An Electronic Structure Study: The Case of YbRh$_2$Si$_2$

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The electronic properties of YbRh$_2$Si$_2$ are studied by detailed band structure calculations in a relativistic framework including correlation corrections and magnetization of the Yb ion, and angle-resolved photoemission experiments. The calculated band structure manifests a 4$f^{13}$ spin-polarized configuration leaving the unoccupied state at 1.4 eV above the Fermi energy. At the band theory level, the 4$f$ bands are located far below the Fermi level and the anisotropic Coulomb interaction within the 4$f$ shell spreads the multilevel into broader 4$f$ complexes below -2.5 eV. The first photoemission spectra obtained on YbRh$_2$Si$_2$ show a clear f-multilevel splitting into $j = 7/2$ and 5/2 excitations. An analysis according to Anderson’s simple impurity model, explains the photoemission spectra in accordance with the results of the band structure calculations and various macroscopic experiments. The Kondo coupling to the valence bands shifts the spectral weight of the 4$f_{7/2}$-level close to the Fermi energy opening visible hybridization gaps. The recently suggested mixed-valency of YbRh$_2$Si$_2$ is opposed from both theoretical and experimental viewpoints. We discuss our findings with respect to two rivaling theories for quantum criticality, i.e. spin-density-waves versus composite quasiparticles.

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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 [1] because of their anomalous low-temperature thermodynamic, transport and magnetic properties that deviate strongly from Landau Fermi Liquid (LFL) theory. Recently, an increasing number of examples of Ce and U based systems such as CeCu$_2$Au$_2$, CePd$_2$Si$_2$, CeRh$_3$ and U$_2$Pt$_2$In have been found to exhibit magnetic quantum criticality by either doping- or pressure-tuning.[2–5] YbRh$_2$Si$_2$ has attracted attention as the first observed Yb-based and stoichiometric HF system with competing Kondo and Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, the dominant exchange mechanisms in metals where the moments interact through the intermediary conduction electrons [6]. Pronounced non-Fermi Liquid (NFL) behavior has been observed in the resistivity $\rho(T)$ and the electronic specific heat $\Delta C(T)$ at low temperatures showing $\Delta \rho = \rho - \rho_0 \propto T$ and $\Delta C/T \propto -\ln(T)$, respectively.[7, 8] The ground state properties of YbRh$_2$Si$_2$ can be easily tuned around the magnetic quantum critical point (QCP) by control parameters such as pressure, magnetic field or doping.[1] 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.[7, 9] On the other hand, expanding the lattice by replacing Si by Ge [10] 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 (ESR) and nuclear magnetic resonance (NMR) experiments have demonstrated the importance of magnetic fluctuations at low $T$.[11, 12] A Hall effect measurement suggests a discontinuity in the FS volume of 1 charge carrier across the quantum phase transition.[13] Based on a local density approximation (LDA) calculation, the change in the FS volume by 1 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.[14] At intermediate temperatures, a regime establishes itself where the quantum critical fluctuations dominate, and for which it is believed that the notion of a well defined quasiparticle breaks down. Remarkably, in YbRh$_2$Si$_2$ this regime extends up to 10 K.[8]

