ARPES view on surface and bulk hybridization phenomena in the antiferromagnetic Kondo lattice CeRh$_2$Si$_2$

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The hybridization between localized 4$f$ electrons and itinerant electrons in rare-earth-based materials gives rise to their exotic properties like valence fluctuations, Kondo behaviour, heavy-fermions, or unconventional superconductivity. Here we present an angle-resolved photoemission spectroscopy (ARPES) study of the Kondo lattice antiferromagnet CeRh$_2$Si$_2$, where the surface and bulk Ce-4$f$ spectral responses were clearly resolved. The pronounced 4$f^0$ peak seen for the Ce terminated surface gets strongly suppressed in the bulk Ce-4$f$ spectra taken from a Si-terminated crystal due to much larger f-d hybridization. Most interestingly, the bulk Ce-4$f$ spectra reveal a fine structure near the Fermi edge reflecting the crystal electric field splitting of the bulk magnetic 4$f^{15/2}$ state. This structure presents a clear dispersion upon crossing valence states, providing direct evidence of f-d hybridization. Our findings give precise insight into f-d hybridization phenomena and highlight their importance in the antiferromagnetic phases of Kondo lattices.

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n intermetallics, Ce is close to the trivalent $4f^1(5d6s)^3$ configuration with slight to moderate $4f^0(5d6s)^3$ and $4f^2(5d6s)^2$ admixtures. The $4f^2$ configuration with double $f$ occupancy is rather unfavourable due to the strong onsite Coulomb repulsion compared to the $4f$ binding energy, and its contribution usually does not exceed a few percent. In contrast, the tetravalent $4f^0$ lies energetically closer to $4f^1$ which often leads to a fluctuating valence between both configurations. Therefore, the unusual phase diagrams in many Ce systems result from a competition between the non-magnetic $4f^0$ and the magnetic $4f^1$ ground state configuration with momentum $f = 5/2$.

At the level of the Anderson impurity model with hybridization between $4f$ and valence band states, the competition is resolved through the Kondo quenching of the $4f^1$ magnetic moment and the resulting appearance of the Kondo resonance at the Fermi energy ($E_F$) in the single-particle spectral function. The resonance reflects final states with a predominantly $4f^1$ contribution for both the electron removal and addition spectrum. In Kondo lattices, it can be understood as the momentum integrated coherent quasi-particle part of the single particle spectrum. In a crystalline environment, the degeneracy of the Ce $4f^1_{5/2}$ sextet is lifted due to the interaction with the nonspherical electrostatic field of the ligands, which is called the crystal electric field (CEF). The resulting CEF splitting strongly influences the magnetic properties of the compound. The Kondo lattice quasi-particles form heavy bands originating from the CEF split $4f^1$ states. If the magnetic moments are Kondo quenched, then these bands disperse across $E_F$ so that the $4f$ electrons enter the Fermi volume, resulting in the so-called large Fermi surface. However, for a magnetically ordered state configuration as expected from the ionization of the trivalent $4f^1$ ground state, and a second feature at $E_F$, commonly ascribed to the tail of the Kondo resonance that is centered slightly above $E_F$ (refs 1,19). Theoretically, this spectral function is well-understood and well-described within the Kondo and Anderson lattice models. The $\sim 2\text{eV}$ feature, which carries most of the $4f$ spectral weight, reflect the localized, ionization-like aspect of the Ce $4f$, while the weaker feature at $E_F$ reflects the hybridized, quasi-particle aspect. However, a precise experimental confirmation of all expected features faced strong problems connected with differenntiating between surface and bulk electronic contributions. So far, however, poorly defined surfaces have resulted in a mixture of surface- and bulk-related features in ARUPS, preventing a precise analysis and assignment.

