Orbital selective coupling in CeRh$_3$B$_2$: co-existence of high Curie and high Kondo temperature

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We investigated the electronic structure of the enigmatic CeRh$_3$B$_2$ using resonant inelastic scattering and x-ray absorption spectroscopy in combination with $ab$-initio density functional calculations. We find that the Rh 4$d$ states are irrelevant for the high-temperature ferromagnetism and the Kondo effect. We also find that the Ce 4$f$ crystal-field strength is too small to explain the strong reduction of the Ce magnetic moment. The data revealed instead the presence of two different active Ce 4$f$ orbitals, with each coupling selectively to different bands in CeRh$_3$B$_2$. The inter-site hybridization of the |$J = \frac{5}{2}$, $J_z = \pm \frac{5}{2}$⟩ crystal-field state and Ce 5$d$ band combined with the intra-site Ce 4$f$–5$d$ exchange creates the strong ferromagnetism, while hybridization between the |$J = \frac{5}{2}$, $J_z = \pm \frac{5}{2}$⟩ and the B sp in the ab-plane contributes to the Kondo interaction which causes the moment reduction. This orbital selective coupling explains the unique and seemingly contradictory properties of CeRh$_3$B$_2$.

I. INTRODUCTION

A. Properties and questions

Cerium-based intermetallic compounds have been widely studied thanks to the variety of exotic properties that arise from the coexistence of localized Ce 4$f$ magnetic moments and itinerant electrons. A widely accepted picture for such “dense” impurity systems is the Doniach phase diagram [1] that describes the competition between the Ruderman–Kittel–Kasuya–Yosida (RKKY) coupling and the Kondo-lattice effect as a function of the interaction strength J between local rare-earth moments and itinerant conduction electrons. In the (weak interaction) RKKY limit, a spin polarization of the itinerant conduction electrons leads to magnetic order below temperatures that grow like $T_{RKKY} \propto J^2$. With stronger interactions, however, the Kondo effect starts to dominate. Here, the formation of singlets between localized and itinerant electrons starts at a characteristic Kondo temperature $T_K \propto e^{-1/J}$ and effectively leads to a screening of the local moments by the conduction electrons, and consequent suppression of magnetic order. The ordering temperature therefore grows through a maximum as a function of J and is suppressed completely at the so-called quantum critical point in the region where $T_{RKKY} \approx T_K$. At that point superconductivity is often observed. Beyond, in the regime where $T_{RKKY} < T_K$ an intermediate valent Kondo state and composite heavy quasiparticles emerging from local 4$f$ and itinerant conduction electrons determine the near ground state properties [2, 3].

The majority of cerium compounds orders antiferromagnetically, but there are also a fair number of ferromagnetic cerium-based compounds. They all have in common that the ordering temperatures tend to be lower than 20 K [4]. CeRh$_3$B$_2$ is the most extreme exception; it
orders ferromagnetic at $T_C = 115$ K [6,7], which is by far the highest magnetic ordering temperature recorded for Ce-based intermetallic compounds. Its $T_C$ is even higher than that of GdRh$_3$B$_2$, $(T_C = 91-105$ K [8]). It is actually two orders of magnitude larger than expected from de Gennes scaling, which works well for localized moments within the rare earth (RE) series. CeRh$_3$B$_2$ is exceptional in another respect as well. It forms in the hexagonal CeCo$_3$B$_2$-type crystal structure (P6/mmm), that consists of alternating layers of Rh and Ce surrounded by B, and its Ce-Ce distances along the c direction are extraordinary short (see Fig. 1), shorter than the Hill limit of about 3.5 Å and shorter than in the valent ground state [9,10]. The latter material has a non-magnetic, strongly intermediate valent ground state [9,10]. The a parameter in CeRh$_3$B$_2$ exhibits a shallow minimum as function of temperature at about 200 K so that its net decrease between 1200 and 5 K is minor (about 0.2%). In the same temperature interval, the c parameter decreases by about 2% and also more drastically than e.g. in the La or Pr compound of the family [4].

Despite its large $T_C$, the magnetic moments in CeRh$_3$B$_2$ are strongly reduced compared to values of a free Ce$^{3+}$ ion, actually more so than what can be expected within a localized crystal-field model. The saturated moments at low temperature measured by magnetic susceptibility are 0.45 $\mu_B$ in the basal plane (with a small in-plane anisotropy) and 0.04 $\mu_B$ along the hexagonal c axis [6,11]. The magnetic anisotropy can be related to the crystal structure, characterized by a large crystalline anisotropy (see Fig. 1).

There is consensus about the filling of the 4$f$ shell being non-integer ($n_f \approx 0.88$) in CeRh$_3$B$_2$ [12,21] and, according to photoemission, the Kondo temperature $T_K$ is of the order of 400 K. This is large, although not as large as in superconducting CeRu$_3$B$_2$ with its $n_f \approx 0.76$ and $T_K = 2000$ K. Actually, in the substitution series Ce(Rh$_{1-x}$Ru$_x$)$_3$B$_2$, the substitution of Rh by Ru quickly destroys the magnetic order [12,19].