We distinguish various theories about antiferromagnetic metallic Kondo lattices. In the weak coupling limit, the magnetism is viewed as a spin-density wave (SDW) instability that develops out of the parent heavy Fermi-liquid state and a small magnetic moment is observed. Using Gaussian critical fluctuations, Hertz,[15] and in a refined version Millis,[16] have given the first phase diagrams for the weak-coupling limit. The internal structure of the quasiparticle is unimportant and the interaction between the Fermi surface (FS) and the critical antiferromagnetic spin fluctuation dominate at low temperatures. Indeed, in YbRh$_2$Si$_2$, a very weak antiferromagnetic (AFM) order with a tiny magnetic moment of $\mu_{\text{Yb}} \approx 10^{-2} - 10^{-3}\mu_B$ [11] is observed at ambient pressure below the Néel temperature $T_N \approx 70$ mK. This initially favored the idea that YbRh$_2$Si$_2$ belongs to the class of SDW metals close to the magnetic QCP, but severe conflicts with several experiments raise doubts. In the strong-coupling limit, the localized f-states, giving rise to a large high-temperature magnetic moment, cou-
ple through the Kondo effect to itinerant states. This induces a Fermi surface of heavy composite quasiparticles. Recently, a detailed phase diagram for heavy fermions in this strong-coupling limit was given by Senthil and collaborators.[17, 18] The ground state at the QCP is described by an exotic phase where the heavy quasiparticles decay into a magnetic (neutral spinon) and an electronic (spinless fermion) excitation. This effect is called the fractionalization of the FS, i.e. the fragmentation of the FS into a ‘cold’ and a ‘hot’ sheet.[17, 19] The latter consists of heavy quasiparticles derived from electronic states with $f$-symmetry. More recently, Si and coworkers introduced a local quantum critical point (LQC), named so because long wavelength and spatially local critical modes coexist at this point.[20, 21] Again, for material close to LQC points, a large magnetic moment at high temperatures is allowed which is then progressively screens by the Kondo effect at low temperatures. In either the SDW or the LQC case, the $f$-electrons are expected to be partly integrated into a large Fermi surface (FS), however for the latter the quasiparticle residue $Z$ vanishes at the QCP and hence no Kondo resonance is expected to appear in the photoemission (PE) spectrum.[21]

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.[22]

In this article, we report state-of-the-art band structure calculations and the first ARPES experiments for YbRh$_2$Si$_2$ in the ordinary high-temperature FL state where the quasiparticles are expected to be well defined. We perform an analysis of the 4$f$-derived spectrum $ρ_ν(ε)$ within the single-impurity Anderson model (SIAM).[23] This analysis explains $ρ_ν(ε)$ using the results from the band structure calculation in agreement with the results from macroscopic experiments. The hybridization of the electronic $f$-levels with the valence bands shifts the spectral weight close to $E_F$ and opens electronic gaps of 91 and 45 meV, respectively. This combined theoretical-experimental project focuses on the electronic 4$f$-excitations, their positions and degeneracies and especially their interactions with the valence bands. A satisfactory agreement between the ARPES spectra and the band structure calculation was obtained.

II. ELECTRONIC STRUCTURE CALCULATIONS

A. Structure

The crystal structure of YbRh$_2$Si$_2$, displayed in Fig. 1, is bct with $I4/mmm$ space group (No. 139). The Yb ion occupies the $2a$ site which has full tetragonal $I4/mmm$ 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 4$e$ site (4$mm$): the Si-Si interatomic distances 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 ($a, a, δ$)]: Yb (0,0,0), Rh (0, $1/2$, $1/2$), Si (0,0,0.375); note that the Si height is not determined by symmetry and is accidentally equal to $\frac{1}{3}$. The experimental lattice constants $a = 4.010$ Å and $c = 9.841$ Å have been used in our calculations.

B. Methods

Rare earth atoms, and other atoms with strong effective intraatomic 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. For interpreting single-particle-like excitations, which is the main topic of this paper, one wants to obtain the $j = ℓ ± \frac{1}{2}$ character of the excitations (which is evident in spectra). 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 an $4f^{13}$ configuration (at elevated temperature, at least), corresponding to $S = \frac{1}{2}$, $L = 3$, $J = \frac{7}{2}$ in the absence of crystal fields.

To be able to include the necessary combination of exchange splitting (magnetic order), SOC, and also the LDA+U approach that is necessary for rare earth atoms, we used the Wien2k electronic structure code.[24] With magnetization along (001) direction, spin-orbit coupling reduces the symmetry to $\text{Abm}_2$ (#39). The around-mean-field version of LDA+U was used, with $U = 8$ eV, $J = 1$ eV. In the results presented below, the $m=0$ 4$f$ orbital was unoccupied. We have also obtained a solution with the $m=-2$ orbitals 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 4$f$ bands. We use a k mesh of $20^3$ (641 k-points in the IBZ), $R K_{\text{max}} = 9$, and the Perdew-Burke-Ernzerhof generalized gradient approximation[25] for exchange correlation potential. An energy range from -7 Ry to 7 Ry is used when SOC is incorporated.