High-energy PES strongly enhances the bulk part of the signal, but the much poorer energy resolution prevents the detection of fine structures, in particular close to $E_F$. Taking advantage of our expertise gained in the course of extended ARUPS studies on the homologues YbRh$_2$Si$_2$ and EuRh$_2$Si$_2$, we were able to obtain spectra for the Ce-terminated and the Si-Rh-Si terminated surfaces of CeRh$_2$Si$_2$, which are representative for weakly and strongly hybridized $4f$ states, respectively. Comparing both spectra provides an unprecedented view into the effects of $f-d$ hybridization on the electronic spectral function, revealing features such as a CEF induced fine structure near the Fermi edge for the Si – Rh – Si surface. For this surface, which is representative for bulk CeRh$_2$Si$_2$, we observe a strong interaction between valence and $f$ electrons at a temperature well below $T_N$, which demonstrates the importance of hybridization effects in the antiferromagnetic phases of Kondo lattices.

Here we study the single particle spectrum of the Ce $4f$ electronic states in the antiferromagnetic (AFM) Kondo lattice CeRh$_2$Si$_2$ by means of high-resolution angle-resolved photoemission spectroscopy (ARPES). Generally, the Ce $4f$ photoemission spectroscopy (PES) spectrum shows a characteristic double-peak structure with one peak at about 2 eV binding energy (BE) corresponding roughly to the $4f^0$ final state configuration as expected from the ionization of the trivalent $4f^1$ ground state, and a second feature at $E_F$, commonly ascribed to the tail of the Kondo resonance that is centered slightly above $E_F$ (refs 1,19). Theoretically, this spectral function is well-understood and well-described within the Kondo and Anderson lattice models. The $\sim 2\text{eV}$ feature, which carries most of the $4f$ spectral weight, reflects the localized, ionization-like aspect of the Ce $4f$, while the weaker feature at $E_F$ reflects the hybridized, quasi-particle aspect. However, a precise experimental confirmation of all expected features faced strong problems connected with differentiating between surface and bulk electronic contributions. So far, however, poorly defined surfaces have resulted in a mixture of surface- and bulk-related features in ARUPS, preventing a precise analysis and assignment.

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The non-dispersive structure at about 1.9 eV BE and the flat spectral feature close to $E_F$ are intensified indicating their Ce 4$f$ origin. For Si termination (Fig. 2b), Rh 4$d$ emission is similarly reduced, but now three flat bands appear right below $E_F$, which did not show in the off resonance spectrum. These flat bands can be attributed to 4$f$ emission from the bulk-type Ce layer buried beneath the Si–Rh–Si covering. The fine structure of the bulk Ce 4$f$ emission consists of a spin-orbit side band at ~0.3 eV BE corresponding to the Ce 4$f^{3/2}$ final state and weakly dispersive bands packed within tens of meV below $E_F$.

The aforementioned spin-orbit sideband shows up for Ce termination as well. The intense 4$f$ feature at $E_F$, however, does not show a similar splitting as observed for the Si termination. The latter is nicely seen in the angle-integrated spectra shown in Fig. 2c,d, obtained by summing up the k-distributed spectral weight of the on-resonance data. These features lie within the dotted rectangles. As will be discussed below, the splitting seen in the Si-terminated data is the CEF splitting of the Ce 4$f^{1/2}$ sextet under $D_{4h}$ symmetry. It is interesting to note that large intensities of the $E_F$ peak are restricted to a narrow region around the $\Gamma$ point at the Ce-terminated surface. A similar, but less pronounced, phenomenon is also observed for Si-termination. Large intensity of the $E_F$ peak denotes strong $f$–d hybridization and the latter is particularly large at points in k space where valence bands approach or even cross $E_F$ (refs 21,22). This is nicely reflected in the data for the Si-terminated surface where the $E_F$ peak intensity increases just below the $E_F$ crossing of a band close to the $\Gamma$ point.

The large intensities around the $\Gamma$ point may, thus, be attributed predominantly to hybridization with the apex of the Dirac cone. We note that the apparent sizeable $f^1$ spectral weight in the ‘bulk’ spectra does not correspond to a large departure of the expectation value of the 4$f$ occupancy $n_f$ from the integer value 1. X-ray absorption spectroscopy measurements, which provide the most reliable information, determine an $n_f$ of the order of 0.975, but this small decrease in $n_f$ is typical for systems close to the transition from localized to itinerant 4$f$ states, as for example, in CeCu$_2$Si$_2$ with $n_f = 0.97$ (ref. 17).