Itinerant magnetism associated with the Rh 4$d$ bands seemed to be a plausible explanation for the unusual magnetism in CeRh$_3$B$_2$ since it is not obvious how the RKKY interaction in the presence of localized moments could produce such a high ordering temperature. However, many facts contradict this; for example, LaRh$_3$B$_2$ is not ferromagnetic [13] and the Rh sites do not seem to carry a magnetic moment [22,24]. Many other models have been put forward [12,13,16,19,20,33], models that include the strong crystal-electric field along the c-axis and the Kondo effect. Until today, however, it is not so clear which states would be involved to establish the magnetism and which states would contribute to the reduction of the Ce moment. The possible importance of the crystal-electric field has been recognized but the crystal-field scheme has yet not been fully determined despite measurements of the magnetic anisotropy [34], neutron scattering work [35,36] and x-ray absorption efforts [18,37,39].

In this study we aim to determine the electronic structure of CeRh$_3$B$_2$ including the full 4$f$ crystal-field scheme in order to obtain answers to the following questions: which states are responsible for the ferromagnetism with the anomalously high ordering temperature, and why at the same time is the saturated magnetic moment so strongly reduced; how strong are the crystal field effects, and which states provide the Kondo screening? To this end we performed a combination of spectroscopic experiments and theoretical calculations. We used temperature ($T$) dependent x-ray absorption (XAS) and resonant inelastic x-ray scattering (RIXS), as well as ab-initio density functional theory (DFT) calculations. In the past we have shown that XAS with linear polarized light at the Ce $M$-edge gives access to the ground state symmetry when measuring at low $T$, while information about low lying excited states can be obtained by taking XAS data at elevated temperatures [40,42]. RIXS, on the other hand, has direct access to the crystal-field transition energies and is particularly suited for a compound where large or even giant crystal-field effects are expected. Today, state-of-art beamlines may reach resolutions of 30 meV at the Ce $M_5$-edge and this resolution does not change over a large energy transfer range. RIXS also has a very good contrast of signal to background, and a strong cross-section for all multiplet states, and, being a two photon process, the selection rules allow excitations beyond those of neutron spectroscopy [43,45]. The experimental results are then interpreted in light of the relevant projections of the partial density of states and hybridization functions from the DFT calculations.

II. METHODS

XAS and RIXS experiments at the Ce $M$-edge (3$d^{10}$4$f^1 \rightarrow 3$d^{2}$4$f^2$) were performed at the Dragon beamline at the NSRRC (National Synchrotron Radiation Research Center) in Hsinchu, Taiwan and the soft-RIXS beamlines I21 at DIAMOND Light Source in the UK [46] and ID32 [47] at the European Synchrotron Radiation Facility (ESRF) in France. All experiments were performed on Czochralski-grown single crystals. Appendix VI A. At I21 RIXS data were taken at 15, 135, and 295 K, at ID32 RIXS measurements were performed with smaller temperature intervals, namely 20, 80, 165, 250, and 318 K. The data were analyzed with full multiplet calculations using the QUANTY code [48]. Greater details about experimental set-ups, data analysis, and the density functional calculation can be found in the Appendix VI B.

III. EXPERIMENTAL RESULTS

A. XAS

With XAS at low $T$ we determine the crystal-field wave function of the ground state. Figure 2 shows the XAS
JAS spectra of pure $4f$ electric field vector $\vec{E}$.

**FIG. 3.** Respective charge densities.

FIG. 2. (a) XAS spectra of CeRh$_3$B$_2$ taken at 20 K with the electric field vector $\vec{E}$ parallel $c$ (red) and in the hexagonal $ab$ plane (blue). The arrows indicate the satellites due to the $4f^1$ contribution in the ground state. Inset: simulation of XAS spectra of pure $J_z$ states of the $2F_2$ multiplet and their respective charge densities.

The general spectral shape of our XAS data agrees well with the XMCD data of Imada et al. who also finds, in addition to the main absorption due the $4f^1$ configuration in the ground state, a small satellite at the higher energy side of the $M_5$ and $M_4$ absorption lines due to the presence of some $4f^0$ in the initial state (see arrows in Fig. 2).

We compare the data with a full multiplet calculation (see Appendix [VI C] for details) in order to confirm the anticipated ground state symmetry. This is different from the intentions of Yamaguchi et al. who were aiming to find values for the Kondo and Curie temperature when fitting their $N$-edge data within an Anderson impurity model.