C. Band Structure Results

The band structure 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 $4f_{5/2}$ complex and a $4f_{7/2}$ complex separated by the spin-orbit splitting of roughly 1.3 eV. Although each $4f$ band is quite flat, each of these complexes of $2j+1$ bands ($j = \frac{5}{2}, \frac{7}{2}$) is split somewhat due to the anisotropy of the Coulomb interaction[26] within the $4f$ shell, which is included fully in the LDA+U method. However, the $4f$ electrons are polarized (one hole, $S = \frac{1}{2}$) so there is also an exchange splitting which complicates the identification in the figure of the $4f_{5/2}$ and $4f_{7/2}$ states separately. However, the result that is pertinent to this paper is that this electronic structure calculation fully includes magnetic and relativistic effects, and 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. 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. 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 4$d$ and total Yb 5$d$ character are shown separately in the fatband representations in Fig. 2. Much of the Rh 4$d$ bands is occupied, while most of the Yb 5$d$ bands are unoccupied, however there is Yb 5$d$ character
around and 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 $a_g (d_{3z^2-r^2}), b_{1g} (d_{x^2-y^2}), b_{2g} (d_{xy})$ or $e_g (d_{xz}, d_{yz})$ of the Rh and Yb 4d states.

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

From the bands in Fig. 2 it can be observed that a hole-type surface nearly closes at the $X=(\pi/2,0,0)$ 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 $\mathcal{J}$. The largest part of this surface encircles nearly all of the upper zone face centered on the $Z=(0,0,\pi)$ point. The character near X is Rh 4$d_{xz}, 4d_{yz}$, and some Yb 5d character. There is also strong Rh 4$d_{xz}, 4d_{yz}$ character in the flat band along Γ − Z near -3 eV. Rh 4$d_{xy}$ character dominates the flat band 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 $\mathcal{D}$ 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 $\mathcal{D}$ surface contains electrons.

D. Aspects of Kondo Coupling

$\text{YbRh}_2\text{Si}_2$ is a heavy fermion compound, whose $J = L + S = \frac{3}{2}$ 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 $\text{YbRh}_2\text{Si}_2$). Thus, while our ferromagnetic state with $S = \frac{3}{2}$ is not expected to describe the interacting ground state, it has the virtue of providing 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 spheroid 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 wavefunctions on the different past of the surface. For points on the $\mathcal{J}$ surface near the $X$ point, the exchange splitting is 20 meV at both $(0.95,0,0)$ and $(1.0,2.0,0)$. Thus the Kondo coupling, and likewise the carrier scattering by the moments, differs by at least a factor of five 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 those of Norman,[14] who presented unpolarized relativistic LDA predictions. Not surprisingly there are substantial differences, as expected from Norman’s 4$f^{14}$ configuration versus our magnetic 4$f^{15}$ 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. As a result, the flat Rh 4$d_{x^2-y^2}$ 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 different predictions for the Hall coefficient.

On the qualitative level, our Fermi surfaces include large sheets with cancelling 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. Discussion of the Hall tensor will be deferred to a future publication. No doubt it will be quite anisotropic, given the strong tetragonal symmetry of the FSs. The edges of the pillbox $P$ may give large contributions.
FIG. 4: The three calculated Fermi surfaces of YbRh$_2$Si$_2$ with 4$f^{13}$ configuration, pictured within the crystallographic Brillouin zone. Top panel: fluted donut $D$ surface centered around the upper zone face midpoint $Z$. Middle panel: multiply-connected jungle gym $J$ surface. Bottom panel: tall pillbox surface $P$, containing electrons at the zone center $\Gamma$.

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 subsection, this coupling varies strongly over the Fermi surface. Hence this system is an example of a multiband (correlated) metal with large Fermi surfaces of varying curvature, having anisotropic scattering. Its Hall tensor, versus temperature, field, and magnetic ordering, promises to be very challenging to understand.