The broader peak emerging at ~1.9 eV BE for Ce termination deserves particular attention. It arises from pure charge excitations of the trivalent Ce ion (4$f^{3/2}$–4$f^1$), and is usually referred to as the ionization peak30,31. A shoulder of this peak observed at 2.4 eV BE in the k-integrated spectrum reflects hybridization spreading due to structure in the valence band density of states. For Si termination, the intensity of the ionization peak is strongly reduced relative to the emissions close to $E_F$ and consists of a broad bump at ~1.5 eV BE, again with a shoulder due to hybridization spreading. The large intensity of the Fermi level peaks with respect to the ionization peak is indicative of strong $f$–d hybridization, much larger than that in the Ce surface layer, and is also reflected by the dispersive properties of the ionization peak in the k-resolved data. The larger BE of the leading ionization peak for the Ce-terminated surface is due to the surface-core-level shift, which is on the order of 0.4 eV for trivalent rare-earth systems, in good agreement with the shift of the peak from 1.5 to 1.9 eV observed here.

Interestingly, the difference in the ionization peak signal between the weakly hybridized surface spectra and the stronger hybridized bulk spectra is very similar to the difference predicted for the $f$ states within LDA + DMFT between CeFeAsO (weak hybridization) and CeFePO (strong hybridization)32.

In Fig. 3, we take a closer look at the fine Ce 4$f$ spectral structure near the $\Gamma$-point. For the Si-terminated surface (Fig. 3a), two prominent features can be seen. An intense and weakly dispersive band bending down to ~20 meV BE near the $\Gamma$-point and a heart-shaped feature, which indicates hybridization of the Dirac cone apex with CEF 4$f$s running
parallel to $E_F$ and packed in a $\sim 50$ meV range (Fig. 2b). The weakly dispersive band close to $E_F$ is similarly found for Ce termination as shown in Fig. 3b except that the heart feature is missing. Since CeRh$_2$Si$_2$ is AFM ordered at the experimental temperature, we interpret non-zero BE as a characteristic feature arising due to the magnetically ordered ground state of the Ce 4$f$ electrons. Although appendix F in ref. 33 treats a ferromagnetic ground state, the underlying concept for a Kondo peak away from $E_F$ should be valid also for an AFM. Note that the magnetically ordered ground state is separated from the Kondo resonant state by an energy corresponding to the stabilization of the magnetic state ($T_N \approx 3$ meV for CeRh$_2$Si$_2$). Consequently, a PES feature appears just below $E_F$ carrying a large weight due to the degeneracy of the Ce 4$f$ orbital.

In the off-resonance spectrum (Fig. 3c), where 4$f$ emission is suppressed and the spectrum is dominated by valence-band emission, a similar feature is visible. This indicates the important role of Rh valence-band states in the formation of the fine spectral structure close to $E_F$. Similar dispersions and $E_F$ crossings of 4$f$-derived quasiparticle bands have already been observed in YbRh$_2$Si$_2$ (ref. 22) and CeFePO as well.

**ARPES insight into the CEF splittings of 4$f^1$ state.** Let us turn now to the discussion of the 4$f$ CEF splittings detected by ARPES. We first note that according to standard theoretical modelling of PES on Kondo lattices, the physics behind the CEF split lines in Ce-systems is quite different from that in Yb systems: In Yb-compounds, the 4$f^{13}$ final state is predominantly a result of a direct ionisation of a 4$f^{14}$ configuration admixed to the 4$f^{13}$ ground state. The amount of this admixture could be estimated parallel to $E_F$ and packed in a $\sim 50$ meV range (Fig. 2b). The weakly dispersive band close to $E_F$ is similarly found for Ce termination as shown in Fig. 3b except that the heart feature is missing. Since CeRh$_2$Si$_2$ is AFM ordered at the experimental temperature, we interpret non-zero BE as a characteristic feature arising due to the magnetically ordered ground state of the Ce 4$f$ electrons. Although appendix F in ref. 33 treats a ferromagnetic ground state, the underlying concept for a Kondo peak away from $E_F$ should be valid also for an AFM. Note that the magnetically ordered ground state is separated from the Kondo resonant state by an energy corresponding to the stabilization of the magnetic state ($T_N \approx 3$ meV for CeRh$_2$Si$_2$). Consequently, a PES feature appears just below $E_F$ carrying a large weight due to the degeneracy of the Ce 4$f$ orbital.

