We studied the electronic structure of the heavy fermion compound YbRu$_2$Ge$_2$ with $x = 0$ and nominally $x = 0.125$ using ARPES and LDA calculations. We find a valence band structure of Yb corresponding to a non-integer valence close to 3+. The three observed crystal electric field levels with a splitting of 32 and 75 meV confirm the suggested configuration with a quasi-quartet ground state. The experimentally determined band structure of the conduction electrons with predominantly Ru $4d$ character is well reproduced by our calculations. YbRu$_2$Ge$_2$ undergoes a non-magnetic phase transition into a ferroquadrupolar ordered state below 10.2 K and then to an antiferromagnetically ordered state below 6.5 K. A small hole Fermi surface shows nesting features in our calculated band structure and its size determined by ARPES is close to the magnetic ordering wave vector found in neutron scattering. The transitions are suppressed when YbRu$_2$Ge$_2$ is doped with 12.5% Rh. The electron doping leads to a shift of the band structure and successive Lifshitz transitions.

I. INTRODUCTION

Heavy-fermion systems are an ideal playground to study quantum critical phenomena$^1$. Multipole ordering is an exotic symmetry breaking$^2$ that offers the possibility of interesting types of quantum criticality$^{3,4}$. A prominent example for multipole ordering is CeB$_6$ with an antiferroquadrupole ordering.$^{5,6}$ It has a cubic symmetry with a quartet crystal electric field (CEF) ground state. Another example is the series of Pr$_2$T$_2$X$_{20}$, which contains a number of compounds with quadrupolar order.$^{7-9}$ Here, the CEF from the cubic lattice results in a non-magnetic ground state of the Pr 4$f^2$ which has a nonzero matrix elements for quadrupoles.

Of the various types of multipolar order, ferroquadrupole (FQ) order is particularly interesting in light of recent results on nematicity in the iron-based high-temperature superconductors (FeSC).$^{10}$ Both ordering phenomena break rotational but not translational symmetry. While nematicity in the FeSC is driven by an instability of the itinerant Fe 3d electrons, FQ order in heavy fermion systems involves local 4f electrons. The coupling of orbital, spin and lattice degrees of freedom was explored extensively in the FeSC using for example strain as a tuning parameter for the nematic order.$^{11,12}$ However, the underlying physics of the nematicity in FeSC is complex with several other intertwined orders. In contrast, the driving force behind FQ order of local 4f orbitals is well understood$^2$. Consequently, materials that undergo a FQ phase transition can serve as model systems to study the effects of nematic fluctuations on conduction electrons, motivating detailed study of their electronic properties.

Here we investigate YbRu$_2$Ge$_2$, which presents a recent example of FQ order. It shows weak Kondo lattice behavior with a Sommerfeld coefficient of $\gamma = 100 \text{mJ/K}^2$.$^{14}$ The crystal electric field (CEF) of the tetragonal crystal structure splits the Yb 4f levels into four Kramers doublets. However, the ground state is a quasi-quartet with a splitting of less than 1 meV.$^{14-16}$ Neutron scattering determined the splitting to the third CEF level to be 32 meV.$^{17}$ The splitting to the fourth level was estimated to be 91 meV.$^{15}$ Three phase transitions were observed at $T_0 = 10.2 \text{K}$, $T_1 = 6.5 \text{K}$ and $T_2 = 5.7 \text{K}$.$^{14}$ $T_1$ could be ascribed to an antiferromagnetic ordering with an incommensurate wave vector of $q = (0.352, 0, 0)$.$^{14,17}$ A slight change of the propagation vector appears at $T_2$.$^{17}$ No signatures of magnetic order were found at $T_0$ in neutron scattering or muon-spin resonance and a theoretical analysis based on the quasi-quartet ground state suggested a FQ order.$^{14,18}$ Recent low-temperature x-ray scattering experiments confirm the presence of a tetragonal to orthorhombic phase transition at $T_0$.$^{16}$ Measurements of the quadrupole strain susceptibility reveal a Curie behavior demonstrating that the FQ order is primarily driven by magneto-elastic coupling.$^{16}$