III. EXPERIMENTS

Single crystalline platelets of 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 Stanford Synchrotron Radiation Laboratory (SSRL) and a second vacuum system equipped with a Scienta SES2002 analyzer and a microwave driven monochromatized He-discharge lamp (Gammatdata VUV5000). At SSRL, we used linearly polarized photons of 21.4 eV. We intentionally refrained from tuning the photon energy to resonance with Yb-core levels which enhances the photoelectron yield of the Yb 4f-electrons but worsens the energy resolution by approximately 6-8 times. An energy resolution of $\sim$ 40 meV or more hides the relevant hybridization features 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, and 22 meV for the 21.4 eV beam, respectively. The chamber pressure was below 4·$10^{-11}$ torr. The samples were cleaved in situ at $T \sim 14$ K. 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

Fig. 5 shows the angle-integrated spectrum (red curve) for angles between -5$^\circ$ and 17$^\circ$ measured with He-II radiation. The broad distribution of intensity between -11 and -7.5 eV, indicated by the shaded area in Fig. 5, is due to the Si 3s bands, as suggested 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 plot for $h\nu = 21.2$ eV does not display any pronounced intensity at these energies. Hence, these are the bulk 4$f^{14}$ to 4$f^{13}$ transitions, separated by 1.3 eV as suggested by the band structure calculation (see section IV C). The very intense flat bands at 650 meV and at 2 eV can be attributed to the spin-orbit split surface bands [27] originating from Yb-ions at or close to the sample surface. (The relative intensity of surface vs. bulk peak decreases strongly when the photon energy is increased from 21 to 41 eV.)
and considering Refs. [22, 28, 32]). The intensity around 3 eV is not due to flat bands but is a result of various co-terminating band edges having high intensities in that energy region (see therefore the angle-resolved spectrum in Fig. 6). In the angle-resolved spectrum (not shown here), we observe a very flat band also at ~5 eV. Little dispersion is observed in the angle-resolved photoemission spectrum which makes us believe that this peak at ~5 eV can be attributed to the bonding Rh $4d_{x^2-y^2}$ orbitals. The photoemission process from $4f^{13}$ to $4f^{12}$ cannot clearly be identified at these low photon energies. For example, the peaks at $\sim$ 10 and 12 eV are two or more of the $4f$-intensities as calculated by Gerken [29] and observed in numerous previous experiments [27, 30, 32]. However, this paper focuses on the excitations close to the Fermi energy.

B. Photoemission spectra for $h\nu = 21.4$ and 21.2 eV

Within the sudden approximation [22] angle-resolved photoemission measures the single-particle spectral function $A(\overrightarrow{k}, \omega)$. In the Landau theory of Fermi liquids, the spectral function is determined by the bare band structure $\epsilon_k$ and the complex self energy $\Sigma = \Sigma' + i \Sigma''$ as:

$$A(\overrightarrow{k}, \omega) = \frac{1}{\pi} \frac{\Sigma''(\overrightarrow{k}, \omega)}{[\omega - \epsilon_k - \Sigma'(\overrightarrow{k}, \omega)]^2 + [\Sigma''(\overrightarrow{k}, \omega)]^2}$$ (1)

The upper panel of Fig. 6 shows an angle-resolved photoemission spectrum $A(\overrightarrow{k}, \omega)$ in the $\Gamma-X-Z$-plane, where $\overrightarrow{k}$ is the angular momentum in plane and $\omega$ the photohole energy, taken at a beam energy $h\nu = 21.4$ eV. In order to connect to the calculations, we use $\omega$, $\epsilon$ and $E-E_F$ on an equal basis in the following discussions. $\Gamma$ denotes the center (equivalent to $\Gamma$), the thin white line indicates the $X$-point. The distance $\Gamma X$ is equivalent to $\Gamma X$ in the center of the Brillouin zone (BZ). Comparing the
EDC and the FS images to the results of the band structure calculations we conclude that \( \tilde{\Gamma} \) lies approximately at 2/3 of the distance between \( \Gamma \) and \( Z \). Two different flat bands display a pronounced intensity, band \( (f_{b1}) \) located very close to \( E_F \), and band \( (f_{s1}) \) with a maximum intensity at \( \approx 680 \) meV below \( E_F \). The latter derives from electronic states of Yb atoms close to the sample surface (see subsection IV A). Previous spectroscopic experiments \[33\] and fully relativistic calculations (see Fig. 2) revealed that the spin-orbit interaction in Yb-based materials is considerable. The \( 4f \) bands (1) with band width less than 35 meV hybridizes weakly with the \( 4d \) band leading to a dispersion of \( \approx 10 \) meV. A gap between the peaks of the two bands of approximately 80 meV is observed. For \( \omega \lesssim 20 \) meV, \( (f_{d1}, \omega) \) rises again towards lower binding energies indicating a double peak structure. A comparison to the band structure calculations suggests that this additional feature originates from the Rh \( 4d_{x^2-y^2} \) band crossing \( E_F \) at \( \tilde{\Gamma} \) and hybridizing weakly with the \( 4f \) band. This effect shifts the spectral weight from the band closer to \( E_F \) and flattens it, so nearly no dispersion is observed. 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 \( \tilde{\Gamma} \). In analogy, the spectra for LuRh\(_2\)Si\(_2\) shows a similar double peak structure between two dispersing Rh-bands, although the bands are slightly more separated and disperse oppositely more clearly.\[28\]

