Electronic band structure and Kondo coupling in YbRh$_2$Si$_2$

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The electronic band structure of YbRh$_2$Si$_2$ is calculated in a relativistic framework including correlation corrections and magnetization of the Yb ion and compared to detailed angle-resolved photoemission spectra. The photoemission spectra for LuRh$_2$Si$_2$ are used as reference to identify electronic bands with no $f$ symmetry. The calculated band structure manifests a $4f^{13}$ spin-polarized configuration leaving the unoccupied state at 1.4 eV above the Fermi energy. At the band theory level, the $4f$ bands are located far below the Fermi level and the anisotropic Coulomb interaction within the $4f$ shell spreads the multilevel into broader $4f$ complexes below −2.5 eV. The photoemission spectra obtained on YbRh$_2$Si$_2$ show a clear $f$-multilevel splitting into $j=7/2$ and $5/2$ excitations. The interaction of the $4f_{7/2}$ levels close to the Fermi energy with two conduction bands shows visible hybridization gaps of 45 and 80 meV, respectively. We discuss the origin of these excitations and provide an analysis according to Anderson’s single-impurity model with parameters suggested by the band-structure calculation and the photoemission spectra. Both experiment and theory indicate nearly identical Fermi surfaces for LuRh$_2$Si$_2$ and YbRh$_2$Si$_2$. The valency of Yb in YbRh$_2$Si$_2$ is estimated to be close to +3.

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I. INTRODUCTION

Heavy fermion (HF) systems on the border of a zero-temperature magnetic transition have been particularly attractive in the past years because of their anomalous low-temperature thermodynamic, transport, and magnetic properties that deviate strongly from Landau Fermi liquid theory. Recently, an increasing number of examples of Ce- and U-based systems such as CeCu$_6$−$x$Au$_x$, CePd$_2$Si$_2$, CeIn$_3$, and U$_3$Pt$_2$In have been found to exhibit magnetic quantum criticality by either doping or pressure tuning. YbRh$_2$Si$_2$ has attracted attention as the first observed Yb-based and stoichiometric HF system with competing Kondo and anisotropic Coulomb interaction within the 4$f$ shell leading to an increase of the magnetic fluctuations at low temperatures, showing a tiny magnetic moment of

$$\mu_{\text{Yb}} = (10^{-2} - 10^{-3}) \mu_B$$

at ambient pressure below the Néel temperature $T_N = 70$ mK. Pronounced non-Fermi liquid behavior has been observed in the resistivity $\rho(T)$ and the electronic specific heat $C(T)$ at low temperatures, showing $\Delta \rho = \rho - \rho_0 \propto T$ and $\Delta C/T \propto -\ln(T)$, respectively. The ground-state properties of YbRh$_2$Si$_2$ can be easily tuned around the magnetic quantum critical point by control parameters such as pressure, magnetic field, or doping. An external pressure compresses the atomic lattice leading to an increase of the antiferromagnetic coupling with a maximal Néel temperature of 1 K at 2.7 GPa. On the other hand, expanding the lattice by replacing Si by Ge (Ref. 12) or Yb by La favors the Kondo coupling and reduces $T_N$. Approximately 5% Ge or La doping completely destroys the antiferromagnetic order in YbRh$_2$Si$_2$. Electron-spin-resonance and nuclear-magnetic-resonance experiments have demonstrated the importance of magnetic fluctuations at low $T$. At intermediate temperatures, a regime emerges for which it is believed that the quantum critical fluctuations dominate and the notion of a well defined quasiparticle breaks down. Remarkably, in YbRh$_2$Si$_2$, this regime extends up to 10 K.

A Hall-effect measurement suggested a discontinuity in the Fermi-surface (FS) volume of one charge carrier across the quantum phase transition. Based on a local-density approximation (LDA) calculation, the change in the FS volume by unit charge was suggested to arise from a shift of the $f$ levels across a quantum transition from the antiferromagnetic phase to the Kondo Fermi liquid. Concurrent theories on critical heavy Fermi liquids assume $f$ electrons to be partly integrated into a large FS and distinguish between visible quasiparticle peaks (spin-density wave case) versus a vanishing Kondo resonance. A direct measurement of the electronic band structure and especially the location and renormalization of $f$-derived electronic bands, their hybridization with the conduction bands, and their incorporation into the FS could provide a stringent test of such theories. Angle-resolved photoemission spectroscopy (ARPES) has proven to be uniquely powerful in its capability to directly probe the electronic structure of solids.

We report here the band-structure calculations reflecting the Yb$^{5+}$ ion that is observed by macroscopic experiments at elevated temperatures. Previous calculations have only modeled a nonmagnetic Yb$^{5+}$ ion. We compare the angle-resolved photoemission spectra for YbRh$_2$Si$_2$ in the ordinary Kondo-screened state with those for LuRh$_2$Si$_2$. The comparison of the Yb and Lu compounds provides a definitive identification of the $4f$-derived states in the Yb compound. Most importantly, we have directly observed evidence of hybridization between the $4f$ state and valence states, yielding hybridization gaps ranging from 30 to 80 meV. We performed an analysis of the $4f$-derived spectrum $\rho_s(\varepsilon)$ within the single-impurity Anderson model using parameters sug-
suggested by the band-structure calculation, which leads to a picture that differs from those presented in previous studies. This analysis explains $\rho_p(e)$ and macroscopic parameters such as the Kondo temperature $T_K$ in reasonable agreement with the experiments.