We recall that the crystal-field Hamiltonian is expressed as a sum of tensor operators $C_k$ which transform in the same way as the (renormalized) spherical harmonics $C^m_k(\theta, \phi)$ for the hexagonal point symmetry of Ce$^{3+}$ in CeRh$_3$B$_2$ the crystal-field Hamiltonian is

$$H_{CEF} = A^m_4 C^0_4 + A^m_6 C^0_6 + A^m_6 (\hat{C}^6_0 + \hat{C}^{-6}_0),$$

where $A^m_k$ are the crystal-field parameters, expressed using the Wybourne normalization [39]. The $A^m_k$ have to be determined experimentally. The crystal field splits the $2F_2$ and $2F_\pm$ multiplets into three and four Kramers doublets, respectively. Usually, in Ce compounds the crystal-field splitting is much smaller than the spin-orbit splitting, so that for hexagonal point symmetry the eigenstates of the crystal-field Hamiltonian are pure $|J_z\rangle$ states, with the exception of $|J = \frac{7}{2}, J_z = \pm \frac{7}{2}\rangle$ and $|J = \frac{7}{2}, J_z = \mp \frac{7}{2}\rangle$ that can be mixed by the action of the $A^6_6$ parameter. In case of larger crystal-field splittings, however, the two multiplets $2F_\pm$ begin to intermix, and, former pure $|J_z\rangle$ states, will have the form $\alpha |J = \frac{5}{2}, J_z = \mp \frac{3}{2}\rangle + \sqrt{1 - \alpha^2} |J = \frac{7}{2}, J_z = \mp \frac{7}{2}\rangle$. In the giant crystal-field scenario, the entire L-S-J coupling scheme may break down.

The inset of Fig. 2 shows the full multiplet simulation for the polarization dependence of the pure $|\frac{7}{2}, J_z\rangle$ states of the $2F_\pm$ multiplet. The polarization dependence of the $|\frac{7}{2}, \pm \frac{1}{2}\rangle$ and $|\frac{7}{2}, \pm \frac{3}{2}\rangle$ has the same sign as the experiment. The experimental dichroism is much stronger than the simulation for $|\frac{3}{2}, \pm \frac{1}{2}\rangle$ so that it can be excluded as a solution. The data almost resemble the simulation of the $|\frac{5}{2}, \pm \frac{1}{2}\rangle$ state with its cigar shaped charge density, in agreement with the ordered moment in the $ab$ plane and many earlier studies (see e.g. Refs. [34][39]). In the experiment, however, some dichroism is missing and this was seen in several repeated measurements performed on freshly cleaved samples. According to Givord et al. the $2F_\pm$ should contribute to the ground state so that we performed a full multiplet calculation for a mixed ground state, but we find that the multiplet mixing cannot account for the discrepancy between data and simulation (see the simulation of coherent sums [58] of $|\frac{7}{2}, \pm \frac{1}{2}\rangle$ and $|\frac{5}{2}, \pm \frac{1}{2}\rangle$ in Appendix [VI D] where we also show the simulations of the pure $|\frac{7}{2}, J_z\rangle$ states). We will come back to the missing dichroism in Section IV.

Next we gain some information about excited states from XAS measurements at elevated temperatures (see...
FIG. 4. CeRh₃B₂ RIXS data acquired on I21, with the experimental geometries and incident photon energy hν indicated in the insets (the isotropic XAS spectrum shown was acquired during the experiment). The lines show the fit of the hν = E_{cen} data, used to determine the crystal-field splitting energies. The inelastic peaks were fitted using Voigt curves, to take into account their intrinsic finite broadening, while the elastic line at 0 meV, mostly due to non-resonant elastic processes, was fitted with a resolution limited 40 meV-FWHM Gaussian.

The T-dependent data reveal at first no change in dichroism up to 160 K so that we can exclude low lying states. At 300 K the dichroism has decreased. We can exclude the partial population of the $|\frac{5}{2}, \pm \frac{3}{2}\rangle$ state because it is as high as $\approx 150$ meV according to neutron scattering [36] and it has the same, although weaker polarization dependence than the ground state (compare inset of Fig. 2). The $|\frac{5}{2}, \pm \frac{5}{2}\rangle$, on the other hand, has a strong opposite dichroism and, if its energy were of the order of 50 meV, it would already be partially populated at 300 K, and thus reduce the net dichroism. It should be noted that due to the selection rules of inelastic neutron scattering, $\Delta J_z = 0, \pm 1$, a ground state excitation to a $|\frac{5}{2}, \pm \frac{5}{2}\rangle$ state has zero cross-section.