We performed angle-resolved photoelectron spectroscopy (ARPES) and LDA band structure calculations to shed light on the electronic structure of YbRu$_2$Ge$_2$. We study both the 4f and the conduction electron system. Our results confirm the weak heavy fermion behavior with a non-integer Yb valence close to 3+. Three CEF levels can be identified with a splitting of 32(6) meV and 75(6) meV. The Ru 4d conduction bands hybridize with the local 4f levels. The 4d-electron band structure
is well reproduced by our calculations and we find a small Fermi surface that contains favorable nesting properties with a nesting vector close to the magnetic ordering vector. Doping YbRu$_2$Ge$_2$ with Rh suppresses the magnetic and quadrupole order and we detect three phase transition between 2 K and 3 K at nominally 12.5% doping. We observe a shift in the band structure due to the electron doping which results in two Lifshitz transitions: one very close to and one well below 12.5% Rh doping.

II. EXPERIMENTAL METHODS

High quality single crystals of YbRu$_2$Ge$_2$ and Yb(Ru$_{0.875}$Rh$_{0.125}$)$_2$Ge$_2$ were grown in indium flux as described in Ref. 16. The residual resistivity ratio is 10 for the parent compound$^{16}$. We characterized the phase transitions with specific heat measurements using a relaxation technique performed in a PPMS from Quantum Design. The ARPES measurements were performed at the SSRRL beamlines 5-2 and 5-4 with an energy resolution of 9–25 meV depending on the beamline and photon energy used. The angular resolution is 0.1°. The base pressure stayed below 4·10$^{-11}$ torr. We use linear horizontal (LH) and linear vertical (LV) light polarization to highlight different parts of the band structure. The samples were cleaved in-situ below 30 K.

III. RESULTS AND DISCUSSION

A. 4f Electronic Structure from Photoemission Spectroscopy

First, we study the valence band structure of the Yb 4f electrons. We use a photon energy of 125 eV. It is close to the Cooper minimum of the Ru 4d and Yb 5d states$^{20}$ and therefore suppresses their contribution to the spectral weight. At the same time the photoionization cross-section for Yb 4f states is enhanced at this photon energy. Figure 1(a) presents the photoemission spectrum at 125 eV.

Photoemission of an electron from the 4$^{n}$ configuration leads to a final state configuration 4$^{n-1}$, which is characterized by atomic-like multiplets. Yb has a non-integer valence in heavy-fermion systems. Therefore, both Yb$^{3+}$ (4$^{13}$ → 4$^{12}$) and Yb$^{2+}$ (4$^{14}$ → 4$^{13}$) contribute to the photoemission spectrum. Since the valence is very close to 3+ and the ground state is almost degenerate with the 4$^{13}$ configuration, we find the multiplet corresponding to Yb$^{2+}$ at the Fermi level. The multiplet originating from Yb$^{3+}$ is separated from it by the Coulomb interaction $U$ between f-electrons.