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from the relative intensity of the $4f^{13}$ emission normalized to the whole $4f$ emission, and a more precise calculation within the Anderson model deviates only slightly from this result. In the Ce-compound, however, the admixture of $4f^{2}$ configurations to the ground state are rather small, and the $4f^{1}$ emission originates mostly from strong hybridization of $4f^{1}$ and $4f^{0}$ configurations. Thus, while in the Yb-system the intensity of the crystal-field PES signal is governed by the atomic dipole matrix elements, in Ce-systems its observability reflects its participation in the hybridization process. Accordingly, if the CEF states were not hybridized, then the photoemission spectral function would still show CEF satellites for an Yb valence fluctuating system, but no satellites for a homologue Ce system. Therefore, the observability of the CEF split state in CeRh$_2$Si$_2$ provides on its own a direct evidence for the hybridization of the excited CEF levels.

In Fig. 4a, we show the ARPES data taken at 40 eV photon energy using circularly polarized light from the Si-terminated surface of CeRh$_2$Si$_2$. These experimental conditions allow us to clearly detect both $4f$ and valence band emission together, while still giving good contrast between them. Thus, we can conclusively identify the $k$ space regions where the CEF states reveal their dispersive and non-dispersive behaviours. For each $k$ value the spectra were normalized to constant integrated emission intensity in the BE range from 30 to 70 meV. We also show the $k$-integrated spectrum taken from region C. The ARPES data clearly show strongly dispersing hole-like bands, which stem mainly from Rh 4$d$-derived states. Also, we can see two states A and B that run parallel to $E_F$ and reveal weak dispersions at points in $k$ space where the valence bands approach them and hybridize. Apparently, the mentioned peak A at 48 meV and peak B at 62 meV BE reflect the fine structure of the $4f$ states. Approaching the $\Gamma$ point the component A disperses towards lower BE, due to its interaction with the Rh hole-like band, reaching about 30 meV exactly at $\Gamma$, while component B seems to disperse in the opposite direction. The appearance of two components is in accordance with the expected CEF splitting in the tetragonal environment of $D_{4h}$ point group symmetry, where the ground state Ce $4f^{15/2}$ splits into three Kramers doublets. Note that the ARPES data show certain $f$-$d$ hybrid states that are packed between the ground state (0 meV) and the first excited CEF state (48 meV). Because the CEF split states have identical degeneracy, one may anticipate that the integrated spectral weight of all the CEF split states should be same. However, from Fig. 4 it can be seen that the feature A is more intense as compared with the other states. An apparent explanation for this difference is that the feature B and the $f$-$d$ hybrid states below 48 meV are connected and that their strong dispersion due to hybridization with Rh 4$d$ redistributes their spectral weights over a much larger energy window than that of feature A. Thus, the fine structure that we observe in the $'4f^{1}$ spectra indicates that one of the excited CEF doublets is strongly hybridized, while the other one is less hybridized. Notably, a recent theoretical calculation predicts the hybridization for the $\Gamma_\delta$ doublet in CeRh$_2$Si$_2$ to be much weaker than for the $\Gamma_\gamma$ doublets. Since all present experimental and theoretical studies indicate one of the $\Gamma_\gamma$ to be the CEF ground state and $\Gamma_\delta$ to be at a comparatively high energy, all these observations can then be merged in a picture with a weakly hybridized $\Gamma_\delta$ at 48 meV and a strongly hybridized $\Gamma_\gamma$ distributed in a wide energy range up to about 65 meV. Previous studies of the CEF scheme are far from being conclusive. Early determinations based on the temperature dependence of the magnetic susceptibility have suggested CEF level schemes of 0–32–80 meV (Ref. 27) and 0–27–59 meV (Ref. 28) with an almost pure $| + / - 5/2 \rangle$ CEF ground state. The most recent study is based on inelastic neutron scattering (INS) and X-ray-absorption spectroscopy and proposes a level scheme of $0–30–52$ meV with a strong mixing of $| + / - 5/2 \rangle$ and $| - / + 3/2 \rangle$ in the ground state, which is incompatible with the measured susceptibility and magnetization data. While INS usually is a proven technique to determine the CEF excitation energies, in CeRh$_2$Si$_2$ it revealed a very broad response, extending up to 60 meV, without well-resolved peaks, making the separation between phonon and magnetic excitations far from evident. This broadness of the CEF response in INS is in line with the wide spectral distribution observed for the feature B and the $f$-$d$ hybrid states in the PES $4f^{1}$ signal. The PES results provide direct insight into the origin for this broadness, namely a strong hybridization with the Rh 4$d$ states. On the other hand, assuming the A features in PES to correspond to the $\Gamma_\delta$ doublet, we note that the INS cross section for the transition from a dominantly $| + / - 5/2 \rangle$ CEF ground state to the $\Gamma_\delta$ excited state is comparatively small, thus the sharper peak expected in INS for this transition might be absorbed within the broad response related to the $\Gamma_\gamma$–$\Gamma_\gamma$ transition.