B. RIXS data at room temperature

The XAS data have shown that there are no crystal-field states lower than 30 meV so that at room temperature the population of excited states is still minor. This allows us to start with the discussion of the room temperature data that are well above the Curie temperature, thus avoiding the possible presence of magnon excitations. Figure 4 shows two RIXS spectra of CeRh₃B₂ acquired at beamline I21 at 295 K. The respective scattering geometries are sketched in the insets. The full circles refer to incident energies hν = E_{cen}, the open circles to hν = E_{cen} + 1 eV as depicted in the inset with the $M_5$ absorption edge. The data with hν = E_{cen} + 1 eV were multiplied by three to compensate for the reduction of the cross section when using an incident energy on the tail of the absorption resonance. The comparison of the three data sets demonstrates the cross-section dependence of the RIXS signal and how it allows the identification of the seven expected peaks: the elastic at zero energy transfer and six excitations from the ground state into the excited crystal-field states, two within the Hund’s rule ground state $^2F_{5/2}$ and another four into the excited multiplet $^2F_{7/2}$.

The energies of the crystal-field states were determined more precisely by fitting the spectra with Fityk [51]. The elastic peak at 0 meV was modeled with a Gaussian function of resolution width. The excitations, visibly broader than the elastic signal, probably due to hybridization effects, were modeled with Voigt profiles. The widths were treated as free parameters with an equally constraint. The width turned out to be 72 ± 8 meV. This way we found for the peak positions 0 ± 6, 56 ± 6, 130 ± 6, 267 ± 5, 321±4, 378±4 and 464±10 meV, where the errors take into account the uncertainties of the peak fitting and the absolute energy scale of the experiment. The estimate of the last peak position suffers of a further uncertainty due to the choice of the line used to model the background.

C. RIXS T-dependence

Figure 5 shows the temperature dependence of the RIXS spectra for the same scattering geometry and energies as in the right hand panel of Fig. 4, hν = E_{cen} (top) and hν = E_{cen} + 1 eV (bottom). Some parts of the spectra exhibit a strong temperature dependence others lesser so. The peak at 260 meV does not seem to shift with temperature and, most importantly, it does not broaden when entering the ferromagnetic phase so that the Zeeman splitting of the Kramers doublets does not seem to be important. The peaks at about 150 meV, at about 400 meV, and also the highest peak are shifted by about 50 meV to higher energy transfers. In RIXS, we further observe that the relative peak intensities are strongly affected by temperature. Data with better resolution and also smaller temperature intervals were taken on ID32 (see Appendix VI E). The smaller temperature
RIXS simulations for all six parameter sets using the scattering intervals show that these spectral changes are gradual with $T$.

D. Crystal-field simulation of RIXS data

The phase space ($A^0_1, A^0_4, A^0_6, A^0_8$) was searched for sets of crystal-field parameters that provide the energy splittings obtained from the empirical fit to the data at room temperature. The $A^0_8$ was not scanned because it is less important for the transition energies. Its main impact is the mixing of the $|\frac{7}{2}, \pm \frac{5}{2}\rangle$ and $|\frac{7}{2}, \mp \frac{5}{2}\rangle$. The search procedure is described in detail in the Appendix VI F. It turns out that six clusters of parameters yield the correct ground state. The word *majority* connotes that there is also some contribution from the $^2F_{\frac{7}{2}}$ multiplet. The RIXS simulations for all six parameter sets using the scattering geometries of the data in Fig. 4, with $h\nu = E_{cen}$, $\phi = 90^\circ$ and $105^\circ$, are shown in the Appendix VI H. The RIXS calculations have taken into account the appropriate temperature but excitations from excited states turned out to have negligible intensities so that only the ground state excitations are indicated. The parameter sets that correspond to models with a $|\frac{5}{2}, \pm \frac{5}{2}\rangle$ or $|\frac{5}{2}, \pm \frac{3}{2}\rangle$ ground state can be excluded because they contradict the findings from XAS, and only one of the two models with a $|\frac{5}{2}, \pm \frac{5}{2}\rangle$ ground state has a $|\frac{5}{2}, \pm \frac{3}{2}\rangle$ excited state at 120 meV which is close to the energy of the peak seen in inelastic neutron scattering at room temperature [36]. This is the model that will be further discussed. It corresponds to the red simulation in the Appendix VI H and is displayed in Fig. 6.

The crystal-field model in Fig. 6 with a (majority) $|\frac{5}{2}, \pm \frac{5}{2}\rangle$ ground state and the $|\frac{5}{2}, \pm \frac{3}{2}\rangle$ state at about 120 meV, has a majority $|\frac{5}{2}, \pm \frac{5}{2}\rangle$ at 54 meV. Thus, this model agrees with our working hypothesis derived from the temperature dependence of the XAS data. The crystal-field level scheme and corresponding wave functions are listed on in Table I (left).

We then adjusted the crystal-field parameters of the model above to fit the RIXS data from I21 and I32 at all temperatures (see Appendix VI E). The resulting crystal-field wave functions and energy splittings at 20 K are also given in Table I (right). It is apparent that the multiplet mixing with the $^2F_{\frac{7}{2}}$ multiplet in the ground state has increased considerably. Table III and IV in the Appendix VI H summarize the corresponding crystal-field parameters and transition energies at all temperatures.