Furthermore, as we change the energy, the intensity at \( E_F \) remains almost unchanged (not shown here), characteristic for a band without dispersion in the \( k_z \)-direction. Although the LDA+U+SOC calculation suggests that the anisotropic Coulomb interaction has a substantial influence on the \( 4f \)-multilevel resulting in a clustering of \( 4f \) bands, we only observe two bulk bands centered at \( -1.3 \) eV and at \( -0.045 \) eV. Hence, in the future, we will neglect, for reasons of simplicity, the CEF effects and assume sharp and well defined \( f \)-excitations at energies \( \epsilon_f \) and \( \Delta \epsilon_f \), respectively.

Panels (C) and (D) of Fig. 7 show a photoemission spectrum \( A(k, \omega) \) along the yellow line in Fig. 8. The top-left panel shows the raw data, the bottom left is the corresponding EDC analysis. The red circles are obtained by fitting a single peak and a constant background to the EDC curves and the red line is the Fermi level. A steep band (band \( (P_2) \) in Fig. 6) with strong \( Rh \)-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 \( f \)-spectral weight into the FS.

These spectroscopic data yield the characteristic band structure of Yb-based material exhibiting a Kondo resonance below \( E_F \).\[31,32\] In theory, increasing the temperature far above the Kondo temperature \( T_K \) induces a significant temperature dependence on the peak position and height and finally removes the peak.\[33\] In YbRh\(_2\)Si\(_2\), the peak at \( \tilde{\Gamma} \) however is removed due to the thermal broadening of the Fermi edge. No other temperature dependence of the peak position could be detected within the experimental resolution. Moreover, moving from \( \tilde{\Gamma} \) to \( X \) in reciprocal lattice, the spectrum does not follow the predictions for a Kondo resonance.

C. The analysis according the single-impurity model

Hybridization of electronic \( f \)-bands with a conduction band leads to peaks in the photoemission spectrum far off
the energy of the $f$-levels ($\epsilon_f$) [31, 32, 34]. The double-
peak structure near $\Gamma$ also needs clarification with respect
to Kondo resonance vs. an additional band, i.e. the Rh
$4d_{x^2-y^2}$ band. Hence, a more elaborate data analysis is
required. We employ a second-order perturbative cal-
culation based on the Anderson single-impurity model.
As mentioned in the previous section, we observe in the
photoemission spectrum that the bulk $4f$-multiplet splits
into $4f_{7/2}$- and $4f_{5/2}$-excitations separated by 1.3 eV.
The additional splitting due to an anisotropic Coulomb
interaction is not observed. In the following, the simula-
tion will be referred to as the Gunnarsson-Schönhammer
(GS) scheme. [31] For the Yb-4f shell we use the Ansatz
for the ground state

$$\Phi_0^{(1)} = A \left[ |0\rangle + \int a(E)|E\rangle dE \right]$$

(2)

where

$$|0\rangle = \prod_{\nu=1}^{14} \Psi_{\nu}^{\dagger} \prod_{\epsilon<\epsilon_F} \Psi_{\nu}\langle \text{core} |$$

$$|E\rangle = \frac{1}{\sqrt{N_f}} \sum_{\nu=1}^{N_f} \Psi_{\nu}\Psi_{E\nu}^{\dagger}|0\rangle$$