An established method to check the relevant energy scales of a Kondo lattice, that is, $T_K$ and the CEF splitting, is to study the
evolution of the 4f-specific heat $C_{4f}(T)$ and 4f entropy $S_{4f}(T)$ as a function of $T$ (refs 36,37). Usually one gets reasonable agreement between the experimental $C_{4f}(T)$ and that calculated using parameters obtained from other methods. As an example, we could recently very nicely reproduce the experimental $C_{4f}(T)$ of YbIr$_2$Si$_2$ using the CEF splitting deduced from the ARPES spectra, and thus demonstrate that INS missed the highest CEF level38. Therefore, we determined $C_{4f}(T)$ and $S_{4f}(T)$ of CeRh$_2$Si$_2$ in a wide $T$ range, up to 300 K, and compared with the curves expected for different CEF schemes and different values of the Kondo temperature $T_K$ (Fig. 5)38. There is presently no analytical expression available for the specific heat of a Kondo lattice which includes both AFM order and the Kondo effect on the excited CEF levels. Since in the present study we are specifically interested in the excited CEF levels, we focus on $C_{4f}(T)$ and $S_{4f}(T)$ above $T_K$. In the standard way of modelling $C_{4f}(T)$ the contribution of the excited CEF level is accounted for by a simple Schottky expression and thus broadening of the CEF levels due to the Kondo effect is not taken into account (see section methods). Since in CeRh$_2$Si$_2$ INS results evidence a significant broadening of the CEF levels, in line with the present PES results, we preferred to use the recent model of Romero et al.37, where the broadening of the first excited level can be taken empirically into account. We initially performed two calculations, one with the CEF excitation energies $\Delta_1$ and $\Delta_2$ as deduced from INS37, and one with $\Delta_1$ and $\Delta_2$ as deduced from the present ARPES results. In both cases we took $T_K$ and width $\Gamma_1$ of the first excited CEF level as deduced from INS37. Including AFM order would modify $C_{4f}(T)$ and reduce $S_{4f}(T)$ only in the $T$ range from slightly above $T_N$ to $T = 0$. Above $T_N$, the agreement between the experimental curve and the curve for the CEF scheme deduced from INS is not too bad, while the curve for the ARPES deduced CEF scheme is too much shifted towards high temperatures. However, in both cases the maximum connected with the CEF excitations is much narrower in the theoretical $C_{4f}(T)$ curves than in the experimental ones, suggesting that the width of the CEF level has been underestimated in the analysis of the INS data. A more fundamental problem is that in both cases the calculated 4f entropy in the $T$ range 50 K $< T < 100$ K is significantly smaller than the experimental one. In an attempt to resolve this discrepancy, we first reduced $T_K$ by one order of magnitude. The entropy above $T_N$ is now nicely reproduced, but $C_{4f}(T)$ is now severely underestimated in the $T$ range 50 K $< T < 100$ K. Increasing the width of the first excited CEF doublet does not correct this discrepancy. Furthermore such a low $T_K$ is incompatible with many other properties, for example, the width of the quasi-elastic line in INS and strong hybridization seen in the bulk ARPES signal. The specific heat of a Kondo ion including CEF splitting (with same hybridization strength for ground and excited CEF states) can be calculated exactly in the single ion case, but this requires very demanding numerical calculations which do not allow for ‘fitting’ experimental data. Fortunately, Desgranges38 very recently provided such numerical results for a larger number of cases, and therefore we tried to use them for modelling our experimental $C_{4f}(T)$ data. In this approach, one has first to choose the most appropriate case among those considered in ref. 38, and then to fix the only free parameter which is the Kondo scale in the absence of CEF splitting, $T_{KNN}$. A preliminary survey of the results in ref. 38 suggests that the curve for $\Delta_1 = 1/2 \cdot \Delta_2 = 0.7 \cdot T_{KNN}$ is closest to our experimental data. Matching experimental and calculated $C_{4f}(T)$ in the $T$ range 50 < $T$ < 250 K resulted in $T_{KNN} = 50$ meV. This corresponds to a Kondo scale $T_K = 2.6$ meV for the ground-state doublet and to CEF splitting of $\Delta_1 = 35$ meV and $\Delta_2 = 70$ meV. The agreement between calculated and experimental specific heat data in the $T$ range 50 K $< T < 250$ K is excellent (Fig. 5). A slightly poorer agreement is obtained for the case $\Delta_1 = \Delta_2 = T_{KNN} = 43$ meV (not shown), corresponding to $T_K = 2.3$ meV. However, in both cases the calculated entropy in the $T$ range 50 K $< T < 100$ K is significantly smaller than the experimental values, reflecting the same problem as for the fits with the model of Romero et al. The essence of this problem is that in the case of a CEF ground-state doublet well-separated from the excited CEF states due to a large splitting as in CeRh$_2$Si$_2$, the large Kondo interaction implied by other properties, like for example, the broadening of the CEF contribution to $C_{4f}(T)$ or the (bulk) ARPES response, always reduces the entropy at 40 K significantly below $Rn2$. Resolving this problem requires considering further interactions beyond the single-ion Kondo and the CEF splittings. Despite this intricate problem, the analysis of $C_{4f}(T)$ supports our analysis of the bulk part of the ARPES signal. The broadness of the CEF contribution to $C_{4f}(T)$ at high $T$ implies a strong hybridization of the bulk 4f states, in line with our conclusion from the bulk PES signal, and in line with other properties. This shows CeRh$_2$Si$_2$ to be strongly hybridized even though it has fully localized 4f electrons in the sense of the large size of the AFM