IV. DISCUSSION

A. Orbital quenching

We find that the total crystal-field splitting of the lower multiplet amounts to about 150 meV, thus setting the scale for the strength of the crystal-field potential in CeRh$_3$B$_2$. Although larger than the usual values of $\leq$50 meV, it is still significantly smaller than the spin-orbit interaction separating the two multiplets ($\approx$280 meV). We thus do not confirm the *giant* crystal-field scenario by Givord et al. with a strongly multiplet mixed ground state (10%) and strongly reduced in-plane moment as a consequence [34, 36].

The crystal-field splitting is nevertheless large enough to cause some mixing of the two multiplets. Comparing the wave functions at room temperature and low $T$ in Table I shows that the multiplet mixing increases upon cooling. The 0.4% contribution of the higher multiplet in the ground state at room temperature has increased to about 5% at 20 K. This mixing is not large enough to cause a complete breakdown of the L-S-J coupling scheme, but it modifies the orbital and spin moments of the ground state.

In general, a $|\frac{5}{2}, \pm \frac{1}{2}\rangle$ ground state can be written as $a |L_z = 0, S_z = \pm \frac{1}{2}\rangle + b |L_z = \pm 1, S_z = \mp \frac{1}{2}\rangle$, with $a^2 + b^2 = 1$. In Table II, the coefficients that we find from the RIXS analysis and the resulting expectation values $\langle L_z \rangle = \pm b^2$ and $\langle S_z \rangle = (\pm a^2 \mp b^2) \times = \frac{1}{2}$, as well as the magnetic moments in the basal ab plane are compared to the values in the absence of multiplet mixing. Note, in the absence of multiplet mixing $\langle L_z \rangle$ and $\langle S_z \rangle$ have opposite signs. At room temperature the expectation values are similar to the unmixed case, but at 20 K the multiplet mixing causes an increase of the $|L_z = 0, S_z = \pm \frac{1}{2}\rangle$ part in the ground state, with a consequent reduction of $\langle L_z \rangle$ and with spin and orbital moments having the same sign. We find therefore a partial quenching of the angular moment induced by the increasing crystal-field strength with decreasing temperature, but to a lesser extent than what was discussed in the frame work of bandstructure.

![Image](attachment:Figure_5.png)

**FIG. 5.** Temperature dependence of CeRh$_3$B$_2$ experimental RIXS spectra with incident photon energies $h\nu = E_{cen}$ and geometries as in Fig. 4.
The thermal population of excited states has been considered but only the ground state excitations are indexed because the intensity of non-ground state excitations is negligible. Here the set of parameters is used that describes the data best. It corresponds to the level scheme in Table I, see Appendix VII for the crystal-field parameters.

To summarize, the unbalance of spin and orbital moments can partially account for the moment reduction in the basal plane (see Table II) but not for the entire reduction to $0.45\mu_B$ as suggested in the giant crystal-field scenario proposed by Givord et al. [34, 35].

**B. Kondo effect**

Our *full-multiplet–crystal-field–only* analysis provide a reasonable description of the experimental XAS and RIXS data although there are some discrepancies in the low $T$ dichroism of the XAS spectra and transition matrix elements in the RIXS data, respectively. We believe that these deviations are due to Kondo-type hybridization effects [32, 38-32, 54] that are not accounted for in our simulation. A hybridization-induced mixing of crystal-field levels, as discussed for example in literature [33, 35, 50], could enhance some of the cross-sections that appear too small in the single-ion approach with its pure $|J_z = \pm 1/2\rangle$ ground state.
We start with the discussion of the missing dichroism in the XAS data at 20 K that cannot be explained by thermal population of excited states because the first excited state is as high as 66 meV (see Table I). However, such a high lying state can be mixed into the ground state when the Kondo temperature is sufficiently high, and this is indeed the case for CeRh$_3$B$_2$ which has a Kondo temperature of 400 K [12, 19]. Hence, the $|\frac{5}{2}, \pm \frac{3}{2}\rangle$ state at 66 meV will contribute to the ground state and thus reduce the net polarization because it has a strong and opposite polarization dependence (see inset of Fig. 2).