II. ELECTRONIC STRUCTURE CALCULATIONS

A. Structure

The crystal structure of YbRh$_2$Si$_2$, displayed in Fig. 1, is body-centered tetragonal (bct) with I4/mmm space group (space group 139). The Yb ion occupies the 2a site which has full tetragonal 4/mmm symmetry and forms a bct sublattice, which becomes important in the interpretation of its magnetic behavior. Rh resides in a 4d site (4m2 symmetry) and lie on a simple tetragonal sublattice rotated by 45° in the plane and having lattice constants $a/\sqrt{2}$ and $c/2$. Si is in the 4e site (4mm); the Si-Si interatomic distances of 2.46 Å is only 5% longer than in diamond structure Si, so one view of the structure is in terms of Si$_2$ dimers oriented along the $\hat{z}$ axis. Yb atoms and the dimers form a centered square lattice in the x-y plane. Yb is eightfold coordinated by Rh at a distance of 3.17 Å. The atomic positions are in units of $(a,a,c)$ Yb (0,0,0), Rh (0, $\frac{1}{2}$, $\frac{1}{2}$), and Si (0,0,0.375); note that the Si height is not determined by symmetry and is accidentally equal to $\frac{3}{8}$. The experimental lattice constants $a=4.010$ Å and $c=9.841$ Å have been used in our calculations.

For reference, we have also calculated the band structure of isostructural and isovalent LuRh$_2$Si$_2$ ($a=4.090$ Å, $c=10.18$ Å). In this compound, Lu has a filled 4f shell under all conditions and the compound is a conventional nonmagnetic metallic Fermi liquid.

B. Methods

Rare-earth atoms and other atoms with strong effective intra-atomic Coulomb repulsion $U$ (Hubbard $U$) pose a serious challenge for band theoretical methods. Density-functional theory addresses at the most basic level the ground state, which gives the Hund’s rule ground state of the Yb ion a central role. Hund’s rule implies that one leaves consideration of spin-orbit coupling (SOC) until after the spin $S$ and angular momentum $L$ have been maximized. On the other hand, for interpreting single-particle-like excitations, which is the main topic of this paper, one wants to obtain the $j=\ell \pm \frac{1}{2}$ character of the excitations. Thus, one must include SOC at the one-electron level, and that is the viewpoint that we take here. From the Curie-Weiss susceptibility at high temperature in YbRh$_2$Si$_2$, it is clear that the Yb ion is primarily in a 4f$^{13}$ configuration (at elevated temperature, at least), corresponding to $S=\frac{5}{2}$, $L=3$, and $J=\frac{7}{2}$ in the absence of crystal fields.

To be able to include the necessary combination of exchange splitting (magnetic order), SOC, and also the local-density approximation plus intra-atomic repulsion $U$ (LDA + $U$) approach that is necessary for rare-earth atoms, we have used the WIEN2K electronic structure code.$^{19}$ An $j^{13}$ configuration necessarily requires a magnetic ion, and we consider only the simplest (ferromagnetic) alignment of Yb spins. With magnetization along the (001) direction, SOC reduces the symmetry to Abm2 (space group 39). The around-mean-field version of LDA+$U$ (appropriate for small spin) was used, with $U=8$ eV and $J=1$ eV. In the results presented below, the $m=0$ 4f orbital was unoccupied. We have also obtained a solution with the $m=-2$ orbital unoccupied. (The Hund’s rule state would have $m=+3$ unoccupied.) There is no difference in the results that are discussed here, only minor differences in the placement of the Yb 4f bands. The filled f$^{14}$ shell of Lu does not present any of these complications. To obtain an accurate determination of the Fermi surface, we have used a k mesh of 20$^3$ (641 k points in the IBZ), $R \ K_{max}=9$, and the Perdew-Burke-Ernzerhof generalized gradient approximation$^{20}$ for exchange-correlation potential. An energy range from $-7$ to 7 Ry is used when SOC is incorporated.

C. Band-structure results

The band structure of YbRh$_2$Si$_2$ shown in Fig. 2 is characterized by the expected 4f$^{13}$ spin-polarized configuration of the Yb ion. Without SOC, this would correspond to one hole in the minority 4f shell. With SOC included, as here, the flat 4f band complex is spin mixed and split into a 4f$^{3/2}$ complex and a 4f$^{1/2}$ complex separated by the spin-orbit splitting of roughly 1.3 eV. Although each 4f band is quite flat, each of the complexes of 2j+1 bands ($j=\frac{5}{2}, \frac{3}{2}$) is split...
due to the anisotropy of the Coulomb interaction\textsuperscript{21} within the 4f shell, which is included fully in the LDA+$U$ method. However, the 4f electrons are polarized (one hole, $S=\frac{1}{2}$), which also induces a Hund’s (exchange) splitting that complicates the identification in the figure of the 4$f_{5/2}$ and 4$f_{7/2}$ states separately. However, the result that is pertinent to this paper is that this electronic structure calculation fully includes magnetic and relativistic effects and intra-atomic correlation in a static but self-consistent manner and leaves one hole in the 4f shell consistent with the Curie-Weiss susceptibility.