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**Figure 5** Insight into the specific heat and entropy of the Ce 4f. Temperature dependence of the 4f specific heat (a) and of the 4f entropy (b) in CeRh$_2$Si$_2$. Black dots show the values deduced from experiment. Coloured lines show the curves calculated for different values of the CEF splitting $\Delta_1$ and $\Delta_2$, of the Kondo scale $T_K$, and of the width $\Gamma_1$ of the first excited CEF level, using the model of Romero et al.37 or the numerical results of Desgranges38. This approach does not include AFM ordering, therefore, comparison with experiment is only meaningful for $T > 50$ K. Parameter values are given in meV in the figure. Blue diamonds: values as deduced from INS. Magenta stars: same as before, but with $\Delta_1$ and $\Delta_2$ taken from our PES results. Red triangles: Parameter as deduced from INS, but with $T_K$ reduced by a factor of 10 to account for the observed entropy at 50 K. Green circles: same as before, but with $\Gamma_1$ increased by a factor of 3 in an attempt to reproduce the observed large Cp(T) for $40 < T < 100$ K despite a low $T_K$. Brown triangles: scaled numerical results of Desgranges38. It corresponds to the case $\Delta_1 = 35$ meV, $\Delta_2 = 70$ meV and $T_K = 2.6$ meV.
ordered moment, the large entropy at \( T_N \), and the small Fermi surface deduced from dHvA experiments. The comparison of experimental \( C_{\text{HvA}}(T) \) with exact numerical results for the Kondo + CEF single-ion model indicates the broadening of the excited CEF level to be even larger than the value deduced from INS results, but of the size expected when the hybridization of the CEF ground and excited states are identical. This suggests that in previous similar studies the broadening of the excited CEF states were cleaved in situ.