A more detailed comparison of data and RIXS calculation in Fig. 6 shows that the intensities for transitions with $\Delta J_z = \pm 2$ are underestimated in the simulation, and the transition with $\Delta J_z = \pm 3$ should have no cross-section at all but it exists in the experiment. These are the transitions into (majority) $|\frac{5}{2}, \pm \frac{3}{2}\rangle$, $|\frac{5}{2}, \pm \frac{5}{2}\rangle$, and $|\frac{7}{2}, \pm \frac{5}{2}\rangle$ states. This cannot be fixed by adjusting the $A^6_0$ parameter that mixes the $|\frac{7}{2}, \pm \frac{5}{2}\rangle$ and $|\frac{7}{2}, \mp \frac{5}{2}\rangle$. The thermal occupation of the excited states is also taken care of in the simulation so that something else must be missing in the calculation. We believe that also here we see the impact of the Kondo effect, namely the Kondo-induced mixing of the first excited state into the ground state. The presence of some $|\frac{5}{2}, \pm \frac{3}{2}\rangle$ in the ground state would then allow $\Delta J_z = 0$ and $\pm 1$ transitions into the before-mentioned states, and these transitions usually have a stronger cross-section than $\Delta J_z = \pm 2$ transitions [45]. This explanation is supported by revisiting the inelastic neutron data of Givord et al. In their spectra (see Fig. 2 in [36]), some unidentified scattering occurs at about 60 meV, i.e. at the energy of the $|\frac{5}{2}, \pm \frac{5}{2}\rangle$ state, and this transition can only be seen with neutrons when the ground state has components different from $J_z = \pm 1/2$.

C. Low impact of Rh $4d$ states

We next discuss the temperature dependence of the crystal-field energies. They are summarized in Figure 7 (see also Table IV). Also here the states are indexed according to their majority $|J, \pm J_z\rangle$ contribution. The corresponding charge densities are shown on the right. It turns out that the energy difference of ground state and the states with charge densities in the basal plane or along the $c$ axis remain unaffected by cooling and the shortening of the $c$ axis that goes along with it. This is very different for the states $|\frac{3}{2}, \pm \frac{3}{2}\rangle$, $|\frac{5}{2}, \pm \frac{5}{2}\rangle$, $|\frac{7}{2}, \pm \frac{5}{2}\rangle$ states that have charge densities extending out of the hexagonal $ab$-plane, away from the $c$ direction, and towards the Rh ions (see Fig. 1). The energy of these states increases upon cooling as much as 50 meV. This effect becomes even more apparent when comparing the crystal-field level scheme of CeRh$_3$B$_2$ with that of pseudo-hexagonal CeRh$_3$Si$_2$ [45]. The latter compound is a low $T_K$ Kondo system that orders antiferromagnetically with $T_N \leq 4.7$ K [57]. In CeRh$_3$Si$_2$ the Ce–Ce distances are distinctively larger than in CeRh$_3$B$_2$ (see lattice constants in Appendix IV) and the Ce orbitals that point towards the Rh ions are lower in energy (see Fig. 7). Hence, the shorter the Ce–Ce distances (when going from CeRh$_3$Si$_2$ to CeRh$_3$B$_2$ at room temperature, and upon cooling in CeRh$_3$B$_2$ to enter the ferromagnetic regime), the higher in energy the Ce orbitals pointing to the Rh ions become i.e. these orbitals become less important for the ground state properties. In short, Rh states play a marginal role to induce the ferromagnetism and/or Kondo hybridization.

It should be pointed out that the Zeeman splitting cannot be responsible for the temperature dependence of the crystal-field states. The full multiplet calculation with an exchange-field in the basal plane shows that only the two $|J, \pm \frac{5}{2}\rangle$ states are Zeeman split but their energies are not subject to changes with temperature nor does the line width or shape of the $|\frac{5}{2}, \pm \frac{3}{2}\rangle$ change with $T$ (see Fig. 5).
D. Impact of $4f \mid J_z = \pm \frac{1}{2} \rangle$ states

![Diagram showing the crystal-field potential](image)

**FIG. 8.** Effective angular part of the crystal-field potential as calculated from weighing the sums of the spherical harmonics with the respective crystal-field parameters. The potentials, depicted on the Ce sites in the hexagonal unit cell of CeRh$_3$B$_2$ at 320 and 20 K, and in the pseudo-hexagonal unit cell of CeRh$_3$Si$_2$, have the same relative arbitrary scale. The blue (red) color indicates the directions more (less) favorable for the electrons. The Si compound has the distinctively larger $c$ parameter (see Fig. 5 in Appendix VI). Figure 8 summarizes the effect of the crystal-field potentials over a Ce site in the crystal structure. Shown are the effective angular parts of the crystal-field potentials (in which the expectation values of the radial part are included in the coefficients) using the sum of spherical harmonics $C_{lm}^{\theta \phi}$, weighted with the $A_{lm}$ parameters from Table III for CeRh$_3$B$_2$ and from Ref. 45 for CeRh$_3$Si$_2$. The same (arbitrary) scale within the unit cell is used for the three plots. The relative sizes cannot be understood intuitively due to the complex and non-linear relationship of the crystal-field parameters and splittings (see Table III and IV). The directions more energetically favorable for the $4f$ electrons are indicated in blue, and the least favorable in red. These plots show that the crystal-field potential stabilizes the $\pm \frac{1}{2}$ in CeRh$_3$B$_2$ at low $T$ with respect to room temperature, and especially with respect to the RKKY compound CeRh$_3$Si$_2$. This confirms that the dominant interactions are along the Ce-Ce chains in the $c$ direction.