(3)

are the $4f^{14}$ and the $4f^{13}$ ions, respectively, and $\Psi_{E\nu}\langle \text{core}$
creates an electron in an unoccupied state. $N_f$ is the
degeneracy of states. Considering the large degeneracy,
we calculated the energy-difference upon hybridization
between the $4f^{14}$ ion and the hybridized state $\Delta E$ in first
order, and obtained the same result as GS obtained for
Ce-materials. The photoemission process $T$ of relevance
reduces the $4f$-shell by one electron, i.e.

$$T\Phi_0^{(1)} = \sum_{\nu} \omega_\nu \Psi_{E\nu}^{\dagger} \Psi_{\nu}\Phi_0^{(1)}$$

(4)

Contrary to previous postulations, there is no need for
a mixed valency to observe the two sharp peaks at $E_F$
and -1.3 eV. In a hole language, this process adds a hole
a mixed valency to observe the two sharp peaks at

The subtraction is rather tedious and a perfect agree-
ment with the calculation cannot be expected. The fea-
tures of interest are two strong intensity regions, one
centered at -1.35 eV and one close to $E_F$. The feature at
higher binding energy is slightly asymmetric, and some
additional intensity around -1.1 eV could not be removed
properly. The intensity maximum in $\rho_0(\epsilon)$ in the vicin-
ity of $E_F$ originates from the $4f_{7/2}$ hole final state and is
about 25% higher than the $4f_{5/2}$ peak. The emission from
the $4f_{7/2}$ surface state at 680 meV is approximated
by a Lorentzian with line width $\sim 230$ meV (see black
dashed line). The result is shown as a red solid line in
the lower left panel of Fig. 7. The energy difference
between the $4f^{14}$ and the hybridized state close to the
$4f^{13}$-configuration is $\Delta E \sim -4.9$ eV. From the simulation
we can extract in first-order two hybridization strengths
and 2 splittings separately. The gap for the interaction
with parabola ($P_1$) yields $\Delta_1 \sim 91$ meV comparable with
the experimental gap of $\approx 80$ meV observed in panel (A)
of Fig. 7. The interaction with parabola ($P_2$) yields $\Delta_2$
$\approx 45$ meV. This is the gap observed in the right panels
of Fig. 7. The simulation yields a hole concentration of
0.98 in the $4f^{14}$ shell, i.e. yielding a valence of $+2.98$, i.e.
close to +3. The asymmetry of the peak at 50 meV can
be explained by the arguments of Doniach and Sunjic.

[36]

Haldane and Jefferson showed that using the “poor-
man’s scaling” technique, a single dimensionless energy
scale is needed,[43] which for YbRh$_2$Si$_2$ leads to

$$\epsilon_f^{\ast} = \frac{\epsilon_f}{N_f\Delta} \approx -5.6 eV$$

(5)

A very important temperature scale in a material with
unfilled $f$-shells is given by the Kondo temperature $T_K$.
We calculated the Kondo energy self-consistently using the
expression in the GS-scheme to be $T_K = \delta/k_B \approx
(23\pm 3) K$, where $k_B$ is the Boltzmann constant. This
Kondo temperature is in excellent agreement with the re-
results from macroscopic experiments which yielded $T_K \approx
24 K$ [7, 8], considering the fact we used a simple second-
order perturbative analysis of the experimental data.
Employing the dynamical theory of the degenerate Anderson model derived at zero temperature by Kuramoto and Müller-Hartmann, \cite{Kuramoto} or in a more approximate form by Newns and Hewson \cite{Newns} yields the zero-temperature susceptibility

\[
\chi_0(T=0\text{K}) = \frac{1}{3} \frac{\pi^2 \hbar^2 \mu_0 N_A}{2 j_1 + 1} \left( 1 + \frac{n_f^2}{n_f^2 - 1} \right) \approx 1.4 \cdot 10^{-5} \text{mole/m}^3 ,
\]

(6)

comparable to the result of \( \sim 1.1 \cdot 10^{-5} \text{mole/m}^3 \). Thus the Kondo coupling leaves a small moment which orders below 70 mK.\cite{Kuramoto} Additionally, we calculate the magnetic relaxation rate of the 4f electrons

\[
\Gamma_M = \lim_{\omega \to 0} \frac{\text{Im} \chi(\omega)}{\omega} \approx \frac{|N_f e^2|}{\pi n_f} \approx 10.8 s^{-1} .
\]

(8)

This value again is in very good agreement with the previously obtained results from ESR/NMR experiments on YbRh\(_2\)Si\(_2\) at temperatures above 10 K, \cite{Kuramoto,Kuramoto} or for various other Yb-based materials, such as YbCu\(_2\), YbAl\(_2\) \cite{Kuramoto} in the regime where no field-dependence is observed.