ARPES measurements

ARPES studies were performed at the \( 3^{\text{rd}} \) ARPS instrument of the BESSY-II synchrotron facility. The spectra were acquired using a Scienta D800 electron energy analyzer. The overall energy and angular resolutions were set to 6 m\( \varepsilon \)V and 0.1, respectively. High-quality single-crystalline samples of CeRh\(_2\)Si\(_2\) were cleaved \textit{in situ} in ultrahigh vacuum at a base pressure better than 8 \( \times 10^{-11} \) mbar. The sample was kept at a temperature of \( \sim 1 \) K during the measurements. The photon energy was varied to take advantage of a resonant enhancement of the 4f emission cross-section at the Ce 4d\textsuperscript{4f} excitation threshold at 121 eV.

Sample preparation and specific heat measurements

Single crystals were grown by the in-flux technique following the procedure described in detail in ref. 39. Polycrystalline CeRh\(_2\)Si\(_2\) and LaRh\(_2\)Si\(_2\) samples were prepared by arc melting of the constituent elements under a high-purity Argon atmosphere. As-cast ingots were annealed for 2 days at 1200 °C under high vacuum. Chemical composition, crystal structure, and physical properties of single crystals and polycrystals were checked by microprobe, X-ray diffraction and resistivity measurements, respectively. Specific-heat measurements were performed on polycrystalline samples of CeRh\(_2\)Si\(_2\) and LaRh\(_2\)Si\(_2\) using the standard specific heat option of the commercial property measurement systems, Quantum Design, USA. LaRh\(_2\)Si\(_2\) is here taken as reference compound for subtracting the non-f part of the specific heat, that is, the phonon and the non-f electron contributions. Since at high temperatures the f contribution is tiny compared to the phonon part, special care was taken to get accurate absolute values. Both the CeRh\(_2\)Si\(_2\) and the LaRh\(_2\)Si\(_2\) samples were measured under identical conditions. For each sample, \( \Delta T_{\text{K}} \) was determined in a first run the addenda (platform and grease) and then in a second run the total specific heat (addenda + sample). The whole procedure was repeated with a different part of the polycrystalline batches in order to get two independent sets of data. Both sets agreed very nicely, and the f specific-heat deduced from the two sets differ by \( \sim 0.1 \) m\( \varepsilon \)V K\(^{-2}\) in the whole T range up to 300 K. The magnetic entropy \( S_m \) was determined by numerically integrating \( C_{\text{HvA}}(T) \) and using a linear extrapolation for the T range below 2 K.

We used the analytical expression of Romero et al.\(^{27} \) to generate \( C_{\text{HvA}}(T) \) for different CEF schemes (\( \Delta_L \), \( \Delta_0 \), energy of excited levels) and different values of the Kondo temperature (\( T_K \)) and width of the first excited CEF level (\( \Gamma_1 \)). The values for the different parameters were chosen on the basis of previous and present experimental results (see main text). Desgranges provided us with his numerical results for the Kondo + CEF model for the cases \( A_2 = A_4 = 0.7 \times 10^{10} \) and \( A_2 = T_{\text{K06}} \) (nomenclature as ref. 38), which correspond to the cases \( \Delta_L = 2 \times \Delta_0 \) and \( \Delta_L = \Delta_0 \), respectively. \( T_{K06} \) was scaled in order to get the best match for the specific heat data. \( T_{K06} \) (for the ground state doublet) was calculated from \( T_{K06} \) by combining the numerical result \( C_{\text{HvA}}(T) \) \( \sim 20.0 \) and the definition limit of the specific heat data.

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Author contributions
S.P., C.G. and D.V.V. designed the research. N.C.C. and C.G. prepared the samples for experiments. ARPES measurements were done by A.G., M.G., S.P., A.C., T.C.R., A.F.S.-S., S.D. and D.V.V. Thermodynamic measurements were performed by P.K. and C.G. The obtained results were discussed together with K.K., Yu.K., C.L., and J.W.A. The manuscript was written by S.P., C.G. and D.V.V. All authors have read and approved the final version of the manuscript.

Additional information
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