E. Ab-initio DFT calculations

To substantiate our empirical findings, we performed *ab-initio* DFT calculations. Our aim is to find the material-specific parameters that can be used in the periodic Anderson impurity model (pAIM) for CeRh$_3$B$_2$. The DFT calculations are non-spin polarized and fully relativistic with the Ce $4f$ states included as itinerant bands. We used the full potential local-orbital (FPLO) code [58] with a $12 \times 12 \times 12$ $k$ mesh for the Brillouin zone integration. After full self-consistency, we followed a standard downfolding protocol (see e.g. [58]) to project the converged Kohn-Sham states to a Wannier basis which consists of the Ce-$4f \mid J_z$ states as well as all Rh $4d$, B $sp$, and Ce $5d$ bands in an energy window from $-10\text{eV}$ to $10\text{eV}$ around the Fermi level. We thus obtained $\varepsilon_{J_z}$ as the on-site energy of the local Ce $4f$ states (including the local crystal-electric field potentials), $\varepsilon_{c,k}$ which denotes the dispersion relation of the uncorrelated conduction electrons (with the index $c$ labeling the Rh $4d$, B $sp$, and Ce $5d$ orbital character), and $V_{J_z,c}(k)$ which describes the hopping integral between the Ce $4f$ and the conduction electrons. These quantities from the downfolding process are input for the periodic Anderson impurity model, see Appendix VI.

From $\varepsilon_{c,k}$ we get directly the Green’s function $G_{0}^{c}(\omega,k)$ and the partial density of states $\rho_{c}^{0}(\omega,k) = -1/\pi \text{Im}[G_{0}^{c}(\omega,k)]$ of the uncorrelated conduction electrons. Here the superscript "0" denotes that these quantities refer to the uncorrelated part of the Hamiltonian. We note also that the partial density of states of these downfolded bands is not to be confused with the original DFT partial density of states since in DFT the hybridization between the Rh $4d$, B $sp$, and Ce $5d$ bands with the Ce $4f$ states is included. We will also make use of the quantity $A_{J_z}(\omega,k) = \sum_{\omega} |V_{J_z,c}(k)|^2 G_{0}^{c}(\omega,k)$, which is the so-called hybridization function and describes the effective hybridization strength of the downfolded Ce-$4f$ and uncorrelated electron bands as function of momentum and energy. A more concise mathematical description of this procedure is presented in Appendix VI.

For our analysis we have performed calculations for the strongly intermediate valent superconductor CeRu$_3$B$_2$ ($T_{K} \approx 2000\text{K}$), the high $T_c$ ferromagnet CeRh$_3$B$_2$ ($T_{K} \approx 400\text{K}$) that is subject of the present manuscript, and the pseudo-hexagonal low $T_{K}$ RKKY system ($T_{N} = 4\text{K}$) CeRh$_3$Si$_2$ (see Fig. 6(a)–(f)). The two boron compounds have small Ce-Ce distances, and the Si compound has the enlarged $c$ parameter.

At first we discuss our results in a large energy window of about $10\text{eV}$ around the Fermi energy $\epsilon_F$. While the hybridization at these energies is not directly related to the Kondo effect, it is relevant for the magnetic interactions (Fig. 9(a)–(c)). The top of the respective panels shows the $k$-integrated $\rho_{c}^{0}(\omega)$ of CeRu$_3$B$_2$ (a), CeRh$_3$B$_2$ (b), and CeRh$_3$Si$_2$ (c) with the downfolded Ce-$5d$ states in blue, Rh or Ru $4d$ states in orange, Rh or Ru $4p$ states in green, and B or Bi $s$, $p$, and $d$ states in brown. The bottom of the panels shows the $k$-integrated hybridization functions $\Delta_{J_z}(\omega)$ for the respective $\mid \frac{5}{2}, \pm \frac{1}{2} \rangle$ (purple), $\mid \frac{5}{2}, \pm \frac{3}{2} \rangle$ (brown), and $\mid \frac{5}{2}, \pm \frac{5}{2} \rangle$ (blue) Kramer’s doublets.

We find for the two boron compounds, (a) and (b), that the $\mid \frac{5}{2}, \pm \frac{1}{2} \rangle$ state shows very strong hybridization at energies where the Ce $5d$ states also show a very high $\rho_{c}^{0}(\omega)$ (see yellow stars). We recall that this is the state that contributes most to the near ground state of CeRh$_3$B$_2$ according to our XAS and RIXS measurements. On the other hand, we cannot identify such overlap of strong hybridization and strong $\rho_{c}^{0}(\omega)$ for Rh $4d$ (or Ru $4d$) states above $\epsilon_F$ (see blue stars). This hints towards an important entanglement of the electrons in the Ce $5d$ and Ce $4f \mid \frac{5}{2}, \pm \frac{1}{2} \rangle$ states for the magnetic interaction that in case of CeRh$_3$B$_2$ leads to a ferromagnetic ground state. This is contrasted by the transition metal $4d$ electrons that seemingly do not contribute to the formation of mag-
-centric order.