The unoccupied 4f band lies 1.4 eV above the Fermi level $E_F$ and can be seen to mix exceedingly weakly with the itinerant (Rh+Yb+Si) bands, reflecting its very localized character. The occupied levels lie 2.5 eV or more below $E_F$ and also hybridize weakly. Hence, at the band-structure level, the 4f states are well away from the Fermi level. Many-body interactions arising through coupling to the conduction bands may, of course, lead to large renormalizations as reflected in the experimental data (see Sec. I). We focus first on the states near and at $E_F$, and then return to the (Kondo) coupling of the 4f moment to the Fermi surfaces.

The total Rh 4d and total Tb 5d characters are shown separately in the projected orbital character representations in Fig. 2. (See Fig. 3 for the density of states.) Much of the Rh 4d bands are occupied, while most of the Yb 5d bands are unoccupied; however, there is Yb 5d character around and even below the Fermi level. The Si 3p character is spread fairly evenly through the valence and conduction bands. The bands around $E_F$ have mostly Rh 4d character, with some Yb 5d mixed in, and the bands along symmetry lines are clearly associated with certain symmetry-determined irreducible representations $a_g(d_{x^2-y^2})$, $b_{1g}(d_{x^2-y^2})$, $b_{2g}(d_{xy})$, or $e_g(d_{x^2-y^2},d_{z^2})$ of the Rh and Yb d states.

The first noteworthy feature is the band lying 0.2 eV below $E_F$ at $\Gamma$, which is completely flat along $\Gamma-Z$ [(0,0,0) line] and disperses upward in the plane; this is a pure Rh $d_{z^2-r^2}$ band. There is also a strong Rh 4$d_{z^2-r^2}$ character at $-5$ eV (within the 4f bands), presumably the bonding combination of $d_{z^2-r^2}$ orbitals on the two Rh atoms in the cell. The Rh $d_{z^2-r^2}$ band crossing $E_F$ contributes the cylindrical faces of the electron-type tall pillbox $P$ FS with (near circular) mean radius in the plane of $k_z=0.133 \pi$. All three FSS are displayed in Fig. 4. The Fermi level is intersected along $\Gamma-Z$ by a band composed of Rh 4$d_{z^2-r^2}$, Yb 5$d_{z^2-r^2}$ character and 2 eV wide. This band defines the top and bottom faces of the $\Gamma$-centered pillbox, with Fermi wave vector $k_F=0.265 \pi$ along the $\hat{z}$ axis. This pillbox contains $\sim 4 \times 10^{-3}$ carriers/f.u.
character dominates the flatband at −1.5 eV along Γ-Z, which disperses downward from there within the plane.

The other Fermi surface, also shown in Fig. 4, is a fluted donut D centered at the Z point and oriented in the x−y plane. It arises partially from the upward dispersion in the x−y plane of the band that lies at −30 meV at Z. This donut D surface contains electrons.

The FS of LuRh$_2$Si$_2$ is nearly identical, as anticipated from the identical structures and the isovalence of the rare-earth ions. One change occurs due to a small difference in band energy at and near the X point. The J surface changes its connectivity and shape as a result but remains a large (and generally similar) FS.

D. Aspects of Kondo coupling

YbRh$_2$Si$_2$ is a heavy fermion compound, whose J=L+S = 7/2 ion and associated local moment will be affected by crystal fields and finally screened by conduction electrons at low temperature (a tiny moment survives and orders in YbRh$_2$Si$_2$; see Sec. I). Thus, while our ferromagnetic state with S=5/2 is not expected to describe the interacting ground state, it has the virtue of providing a measure of the degree of Kondo coupling of the Yb moment to the Fermi surfaces, because the exchange splitting of the Fermi surfaces reflects the coupling of the local moment to the itinerant bands.

The exchange splitting of the Γ cylinder is 6 meV around its waist (in the x−y plane) and 30 meV at top and bottom, a strong anisotropy resulting from the different characters of wave functions on the different parts of the surface. For points on the J surface near the X point, the exchange splitting is 20 meV at both (0.95,0,0)"_a and (1,0,2,0)"_a. Thus, the Kondo coupling, and likewise the carrier scattering by the moments, differs by at least a factor of 5 around the Fermi surfaces.

E. Discussion of bands and Fermi surfaces

This fully relativistic, spin-polarized LDA+U band structure and resulting Fermi surfaces can be compared with previous unpolarized relativistic LDA prediction.15,22,23 Not surprisingly, there are substantial differences, as expected from the LDA’s 4f$^{14}$ configuration versus our magnetic 4f$^{13}$ bands; this difference in Yb 4f charge state puts Norman’s Fermi level one electron lower with respect to the Rh 4d + Yb 5d + Si 3p itinerant bands.15 As a result, the flat Rh 4d_{x^2−y^2} band that lies 0.2 eV below $E_F$ in our bands lies 0.1 eV above $E_F$ in the LDA bands, and the Fermi surfaces are entirely different. These differences will lead to completely different predictions for the Hall coefficient.