We note a remarkable agreement of the parameters obtained using the GS simulation with those from macroscopic experiments. Hence, we confirm that SIAM is a simple but rather accurate tool for a quantification of the photoemission spectra in Yb-based materials \cite{Kuramoto,Kuramoto,Kuramoto} as we are limited to temperatures above the critical behavior. We notice that without the detailed knowledge of the band structure, finding a reasonable agreement between the SIAM calculations and the observed PE spectrum was nearly impossible. A description according the periodic Anderson model (PAM) using an angle-dependent matrix \( V(\mathbf{k}, \mathbf{k}') \) was recently very successful in explaining a photoemission spectrum in YbIr\(_2\)Si\(_2\)\cite{Kuramoto}. The major complications concerning the macroscopic quantities such as resistivity and specific heat in YbRh\(_2\)Si\(_2\) at low temperatures however raises a severe doubt on obtaining more information by employing the periodic model. In the same line of thinking, we have been checking for a temperature dependence of the two peaks in \( A(\mathbf{k}, \omega) \) near \( E_F \) and found no resemblance to a hump feature within the Kondo theory. The GS analysis suggests that the band structure is in good agreement with the experimental data, even though at first sight it seems anything but alike. The Kondo coupling shifts the spectral weight of the \( 4f_{7/2} \) quasiparticles close to \( E_F \). The second peak at \( \Gamma \) in the top panel of Fig. 7 arises indeed from the photoholes belonging to emissions out of the Rh-4\(d_{x^2−y^2}\) band which is a stable component of this and other band structure calculations performed in this group.

We address the recent claim of YbRh\(_2\)Si\(_2\) being a mixed valent. If a d-band overlaps the \( f \)-configuration 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\(^{3+}\) with electronic \( 4f^{13} \) configuration or Yb\(^{2+}\) with \( 4f^{14} \) configuration. The panels (C) and (D) in Fig. 7 however display that the hybridization energy is smaller than the distance to the Fermi level, i.e. 50 meV, and hence no mixed valency occurs.

\[ \text{D. Fermi Surface at 21.2 eV} \]

Fig. 8 shows a cut through the FS of YbRh\(_2\)Si\(_2\) 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 urged by the shift of the spectral intensity of the \( 4f_{7/2} \) excitations by the Kondo interaction. In accordance with the FS from the LDA+U+SOC calculation, the FS splits into three different sheets. At \( \Gamma \), there is a small pocket-like area \( P \) with a high intensity, which we interpreted as the Rh-4\(d_{x^2−y^2}\) FS sheet. At the boundary of the BZ a very distinct FS sheet \( J \) of the form of a butterfly shows a strong inten-
single particle picture, the calculation demonstrates that and a multiply-connected jungle gym surface situated around the upper zone face midpoint through the FS displaying Rh-4m of 4 unoccupied at 1.4 eV above least qualitatively, and probably even quantitatively, correlate.

calculation and the photoemission experiment shows that this FS obtained in the LDA+U+SOC calculation is at least qualitatively, and probably even quantitatively, correct.

V. CONCLUSIONS

In this article we have presented the results of an electronic band structure calculation within a relativistic framework including correlation corrections. Characteristic of the electronic structure is the 4f\textsuperscript{13} ground state as observed in the experiments with the m = 0 state unoccupied at 1.4 eV above E\textsubscript{F}. A small FS cylinder of 4d\textsubscript{z^2-r^2}-symmetry is centered at Γ, a fluted donut D surface situated around the upper zone face midpoint Z and a multiply-connected jungle gym J surface. In the single particle picture, the calculation demonstrates that the 4f-multiplet spreads out into 4f complexes below -3.4 eV. On the other hand, the angle-resolved photoemission spectrum A(\vec{k},\omega) manifests (true many-body) intensities originating from 4f\textsuperscript{13}_{7/2} and 4f\textsuperscript{13}_{5/2} states separated by 1.3 eV, the value for the spin-orbit interaction obtained from the calculation. This discrepancy between the band structure calculation and the photoemission experiment can be understood in the simple words: in the photoemission process, the photon hits an electron out of the 4f\textsuperscript{14} shell. The spectrum now indicates that the surrounding electrons do not have enough time to redistribute properly in order to demonstrate the effects from the anisotropic Coulomb interaction and the exchange hole polarization. Hence, we observe only the two spin-orbit split states, and not the bands as relevant in the Yb-4f\textsuperscript{13} configuration.

