions. The arrows indicate the loci where the bands cross $E_F$. (e) Calculated band structure along symmetry lines for LaCu$_2$Ge$_2$.

We have also performed the band-structure calculation for LaCu$_2$Ge$_2$ by using the WIEN2k package [12], displaying the result of the calculation in Fig.2(e). The predicted electronic structure for LaCu$_2$Ge$_2$ should corresponds to that for CeCu$_2$Ge$_2$ with localized 4f electrons in the occupied side. Indeed, the obtained band structure and Fermi surface topology (not shown here) from our calculation are consistent with those previously reported [13] for CeCu$_2$Ge$_2$ for which the 4f orbitals have been treated as localized core states. The band-structure calculation indicates that there is one band crossing $E_F$ between the Γ and X points whereas three $k_F$s are seen along the Z-X cut. The soft x-ray ARPES result for CeCu$_2$Ge$_2$ at 20 K is thus consistent with the predicted band structure for LaCu$_2$Ge$_2$, indicating that the 4f electrons are localized and hence hardly contribute to the formation of the Fermi surface sheets in ambient pressure.

4. Resonance photoemission for CeCu$_2$Ge$_2$ and LaCu$_2$Ge$_2$

It is well known that the Ce 4f spectral weight highly deviated from the non-4f ones is revealed by the 3d-4f resonance photoemission, at which the 4f spectral weight is enormous relative to the off-resonant non-4f spectral weight [9, 14, 16]. We have also performed the angle-integrated resonance photoemission at the 3d-edge for CeCu$_2$Ge$_2$ as shown in Fig.3(a). There are a sharp
peak at 0.24 eV as well as a shoulder in the vicinity of $E_F$, and another peak at $\sim 2.3$ eV in the on-resonance spectra at $h\nu = 881.9$ eV. The former components are ascribed to the 4f$^1$ final states involving the tail of the Kondo resonance at $E_F$ (4f$^1_{5/2}$ final state), its crystal-field-split partners (other 4f$^1_{5/2}$ final states, not seen as a peak due to the relatively poor energy resolution of 140 meV) and its spin-orbit partner (4f$^1_{7/2}$ final state) at 0.24 eV [15, 16, 17, 18]. The spectral weight of the tail of the Kondo resonance is much weaker than the spin-orbit partner in contrast to the case of a typical heavy fermion system CeRu$_2$Si$_2$ [16, 18], which suggests that the possible 4f-derived quasi-particle spectral weight is negligible in the total 4f spectral weight [9] for CeCu$_2$Ge$_2$. In the case of CeRu$_2$Ge$_2$ where the 4f$^1_{5/2}$ final-state peak height has been rather comparable to the 4f$^1_{7/2}$ one [16, 18], its non-4f electronic structure probed by the soft x-ray ARPES has been basically consistent with the band-structure calculation for LaRu$_2$Ge$_2$ corresponding to the 4f-localized model [7]. Therefore, the result of the Ce 3d-edge resonance photoemission and that of the soft soft x-ray ARPES probing the non-4f states are mutually consistent. The peak at 2.3 eV is due to the 4f$^0$ final state representing the localized 4f component, whose peak energy is distinctly different from that at 2.5 eV seen in the off-resonance spectrum at $h\nu = 876.2$ eV.

Figure 3. Angle-integrated resonance photoemission spectra near the 3d$_{5/2}$ core absorption edge at 20 K for (a) CeCu$_2$Ge$_2$ and (b) LaCu$_2$Ge$_2$ where the Ce 3d-4f on-resonance spectral weight is scaled by multiplying it by 0.3 for comparison of the spectral line shapes. Dashed lines located at the peak and/or shoulder binding energies in the off-resonance spectra (at $h\nu = 876.2$ eV for CeCu$_2$Ge$_2$, at $h\nu = 830$ eV for LaCu$_2$Ge$_2$) are guides to the eye. The insets show the core absorption spectra where the employed photon energies for the resonance photoemission are indicated by arrows.

Figure 3(b) shows the angle-integrated photoemission spectra near the 3d$_{5/2}$ absorption edge (see the inset of the figure) for LaCu$_2$Ge$_2$. The spectral weight from $E_F$ to the binding energy of 3 eV is clearly enhanced in the spectra at $h\nu = 836, 834$ and 834.2 eV located at the La 3d-to-4f absorption relative to that at $h\nu = 830$ eV. Such a enhancement is qualitatively different from that at the 3d$_{5/2}$ edge for CeCu$_2$Ge$_2$ in Fig. 3(a) as pointed out in the following: The magnitude of the spectral enhancement is much weaker for LaCu$_2$Ge$_2$ than for CeCu$_2$Ge$_2$. 