On the qualitative level, our Fermi surfaces include large sheets with canceling positive and negative contributions to the Hall coefficient, as do Norman’s. The Hall coefficient, usually thought of (in the constant relaxation times approximation) as being an average of the Fermi-surface curvature, will bear no relation to the number of carriers. No doubt it will be quite anisotropic, given the strong tetragonality of the FSs. The edges of the pillbox P may give large contributions (and make evaluation difficult); likewise, the sharp edges on the donut D will also have large curvatures.

From the bands in Fig. 2, it can be observed that a hole-type surface nearly closes at the X=(1/2,0,0) point. Because the point we call X is not on the bct Brillouin-zone boundary (the true zone is shown in Fig. 4), this is not a small ellipsoid as might be guessed, but rather part of tubes of a multiply connected jungle-gym surface J. The largest part of this surface encircles nearly all of the upper zone face centered on the Z=(0,0,1/2) point. The character near X is Rh 4d_{x^2}, 4d_{y^2}, and some Yb 5d character. There is also strong Rh 4d_{x^2−y^2}, 4d_{x^2−y^2} character in the flatband along Γ-Z near −3 eV. Rh 4d_{x^2−y^2}
The “curvature” interpretation of the Hall tensor relies on the isotropic scattering time approximation. This situation is unlikely to be the case in YbRh$_2$Si$_2$, where the main scattering arises from the Kondo coupling to local moments. As pointed out in the previous section, this coupling varies strongly over the Fermi surface (by at least a factor of 5). Hence, this system is an example of a multiband (correlated) metal with large Fermi surfaces of varying curvature, having large and anisotropic scattering. Its Hall tensor, versus temperature, field, and magnetic ordering, promises to be very challenging to understand.

III. EXPERIMENTS

Millimeter sized single crystalline platelets of LuRh$_2$Si$_2$ and YbRh$_2$Si$_2$ were grown by the flux-growth method using an In flux in a sealed Ta tube under argon atmosphere. The crystals were washed in HCl acid solution to safely remove excess In flux. The tetragonal crystal structure and the lattice parameters were confirmed by x-ray powder diffraction. The ARPES measurements were performed using a chamber equipped with a Scienta SES200 analyzer attached to the undulator beamline 5-4 of the Stanford Synchrotron Radiation Laboratory (SSRL) and a second vacuum system equipped with a Scienta SES2002 analyzer and a microwave driven monochromatized He-discharge lamp (Gammadata VUV5000). At SSRL, we used linearly polarized photons of 21.4 eV. The photoemission spectra at these photon energies allow a detailed comparison of the electronic states with no core levels, which enhances the photoelectron yield of the Yb 4f electrons but worsens the energy resolution by approximately six to eight times. At these low energies, the photoelectron mean free path becomes very short and care has to be taken regarding identifying surface and bulk states. Fortunately, there are numerous reports having dealt with this issue in Yb-related materials$^{24,26,27}$ and also in YbRh$_2$Si$_2$. An energy resolution of $\sim$40 meV or more hides the relevant hybridization features in the angle-resolved spectra for the critical system YbRh$_2$Si$_2$. The total energy resolution including the monochromator and the analyzer was 8 meV for the 21.2 eV beam from the He source and 22 meV for the 21.4 eV synchrotron beam, respectively. The chamber pressure was below 4$\times$10$^{-11}$ torr. The samples were cleaved in situ at $T\sim 14$ K. As opposed to previous experiments on Yb- or Ce-based material, very clean cleaves with large flat grayish shiny areas can be obtained on these 1-2-2 compounds where the electronic spectra manifest sharp features. The excellent quality of the surface has been determined using high-resolution low-energy electron diffraction. The position of the Fermi level ($E_F$) was calibrated from the Fermi edge of polycrystalline Au for every measurement.

IV. PHOTOEMISSION RESULTS AND DISCUSSION

A. Angle-integrated spectrum at $h\nu=40.8$ eV

Figure 5 shows the angle-integrated spectrum for YbRh$_2$Si$_2$ (solid curve) at angles between $-5^\circ$ and $17^\circ$ in the $\Gamma$-M-Z plane measured with He II radiation. The broad distribution of intensity between $-11$ and $-7.5$ eV, indicated by the shaded area in Fig. 5, included emission from Si 3s states, as indicated by the band-structure calculations. At low binding energies, we can identify two sharp but small intensity maxima at $\sim -1.3$ eV and right at $E_F$ with a peak intensity ratio of approximately 2:3, respectively. The corresponding data for $h\nu=21.2$ eV do not display any pronounced intensity at these energies. Hence, these are single-hole, very weakly hybridized $j=7/2$ and $j=5/2$ states split by the 1.3 eV SOC energy (see Sec. IV C). The intense peaks at 650 meV and at 2 eV can be attributed to the spin-orbit split surface bands$^{28}$ originating from Yb ions at or close to the sample surface. The relative intensity of surface vs bulk peaks decreases strongly when the photon energy is increased from 21 to 41 eV and 110 eV$^{22}$. The intensity around 3 eV is not due to flatbands but is a result of various coterminating band edges having high intensities in that energy region, which is seen in the angle-resolved spectrum in Fig. 7. We refer to Ref. 22 where the 4f intensities can be compared to the atomistic calculations of Gerken$^{29}$. However, this paper focuses on the excitations close to the Fermi energy, related to the Yb 4f$^{7/2}$ excitations.