Nevertheless, it is quite remarkable that an analysis of the 4f-spectrum \rho_\omega(\epsilon) according the degenerate Anderson impurity model using the parameters obtained from the band structure calculations explains the shift of the center of the 4f\textsubscript{7/2} spectral weight to 45 meV below E\textsubscript{F}. The Kondo splittings obtained from the band structure calculations can be compared to the values from the GS calculation. The GS calculation yields a splitting at Γ of V(\epsilon_F) ≈ 28 mev and at the BZ boundaries of ≈ 14 meV. These values agree nicely with those obtained from the LDA+U+SOC calculation. The estimated electronic gaps reproduce quantitatively the observed ones and indicate that the spectral weight of the f-bands is not taking part in actively forming the FS. Hence, YbRh\textsubscript{2}Si\textsubscript{2} is not mixed-valent. The Kondo temperature T\textsubscript{K} ~ 23 K, the valency ~ +2.98, the zero-temperature magnetic susceptibility \chi_0 ~ 1.45\times10^{-5} mole/m^3 and the nuclear magnetic relaxation rate Σ ~ 10.8 s\textsuperscript{-1} are in excellent agreement with the results from macroscopic experiments. We also concluded that the tiny Fermi surface at the zone center reflects the Rh-4d\textsubscript{z^2-r^2} band crossing the Fermi level in accord with our band structure calculations. A FS map taken at 21.2 eV shows three sheets, the Rh 4d\textsubscript{z^2-r^2} cylinder near Γ, a portion with high intensity embracing the X-point of the BZ and a large surface centered at the Z-point of the BZ.

The GS simulation indicates there is significant spectral weight close to the Fermi level. We propose that the resistivity at low temperatures is dominated by the conduction of the electrons and holes in an ordinary way. The main scattering is due of spin-fluctuations having a continuum of low excitation energies as no indication for a preferred mode is seen in the spectrum for the light holes (l\textsubscript{1}) and (l\textsubscript{2}) within experimental resolution. This scattering mechanism displays a resistivity depending linearly on the temperature.

Previous ESR and especially the Hall effect experiments rejected the theory of a SDW instability for the QCP in YbRh\textsubscript{2}Si\textsubscript{2}. Despite having these strong Si-bonds, which induce an easy-cleavage plane, and the observation of relatively sharp electronic bands, the electronic structure has to be considered highly three-dimensional, as can be seen from the results of the electronic band-structure calculation and a strong energy-dependence in A(\vec{k},\omega), i.e. no net reduction in dimensionality is ob-
served. The 4$f$-bands are not participating in actively forming the FS. These observations conflict with the SDW theory. In this coupling regime, according to Senthil et al.,[17] the Fermi liquid phase of a material in the vicinity of the crossover from the RKKY-dominated to the Kondo-regime, form a "cold" and a "hot" FS sheet. The latter consists of the heavy quasiparticles and is considered to be large. The FS centered at $\Gamma$ is a small electronic pocket and hence can be disregarded. Accordingly, the portion $D$ is the prime candidate for the "cold" FS. The FS sheet $J$ would be the "hot" FS which is supposed to transform into a spin fluid with a FS of neutral spinons.[17] This experimental study clearly favors a three-dimensional approach to the theory of the quantum criticality in YbRh$_2$Si$_2$. It is at present not clear to the authors how the obvious electronic three-dimensionality can be reconciled with (quasi-)two-dimensional quantum critical fluctuations.

VI. ACKNOWLEDGEMENT

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[28] We intend to publish a complete discussion on the band structure and the Fermi surface of YbRh$_2$Si$_2$, including results for LuRh$_2$Si$_2$ and LaRh$_2$Si$_2$.