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and the spectral weight of the peak and/or shoulder structures seen in the off-resonance spectrum at $h\nu = 830$ eV are enhanced in the spectra at $h\nu$s in the 3$d_{5/2}$ absorption edge for LaCu$_2$Ge$_2$, which is in contrast to the case of CeCu$_2$Ge$_2$. There are two processes in the photoemission at the La 3$d$ absorption edge for LaCu$_2$Ge$_2$ as

$$3d_{10}^{10}4f^05d^n + h\nu \rightarrow 3d_{10}^{10}4f^05d^{n-1} + e^-, \quad \text{(direct process)} \quad (1)$$

$$3d_{10}^{10}4f^05d^n + h\nu \rightarrow 3d_{10}^{9}4f^15d^n \rightarrow 3d_{10}^{10}4f^05d^{n-1} + e^-, \quad \text{(Auger process)} \quad (2)$$

where $e^-$ denotes a emitted photoelectron. Since the initial and final states are the same between these processes, the 5$d$ contribution can be resonantly enhanced. We thus conclude that the enhanced weight in the photoemission spectra of LaCu$_2$Ge$_2$ taken at the 3$d_{5/2}$ absorption region is due to the resonant La 5$d$ contribution. It should be noted that the 5$d$ resonance enhancement could take place at the 3$d_{5/2}$ edge for Ce compounds while it seems to be completely buried by the 4$f$ contributions in the angle-integrated resonance photoemission spectrum of CeCu$_2$Ge$_2$ as shown in Fig. 3(a). Indeed, the similar 5$d$ resonance enhancement have also been in the Yb 3$d$-edge resonance photoemission for YbRh$_2$Si$_2$ [19], for which there are four processes as

$$3d_{10}^{10}4f^{135}5d^n + h\nu \rightarrow 3d_{10}^{10}4f^{125}5d^n + e^-, \quad \text{(4f-direct process)} \quad (3)$$

$$3d_{10}^{10}4f^{135}5d^n + h\nu \rightarrow 3d_{10}^94f^{145}5d^n \rightarrow 3d_{10}^{10}4f^{125}5d^n + e^-, \quad \text{(4f-Auger process)} \quad (4)$$

$$3d_{10}^{10}4f^{135}5d^n + h\nu \rightarrow 3d_{10}^{10}4f^{135}5d^{n-1} + e^-, \quad \text{(5d-direct process)} \quad (5)$$

$$3d_{10}^{10}4f^{135}5d^n + h\nu \rightarrow 3d_{10}^94f^{145}5d^n \rightarrow 3d_{10}^{10}4f^{135}5d^{n-1} + e^-, \quad \text{(5d-Auger process)} \quad (6)$$

where the initial and final states are the same between the processes (3) and (4), and those (5) and (6), respectively.

5. Resonance ARPES for LaCu$_2$Ge$_2$

The soft x-ray ARPES near the 3$d_{5/2}$ absorption edge has also been performed for LaCu$_2$Ge$_2$ as shown in Fig. 4. One can recognize that the spectral weight due to the dispersive band structure from $E_F$ to the binding energy of ~2 eV is enhanced in all momenta at the on-resonance condition of $h\nu = 834$ eV relative to that at $h\nu = 832$ eV in the off-resonance condition without showing any possible enhancement of non-dispersive localized component. $h\nu = 834$ eV corresponds roughly to $k_z \sim \pi/c$, halfway between the $\Gamma$ and $Z$ points along the $k_z$ direction. There is a band approaching to and crossing $E_F$ on going from (a,a,0) to (0,0) in the off-resonance ARPES spectra at $h\nu = 832$ eV in Fig. 4(a). At $h\nu = 834$ eV in the resonance condition, the spectral weight of this band is clearly enhanced. In addition, another band, which cannot be recognized in the off-resonance ARPES, appears near $E_F$ inside the above band centred at (0,0) in the on-resonance ARPES spectra. Thus, the resonance enhancement seen in the angle-integrated photoemission shown in Fig. 3(b) is due to the itinerant and dispersive La 5$d$ contribution strongly mixed with such other orbital-derived states as Ge 4$sp$ and Cu 4$s$ states.

6. Summary

We have shown that the electronic structure of CeCu$_2$Ge$_2$ at 20 K probed by the soft x-ray ARPES and resonance photoemission is consistent with the band structure predicted for LaCu$_2$Ge$_2$, which suggests the localized Ce 4$f$ character in this system. The 5$d$ resonance enhancement is observed for LaCu$_2$Ge$_2$ in both angle-integrated and angle-resolved photoemission while the magnitude of enhancement is much weaker than the Ce 4$f$ resonance one for CeCu$_2$Ge$_2$. The resonance ARPES of LaCu$_2$Ge$_2$ tells us that the La 5$d$ orbitals are strongly hybridized with the other itinerant orbitals such as Ge 4$sp$ and Cu 4$s$ ones.
Figure 4. (a) Off- and (b) On-resonance angle-resolved photoemission intensity maps for LaCu$_2$Ge$_2$ near the La 3$d_{5/2}$ absorption edge measured at 20 K. Black dotted curves near (0,0) are guides to the eye representing the dispersive band drastically enhanced at $h\nu = 834$ eV.

Acknowledgments
We thank J. Yamaguchi, M. Tsujibayashi, T. Uyama, M. Obara, Y. Nakatsu, S. Komori, S. Itoda, S. Imada, Y. Kato, S. Suga, S. Kitayama, C. Hatakeyama, B.-Y. Hao, T. Matsumoto, H. Fuchimoto and Y. Takeda for supporting the experiments. This work was supported by Grant-in-Aid for Scientific Research (21740229), Innovative Areas (20102003), the Global COE (G10) from MEXT and JSPS, Japan, and by Toray Science Foundation. The photoemission measurements were performed at SPring-8 under the approval of JASRI (2008B1450, 2009A1005, 2009B1014, 2011B1348) and JAEA (2010B3834, 2011A3833, 2011B3834).

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