B. Angle-resolved spectra for LuRh$_2$Si$_2$ and YbRh$_2$Si$_2$

Within the sudden approximation$^{17}$, angle-resolved photoemission measures the single-particle spectral function $A(k,\omega)$, where $k$ is the crystal momentum and $\omega$ is the photo-hole energy taken at a beam energy $h\nu=21.2$ eV. For quasi-two-dimensional materials, it is the in-plane component of the crystal momentum $k_{\parallel}$ that matters. We will plot the data with respect to $k_{\parallel}$; however, we note that the three-dimensional behavior can be important in this material. $\bar{\Gamma}$, $\bar{M}$, $\bar{X}$, and $\bar{Z}$ refer to locations in the Brillouin Zone (BZ).
FIG. 6. (Color online) [(a) and (b)] Angle-resolved PE spectra for LuRh$_2$Si$_2$ taken in our case at 21.2 eV in the $\Gamma\tilde{M}$ direction. The numbers are referred to in the text. (c) Angle-resolved spectrum of LuRh$_2$Si$_2$ in the $\Gamma\tilde{X}$ direction. (d) EDC plot for the $\Gamma M$ direction near $\tilde{\Gamma}$.

close to the $\Gamma$, $M$, $X$, and $Z$ points in the real BZ, respectively. The three-dimensional nature of the bands, and hence of the photoemission process, inhibits more precise identification in $k$ space (i.e., of $k_\text{F}$). The distance $\Gamma\tilde{X}$ is approximately equivalent to $\Gamma X$ in the center of the BZ. In order to connect to the calculations, we use $\omega$, $\epsilon$, and $E-E_F$ on an equal basis in the following discussions.

At the most rudimentary level, LuRh$_2$Si$_2$ and YbRh$_2$Si$_2$ differ only by one electron in the 4f shell on the rare-earth ion. Whereas high-temperature experiments have shown that in these materials Yb is in the magnetic 4f$^{13}$ state, Lu has a filled shell and the 4f-electron levels are expected to be at elevated binding energies. Hence, comparing photoemission results for these compounds can yield insight into the nature of the various electronic bands with no f symmetry.

LuRh$_2$Si$_2$. The top two plots in Fig. 6 show the angle-resolved photoemission spectra for LuRh$_2$Si$_2$ in the $\tilde{\Gamma}-\tilde{M}-\tilde{Z}$-plane with different energy scales measured at 21.2 eV. Comparing the energy distribution curve (EDC) and the FS images to the results of the band-structure calculations, we conclude that $\tilde{\Gamma}$ lies on a point slightly below 1/4 of the line from $-Z$ to $\Gamma$. Several bands — 1, 2, 3, 4, and 5 — cross the Fermi level and form Fermi surfaces. Since the LDA calculation for LuRh$_2$Si$_2$ yields nearly the identical FS as the LDA+$U$+SOC calculation does for YbRh$_2$Si$_2$, these sheets can be compared to the corresponding ones in Fig. 4.

Bands 4 and 5 are already in the neighboring BZ. They can be ascribed to the donut shaped $D$ and jungle gym $J$ FSs, respectively. Band 1, i.e., the Rh 4d band, shows a parabolic dispersion where the spectral weight increases strongly as $E_F$ is approached near $\tilde{\Gamma}$. The lower right panel in Fig. 6 reveals, however, that it is not only a single band but also a steep one (band 1) and a flat one (band 1') meeting at $\tilde{\Gamma}$ without opening a clearly detectable hybridization gap.

YbRh$_2$Si$_2$. The upper panel in Fig. 7 shows an angle-resolved photoemission spectrum in the $\Gamma$-$X$-$Z$ plane measured again at the same 21.2 eV. Compared with the LuRh$_2$Si$_2$, we have evidence for four additional bands between $E_F$ and 2 eV binding energy, suggesting that these are Yb-derived 4f states, an assignment consistent with these bands being extremely flat. Two different flatbands display a pronounced intensity: band ($fb_1$) located very close to $E_F$ and band ($fb_2$) with a maximum intensity at $\approx 680$ meV below $E_F$. The latter is derived from electronic states of Yb atoms close to the sample surface (see Sec. IV A). Previous spectroscopic experiments$^{30}$ and fully relativistic calculations (see Fig. 2) revealed that the spin-orbit interaction in Yb-based materials is of the order of 1.3 eV, consistent with the value obtained within the relativistic calculation (see Sec. II).

Masked in the primary spectra by the high intensity of neighboring bands, the second derivative plot (lower panel in

FIG. 7. (Color online) Angle-resolved PE spectra of YbRh$_2$Si$_2$ taken at $h\nu=21.4$ eV at $T=14$ K in the $\Gamma$-$X$-$Z$ plane. The lower panel shows the second derivative of the spectrum (upper panel). The relevant bands are denoted as ($fb_1$) and ($fb_2$) for the bulk 4f$^{13}$ and ($fs_1$) and ($fs_2$) for the surface 4f$^{13}$ states; $P_1$ and $P_2$ are valence bands with mostly Rh 4d and partly Yb 5d character, for the latter one.
Fig. 7) reveals a third very flat electronic band \((f_{b_2})\) separated from band \((f_{b_1})\) by the spin-orbit splitting \(\Delta_{f}\) of 1.3 eV and a fourth flatband \((f_{s_1})\), i.e., the bulk and surface \(4f_{5/2}\) final states, respectively. Neither a careful investigation of the spectra nor the second derivative plot revealed an additional flatband with \(f\) symmetry as indicated by the LDA+\(U\)+SOC band-structure calculation. This observation reflects the fact that the LDA+\(U\) eigenvalues are not in one-to-one correspondence with photohole energies in open strongly correlated shells, and more especially so when there is important coupling to valence states as is clearly the case in YbRh$_2$Si$_2$. Hence, the \(f\) excitations are split into a \(4f_{5/2}\) peak at \(-1.3\) eV and a sharp band of \(4f\) electrons with \(j = 7/2\) centered at \(-45\) meV with a peak width of \(\Gamma_{FWHM} = 30\) meV obtained from an EDC fit to a Lorentzian shape.