We observe these two multiplets in the spectrum in Fig. 1(a). The 4$^{13}$ → 4$^{12}$ multiplet between 12 eV and 6 eV consists of 13 levels that are split by spin-orbit coupling. The binding energies and relative intensities compare well with theoretical calculations$^{19}$. The multiplet close to $E_F$ corresponds to the transition 4$^{14}$ → 4$^{13}$. Spin-orbit coupling splits the final state into a doublet. The two additional, rigidly shifted peaks seen in Fig. 1(a) indicate photoemission from the surface Yb layer. It has been shown that the lower coordination of the surface atoms generally leads to a shift of the level to higher binding energies for rare earth elements$^{21}$ and similar magnitudes of shifts were observed in Yb systems before$^{22–25}$ YbRu$_2$Ge$_2$ will most likely cleave between the Yb and the Ge atomic layer. This allows for two surface terminations. The large intensity of the surface doublet in Fig. 1(a) indicates that the sample has a Yb terminated surface$^{26}$. The absence of a similar surface Yb$^{3+}$ multiplet indicates that the surface Yb layer has a valence close to 2.$^{26}$ We find a third pair of peaks with very low intensity shifted by ∼ 0.2 eV (Fig. 1(b), Fig. 4(a1,c1)). This shift is larger than the expected CEF splitting. Such a set of multiplets was also observed in YbRh$_2$Si$_2$ which was attributed to the next buried layer of Yb.$^{24}$ We therefore
interpret the third doublet in YbRu$_2$Ge$_2$ to photoemission from the 2nd Yb layer, i.e. the first buried layer. Similar observations of multiplets from the first and the second surface layer have been found in YbAl$_2$. The third doublet is not a signature of a mixed surface termination consisting of both Yb terminated and Ge terminated patches. It has been shown in YbRh$_2$Si$_2$, that both terminations would result in a surface doublet at the same binding energy but with very different intensities relative to the bulk doublet. In our measurements, the 4$f$ levels are generally enhanced in LV polarization for all bulk levels. The surface states in contrast are more pronounced in LH polarization. This could relate to the finite out-of-plane component of the LH polarization due to the finite incident angle of the light.

One can determine the Yb valence from the relative intensities of the Yb$^{3+}$ and the Yb$^{2+}$ multiplets. From the relative peak heights we already expect the valence to be closer to 3+ in YbRu$_2$Ge$_2$ compared to YbRh$_2$Si$_2$ in accordance with thermodynamic and transport measurements. A quantitative analysis requires a subtraction of surface contributions and of a background from inelastically scattered electrons as well as valence band contributions e.g. from Ru 4$d$ electrons. The contributions for the Yb$^{2+}$ multiplet are small and we estimate the background by a linear function. For the Yb$^{3+}$ doublet, the peaks from the surface layer have the largest contribution to the background. We estimate them by fits using a Doniach-Sunjic line shape convoluted by a Gaussian. The resulting intensities of the Yb$^{3+}$ and Yb$^{2+}$ multiplets are shown as shaded areas in Fig. 1(a).

They include photoemission from the bulk and from the first buried Yb layer, which have almost the same valence in YbRh$_2$Si$_2$. We find an estimate for the valence in YbRu$_2$Ge$_2$ of 2.95(4).

Figure 1(b)-(d) shows the CEF splitting at 125 eV and 30 eV. We highlight the ground state CEF level close to the Fermi level in Fig. 1(c-e) by dividing with the Fermi-Dirac distribution. We can resolve three CEF levels at a binding energy of $E_0 = (3 \pm 3)$ meV, $E_1 = (35 \pm 3)$ meV and $E_2 = (78 \pm 3)$ meV. This observation fits well to the CEF scheme described in literature. The splitting of the quasi-quartet of less than 1 meV is below our experimental resolution and we observe a single level at $E_0$. The splittings to the next excited levels are $(32 \pm 6)$ meV and $(75 \pm 6)$ meV. The first agrees with the value from inelastic neutron scattering. The largest splitting was so far only estimated to 91 meV, which is slightly larger than our experimentally determined value.

B. LDA Calculations

We performed LDA calculations of the band structure using the wien2k package including effects of spin-orbit coupling. The calculations are performed for LuRu$_2$Ge$_2$ using the experimentally determined lattice parameters from YbRu$_2$Ge$_2$. The Lu-counterpart has a fully occupied f-shell removing the 4$f$ electrons from the valence band structure. The bands shown in Fig. 2 therefore originate primarily from Ru 4$d$ electrons. The hybridization of these electrons with the renormalized flat 4$f$ electron bands in the Kondo lattice state of YbRu$_2$Ge$_2$ will be clearly visible in the photoemission spectra and will only slightly alter the Fermi surfaces.

We find five Fermi surfaces: a cylindrical almost two-dimensional sheet ($\alpha$), two small hole pockets at Z ($\beta$, $\gamma$) and two large three-dimensional sheets ($\delta$, $\epsilon$). The shape and size of $\epsilon$ strongly depends on the position of the Fermi level. Interestingly, the cylindrical $\alpha$-sheet has a square-like shape implying preferable nesting conditions.
FIG. 3. Photon energy dependence and FS maps in the normal state at 15 K. (a) and (b) show photon-energy dependencies for a cut through the zone center along \(k_x\) at a binding energy of (a) 300 meV and (b) 20 meV. (c)-(e) FS maps for different photon energies that probe different \(k_y\) as marked in (a). The yellow arrow in (e) marks the magnetic ordering wave vector.\(^{17}\) Blue lines indicate the Brillouin zone.

C. ARPES Results in the Tetragonal State of YbRu\(_2\)Ge\(_2\)

Figure 3(a) presents a map of the photon energy \(h\nu\) dependence for a cut along \(k_x\) through the zone center. We find a clear periodic pattern at a binding energy of 300 meV. As we see from Fig. 1 this binding energy probes mainly conduction band electrons and has a low contribution from the f-electron states. We can determine \(k_x\) from the periodicity and indicate the relevant photon energies used throughout this study. In Fig. 3(b) we show a photon energy dependence close to the Fermi level. The star-shaped pattern contains contributions from the \(\alpha\) to \(\delta\) Fermi surfaces. Figures 3(c)-(e) depict Fermi surfaces measured at specific photon energies. We can clearly identify one (42 eV) or two (30 eV, 23 eV) round Fermi surface pockets at the zone center which we attribute to the \(\alpha\) and \(\beta\) sheets. The calculations predicted that parts of the \(\alpha\) Fermi surface is nested. Neutron scattering found an incommensurate magnetic ordering wave vector of \(q = (0.352, 0, 0)\)\(^{17}\), which can be a sign of preferable nesting conditions in YbRu\(_2\)Ge\(_2\). The experimentally determined diameter of the \(\alpha\) Fermi surface fits well to the size of \(q\) (Fig. 3(e)).

We now compare the calculated band structure shown in Fig. 2(b,c) with ARPES spectra taken with corresponding photon energies of 42 eV and 64 eV in Fig. 4. We can clearly identify the flat \(4f\) bands in the ARPES spectra in Fig. 4(a1)-(d1). For comparison we also added the integrated EDC from Fig. 1(a) taken with 125 eV. We highlight the different bulk and surface (1st and 2nd Yb layer) \(f\)-levels on the right side. From Fig. 3(a) we find that (a,b) are close to the Z-plane while (c,d) are close to the Γ-plane. We overlay the second derivative spectra with the calculated band structure from Fig. 2 that contains bands of mainly Ru 4d character.
them with the calculated band structure in Fig. 4(a2)-(d2). The calculated band structure fits well to our experimental results indicating that correlations among the 4$d$ electrons are weak. In contrast to the calculations, the band forming the tiny $\gamma$ Fermi surface pocket is observed below the Fermi level in Fig 4(a2). In compounds with a similar composition such as YbRh$_2$Si$_2$, clear signatures from surface related d bands were observed in ARPES\textsuperscript{25}. Their contribution to the measured spectra depends on the surface termination. Such surface related signatures can be one reason for discrepancies between our ARPES spectra in Fig. 4 and the calculated bulk band structure. A detailed description of such surface related phenomena in YbRu$_2$Ge$_2$ is necessary to perform a precise band assignment for all observed spectral signatures but goes beyond the scope of this manuscript.