A strong intensity is displayed by the band \((P_1)\) which shows a nearly-free-electron parabola with band width \(B\) down to \(-3.6\) eV at the \(X\) point and nearly \(6\) eV at the \(M\) point (see lower left panel in Fig. 6). While the band consists of several overlapping components, comparison with LDA+\(U\) band structure suggests that it is mostly states of Rh 4\(d\) character. While the real band structure is more complicated, we will use a nearly free parabola to mimic this band for continuation \(\epsilon > 0\) eV and simulating the \(4f\) spectral weight later. Moreover, band \((P_1)\) also crosses and mixes with the Yb-derived surface bands \((f_{s_1})\) and \((f_{s_2})\) around \(\bar{\Gamma}\). Since the Si ions form strongly bonded Si$_2$ dimers that encage the Yb ions, the first Yb layer is intermediate between a bulk and a surface layer such that it can be distorted by hybridization with a bulk band.

Halfway between the \(\bar{\Gamma}\) and the \(\bar{X}\) point, a band \((P_2)\), displaying a very weak intensity, hybridizes with the \(f\) band. We will show in Fig. 8 how this hybridization arises. This band \((P_2)\) starts at approximately \(-2\) eV close to \(M\) and crosses \(E_F\) near \(X\) as observed in Fig. 2. Considering the wave-function symmetry of this band, it can be continued in a nearly free parabola to approximately \(2\) eV above \(E_F\) at \(\bar{\Gamma}\). This band induces the hololike FS \(\mathcal{D}\). At \(\sim -20^\circ -25^\circ\), we observe two different bands denoted as \((d_1)\) and \((d_2)\). They form the jungle-gym FS sheet \(\mathcal{J}\) and will be briefly discussed in the Sec. IV D.

The upper left panel in Fig. 8 shows \(A(k_1, \omega)\) measured in the vicinity of \(\bar{\Gamma}\) using a photon energy of \(21.2\) eV. At very small angles, the \(4f_{7/2}\) band \((f_{b_1})\) with peak width less than \(35\) meV hybridizes weakly with the Rh 4\(d\) band leading to a dispersion of \(\sim 10\) meV. A gap between the peaks of the two bands of approximately \(80\) meV is observed. For \(\omega \sim -20\) meV, \(A(k_1, \omega)\) rises again toward lower binding energies indicating a double peak structure. In analogy to the spectra for LuRh$_2$Si$_2$, we observe a similar double peak structure between two dispersing Rh bands, but now they are separated by an Yb \(f\) band. Nearly no dispersion is observed for the peak below \(20\) meV binding energy. We note here that this feature near \(E_F\) does not follow the dispersion behavior of the \(f\) band, but it is rather limited to a small region around \(\bar{\Gamma}\). Furthermore, as we change the photon energy between \(17\) and \(31\) eV, the intensity at \(E_F\) remains almost unchanged (not shown here), characteristic for a band with minimal dispersion in the \(k_z\) direction. Hence, this lowest-energy peak at \(\bar{\Gamma}\) cannot be considered as a candidate for the Kondo resonance as it has a corresponding component in LuRh$_2$Si$_2$.

Panels (C) and (D) in Fig. 8 show a photoemission spectrum along the yellow line in Fig. 9. The top-right panel shows the raw data; the bottom right is the corresponding EDC data. The filled circles are obtained by fitting a single Lorentzian and a constant background to the EDC curves and the vertical thick line sets the Fermi level. A steep band \(\text{[band} (P_2) \text{in Fig. 7]} \) with strong Rh \(d\) character hybridizes with the flat Yb \(f\) band. This induces an opening of a band gap of the order of \(30 - 40\) meV. We note that this gap is too small to incorporate significant \(f\) spectral weight into the FS.

**C. 4f-excitation spectrum**

Now, we now come back to the \(4f\) states. As in Ref. 22, there is a complex \(4f\) spectral weight for binding energies above \(4\) eV, consistent with the LDA+\(U\)+SOC calculation.
FIG. 9. (Color online) In the lower panel, we plotted a Fermi-surface map for LuRh$_2$Si$_2$ taken at 21.2 eV. The upper panel shows the corresponding map for YbRh$_2$Si$_2$. $\mathcal{F}$, $\mathcal{D}$, and $\mathcal{J}$ are three different FS parts as discussed in the text. The dashed line indicates $\pi/a$, where $a$ is the length of the lattice bases. Units are given in $\pi/a$.

in Fig. 2. Unlike band theory, we observe two 4$f$-derived bulk features between $E_F$ and $-1.3$ eV arising from many-body interactions. They are usually related to 4$f_{7/2}$ and 4$f_{5/2}$ excitations and denoted as the Kondo resonance and its spin-orbit side band. The additional splitting due to an anisotropic Coulomb interaction that would lead to distinct energies of different $l=3$ hole orbitals is not observed.

We have performed a Gunnarsson-Schönhammer\footnote{Wigger et al. (2007)} (GS) analysis using parameters suggested by the band-structure calculations which differ significantly from those normally used in the literature.\footnote{Gunnarsson and Schönhammer (1984)} This scheme employs a second-order perturbative calculation based on the Anderson single-impurity model. We will assume $U=\infty$ and a large SOC in order to study only the 4$f_{7/2}$ states with degeneracy $N_f=8$.

As is usual in GS calculations, we model the valence band with a semieliptical density of states, in our case extending from $-6$ to $6$ eV. Based on our earlier discussion, we represent the $P_2$ band with a half-filled semieliptical form ranging from $-1.8$ to $2.4$ eV. The hybridization strength $V$ is related to the gap $\Delta$ by $\Delta=2V^2/B$, where $B$ is the bandwidth of the related conduction band. The solution for the spectrum is equivalent to the solution for the bremsstrahlung isochromat spectroscopy spectrum in cerium material, replacing the electrons by holes and inserting the form for the valence bands obtained from the band-structure calculations. The electronic gaps in the photoemission spectra are given for the interaction with parabola ($P_2$) as $\Delta_1 \sim 80$ meV observed in panel (A) in Fig. 8 and for the interaction with parabola ($P_2$) as $\Delta_2 \sim 45$ meV observed in the panels (C) and (D) in Fig. 8. In order to reproduce the spectrum, we vary $\epsilon_i$, the eightfold degenerate $f$ level.

The spectrum (open symbols in panel (B) in Fig. 8) is obtained by integrating the angle-resolved photoemission data between $0^\circ$ and $20^\circ$ at $21.2$ eV and subtracting the contribution from the Rh 4$d$ band using a Doniach-Sunjic line shape.\footnote{Doniach and Sunjic (1975)} Furthermore, we subtracted the intensity from the 4$f_{5/2}$ surface state centered at $2$ eV using a Lorentzian and a uniform background as in Ref. 24. The subtraction is rather tedious and perfect agreement with the calculation cannot be expected. The features of interest are two strong intensity regions, one centered at $-1.35$ eV and the other at $-45$ meV with intensity ratio of 2:3. The peak at $-1.35$ eV which mimics the 4$f_{5/2}$ excitation is approximated by a Lorentzian with linewidth of $\sim 55$ meV where we subtracted the background. As noted earlier, the feature at $-0.7$ eV is due to a surface state. Its emission is approximated by a Lorentzian with linewidth of $\sim 230$ meV (see the dashed line). The feature at higher binding energy is slightly asymmetric, and some additional intensity around $-1.1$ eV could not be removed properly.\footnote{Wigger et al. (2007)}

The result of the GS simulation is shown as a solid line in panel (B) in Fig. 8. The simulation yields an energy $\epsilon_i=-1.4$ eV and a hole concentration of 0.99 in the 4$f_{14}$ shell, i.e., the full Yb$^{3+}$ moment. The asymmetry of the peak at $50$ meV can be explained by the arguments of Doniach and Sunjic.\footnote{Doniach and Sunjic (1975)} In the spin-fluctuation limit with the $f$-level occupancy very close to 1, an estimate for the Kondo temperature can be obtained in the GS scheme\footnote{Sunjic and Wigger (2007)} as

$$\Delta E=N_f \sum_j \frac{|V_j(\epsilon)|^2}{\Delta E-\epsilon_j-\epsilon}.$$
scheme is justified. The interpretation of these two peaks is likely to be given, in an atomistic framework, by Gerken\textsuperscript{20} and which has been used for SmB\textsubscript{6} and sometimes also for Yb-related material.\textsuperscript{35,36} In this case, the valency is reduced to approximately $\pm 2.9$,\textsuperscript{22} which, however, interferes with macroscopic experiments.\textsuperscript{9} Given the serious deficiency of recent band-structure calculations in getting the correct experimental picture for the Yb $4f^{13}$ ion, which is then progressively screened at low temperature due to the Kondo effect, and given our GS-scheme simulation which provides a reasonable electronic spectrum and $T_K$, in balance, we favor the Kondo interpretation. We expect time-dependent two-photon photoemission spectroscopy and DMFT calculations on pure Yb to yield more information on the nature of these peaks.

We address the recent claim of YbRh\textsubscript{2}Si\textsubscript{2} being a mixed valent.\textsuperscript{15,22} If a $d$ band crosses the $f$ spectrum and the Fermi energy overlaps the $f$ configurational levels to within the hybridization energy, we have a mixed valence compound, i.e., the Yb ions occur both as Yb\textsuperscript{3+} with electronic $4f^{12}$ configuration or Yb\textsuperscript{5+} with $4f^{13}$ configuration. Panels (C) and (D) in Fig. 8, however, display that the hybridization energy is smaller than the distance to the Fermi level, i.e., 50 meV, and hence the valency is close to $+3$.