D. ARPES Across the Ferroquadrupole Order

YbRu$_2$Ge$_2$ undergoes a FQ order at $T_0 = 10$ K. This phase transition admixes further splits the two closely-spaced doublets that comprise the CEF quasi-quartet ground state. Assuming a coupling between the 4$f$ electrons and the conduction electrons, we also expect a two-fold distortion of the Fermi surfaces and corresponding shifts of the binding energies of the 4$d$ bands. Figure 5 shows a representative spectrum taken above and below the FQ order. We do not detect any change in the binding energy of the 4$f$ level within our resolution. This is unsurprising as the splitting of the quasi-quartet in the normal state is already below our measurement resolution. We also do not detect any changes in the 4$d$ bands. This is in contrast to the nematic phase of the FeSC, where a clear band separation between the two orthogonal directions is observed.\textsuperscript{12} For twinned crystals as studied here, this manifests in a band splitting in ARPES. Both FeSC and YbRu$_2$Ge$_2$, however, develop an orthorhombic distortion\textsuperscript{16,29} and a diverging nematic susceptibility\textsuperscript{11,16} of very similar size. The transition in FeSC is driven by the d-electrons, whereas the ordering of the f-electrons are the driving force in YbRu$_2$Ge$_2$.\textsuperscript{16} The unchanged Ru 4$d$ electronic structure in the FQ state indicates a very small coupling to the ordered 4$f$ electronic system.

Doping YbRu$_2$Ge$_2$ with Rh suppresses the magnetic and FQ order. We observe three phase transitions between 2 K and 3 K for $x = 0.125$ in specific heat as shown in Fig. 6(a3,b3). We therefore expect Rh-doping to be a promising route to induce a magnetic and/or a FQ quantum phase transition. Figure 6(a,b) compares two ARPES spectra for $x = 0$ in the normal state and for $x = 0.125$ for a photon energy that probes a $k_z$ close to Z. Rh-doping introduces electrons which shifts the relative Fermi level position. We indicate the positions of three hole bands $\alpha$–$\gamma$. (a3,b3) Specific heat measurements for $x = 0$ reproduced from Ref. 14 and for $x = 0.125$ measured on our samples.
upon Rh-doping. We can compare this value to the shift predicted by the total density of states from band structure calculation. Assuming that each Rh atom contributes one additional electron and that the bands shift rigidly, we derive a shift of 90 meV for $x = 0.125$. This value is close to our measured shift. As discussed above, we cannot exclude, that surface related signatures contribute to the spectral features in Fig. 6(a,b). In particular, different surface terminations can change those surface signatures. The good agreement with the calculations, however, serves as an additional support for our interpretation of a doping induced band shift.

Considering the nesting properties of the $\alpha$ band, its disappearance will likely influence the magnetic order. A change in its size can influence the ordering wave vector while its disappearance can suppress the ordering temperature.

Recent measurements of the quadrupole strain susceptibility in YbRu$_2$Ge$_2$ indicate that the FQ order arises predominantly from magneto-electric coupling. Consequently, changes in the band filling are unlikely to have a profound effect on the FQ critical temperature $T_0$. Rather, the suppression of $T_0$ with Rh substitution is tentatively attributed to local strains induced by the chemical substitution, which act as random fields for the local quadrupoles. Such an effect has previously been observed in other chemically substituted compounds which exhibit a cooperative Jahn-Teller effect similar to YbRu$_2$Ge$_2$, for example TmVO$_4$.

IV. CONCLUSION

In summary, we studied the heavy fermion compound YbRu$_2$Ge$_2$ using ARPES and band structure calculations. We observe a non-integer valence of Yb and three CEF levels, which confirms the suggested quasi-quartet CEF ground state. The band structure of the conduction electrons observed in ARPES fits to our calculated band structure and we observe a hybridization with the local $4f$ levels. We do not resolve any changes in the electronic structure due to FQ order. Doping with Rh suppresses the ferroquadrupolar and magnetic order. The electronic structure changes due to the electron doping and we identify two Lifshitz transitions. The Lifshitz transition close to $x = 0.125$ is connected to a two-dimensional Fermi surface that is predicted to have preferable nesting properties by our calculations. Its size fits to the incommensurate wave vector of the magnetic order.

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