\section{D. Constant energy cuts at 21.2 eV}

The results of our band-structure calculations suggest that the FS of LuRh\textsubscript{2}Si\textsubscript{2} does not deviate significantly from the one of YbRh\textsubscript{2}Si\textsubscript{2}, plotted in Fig. 4.

The lower panel in Fig. 9 shows a FS map of LuRh\textsubscript{2}Si\textsubscript{2} obtained at a photon energy of 21.2 eV. We integrated the intensity over an energy window of 2 meV at $E_F$. This integration window is extremely narrow. It is imposed by the comparison to the FS of YbRh\textsubscript{2}Si\textsubscript{2} where the intensity of the $4f_{7/2}$ excitations appears close to the Fermi level and might falsify the intensity pattern. We distinguish clearly three different regions. Right in the center of the BZ, we observe a bright intensity $\mathcal{J}$ which, according Sec. IV B, is the inner part of the complex jungle-gym sheet forming a tip-like structure. $\mathcal{D}$ is a cut through the donutlike FS sheet centered around the $Z$ point of the BZ. Its intensity is blurred out because of considerable $k$ dispersion. $\mathcal{J}$ is again a cut through the complex jungle-gym sheet at the border of the BZ. For a better understanding, compare to Fig. 4.

The upper panel in Fig. 9 shows a FS map of YbRh\textsubscript{2}Si\textsubscript{2} obtained at the same photon energy of 21.2 eV. We again integrated the intensity over an energy window of 2 meV centered at the Fermi level determined on the gold reference sample. In accordance with the LDA+$U$+SOC calculations, the FS splits again into three different parts. At $\Gamma$, there is a small tip-like area $\mathcal{J}$ with a high intensity. At the boundary of the BZ, the very distinct arms of the FS sheet $\mathcal{J}$ show strong intensities. As indicated by the cut along $\bar{\Gamma}X$ in Fig. 7, it appears that for some particular crystal momenta the sheet $\mathcal{J}$ splits into two parts which have been labeled ($d_1$) and ($d_2$), respectively. An momentum distribution curve and/or EDC analysis reveals that these excitations have a relatively light effective mass of $m_{\text{eff}} \approx 1.2m_e$. The intensity pattern labeled $\mathcal{D}$ shows a cut through the FS displaying Rh $4d$ and Yb $5d$ characters and forming the same donut-shaped sheet as observed in LuRh\textsubscript{2}Si\textsubscript{2}.

We observe that at least qualitatively, the Fermi surfaces of LuRh\textsubscript{2}Si\textsubscript{2} and YbRh\textsubscript{2}Si\textsubscript{2} agree. This confirms the results of the band-structure investigations which obtained nearly identical FS for both materials. Hence, we conclude that the Yb $4f$ electron contribution to actively form the FS is small at 14 K.

\section{V. CONCLUSIONS}

In this paper, we have presented the results of an electronic band-structure calculation within a relativistic framework including correlation corrections for YbRh\textsubscript{2}Si\textsubscript{2}. The characteristic of the electronic structure is the $4f^{13}$ ground state as required by the Curie-Weiss moment that is observed at high temperature. A small FS cylinder of $4d_{2-7/2}$ symmetry is centered at $\Gamma$, a fluted donut $\mathcal{D}$ surface situated around the upper zone face midpoint $Z$, and a multiply connected jungle-gym $\mathcal{J}$ surface. The angle-resolved photoemission spectrum manifests (true many-body) intensities originating from $4f_{7/2}$ and $4f_{5/2}$ final-state excitations separated by 1.3 eV, the value for the spin-orbit interaction obtained from the calculation. These excitations are eightfold (sixfold) degenerate and do not manifest the splitting due to the anisotropic Coulomb interaction inherent to the single-particle energy states.

An analysis of the $4f$ spectrum $\rho_\mathcal{J}(e)$ according the degenerate Anderson impurity model using the parameters obtained from the band-structure calculations explains the appearance of a peak related to the $4f_{7/2}$ excitations at 45 meV below $E_F$. The Kondo splittings obtained from the band-structure calculations can be compared to the electronic gaps in the photoemission spectra. In a GS framework, the splittings are $V(e_F)\approx V/\pi\approx 33$ meV at $\Gamma$ and $16$ meV at the BZ boundaries. These values agree with those obtained from the LDA+$U$+SOC calculation. The Kondo temperature $T_K \approx 30$ K and full Yb\textsuperscript{3+} moment are in agreement with the results from macroscopic experiments.

The band structure and FS of LuRh\textsubscript{2}Si\textsubscript{2} and YbRh\textsubscript{2}Si\textsubscript{2} are compared. The absence of very flat bands in the Lu compound provides confirmation for the $4f$ nature of these bands in the Yb compound. Both compounds show very similar Fermi-surface features. At the center of the BZ, we cut a tip-like sheet which is part of the jungle-gym FS $\mathcal{J}$. The same sheet is visible with high intensity embracing the X point of the BZ. Additionally, at 21.2 eV, we observe a large surface centered at the $Z$ point of the BZ in the form of a donut. There is no clear difference between the FS of both materials observed, neither theoretically nor experimentally. This indicates that the spectral weight of the $4f$ bands do not contribute significantly in forming the FS at 14 K.

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