FIG. 9. Top of each panel: calculated \( \rho_e^0(\omega) \) of the downfolded Ce 5d states in blue, Rh or Ru 4d states in orange, Rh or Ru 4p states in green, and B or Si s, p, and d states in brown. Bottom of each panel: calculated hybridization function \( \Delta_{J_z}(\omega) \) of the three lowest Kramer’s doublets for CeRu\(_3\)B\(_2\) (left), CeRh\(_3\)B\(_2\) (middle), CeRh\(_3\)Si\(_2\) (right). Panels (a)–(c) display the larger energy scale that is most relevant for the magnetic exchange, while panels (d)–(f) expand the region close to the Fermi level \( \epsilon_F \) that is most relevant for the Kondo physics.

The above is in agreement with the suggestion of Takegahara et al.\(^{30}\), Kasuya et al.\(^{31,32}\), and Yamaguchi et al.\(^{37,38}\) that inter-site Ce–Ce hopping of Ce 4f/\( \pm \frac{1}{2} \) (\( f_0 \) in their nomenclature) and Ce 5d electrons in combination with intra-atomic 5d–Ce 4f/\( \pm \frac{1}{2} \) exchange is responsible for the ferromagnetism with high Curie temperature. We do not agree, though, with their suggestion that Ce 4f-Rh 4d hybridization is important.

The zoom to the energy window closer to \( \epsilon_F \), which is most relevant for the Kondo interaction, highlights the differences of the two boron compounds. In CeRu\(_3\)B\(_2\) (panel (d)), the \( \frac{5}{2}, \frac{3}{2} \) state, the state with charge densities pointing towards the transition metal ions (here Ru), has a pronounced maximum at \( \epsilon_F \) where the Ru 4d states have a very high \( \rho_e^0(\omega) \). Hence, in CeRu\(_3\)B\(_2\) the Kondo effect is triggered by the Ru 4d and Ce 4f/\( \pm \frac{3}{2} \) electrons and is strong enough to overcome any instability to magnetic order. This is contrasted by CeRh\(_3\)B\(_2\) (panel (e)) where we find that close to \( \epsilon_F \) the hybridization functions are generally reduced, and also the \( \rho_e^0(\omega) \) of the transition metal Rh 4d is much lower. Hence, in CeRh\(_3\)B\(_2\) the magnetic order prevails. This is very much in line with the interpretation of the substitution series Ce(Ru\(_{1-x}\)Rh\(_x\))\(_3\)B\(_2\) by Allen et al.\(^{19}\).

Nevertheless, also in CeRh\(_3\)B\(_2\) some the Kondo interaction is present and sufficiently strong to reduce the magnetic moments. In contrast to CeRu\(_3\)B\(_2\), we find in CeRh\(_3\)B\(_2\) that the 4f/\( \pm \frac{3}{2} \) with charge densities in the \( ab \) plane are most strongly hybridized at \( \epsilon_F \) accompanied by peaks in the \( \rho_e^0(\omega) \) of B sp that are located in the same plane. Hence, in CeRh\(_3\)B\(_2\) it seems that the Kondo effect is mainly triggered by hybridization in the \( ab \) plane of the disk-like \( |\frac{5}{2}, \frac{3}{2}\rangle \) states with the B sp electrons. The hybridization of Ce 4f/\( \pm \frac{5}{2} \) and \( |\frac{5}{2}, \pm \frac{1}{2}\rangle \) and Rh 4d states, in contrast, seems to be significantly less important. This interpretation of the hybridization function is supported by the experimental findings of the presence of the Ce 4f/\( \pm \frac{5}{2} \) in the ground state and the energetically expensive Ce 4f/\( 2, \pm \frac{3}{2}\rangle \) states in CeRh\(_3\)B\(_2\). It would be an interesting task for future work to find out where in energy the Ce 4f/\( \pm \frac{5}{2} \) states of CeRu\(_3\)B\(_2\) are in a total energy diagram.

Finally, CeRh\(_3\)Si\(_2\) (see Fig. 9 (e) & (f)) shows an overall reduced hybridization function, completely in line with its antiferromagnetic RKKY (i.e. weak hybridization limit in Doniach’s picture) ground state.

V. CONCLUSION

The full crystal-field scheme of CeRh\(_3\)B\(_2\) has been determined with XAS and RIXS. We confirm the Ce 4f/\( \pm \frac{5}{2} \) ground state and find a large but not giant crystal-field splitting. Consequently, the J-L-S coupling scheme remains basically intact despite some multiplet mixing and consequent quenching of the orbital moment. The \(^2\)F\(_{5/2} – ^2\)F\(_{7/2}\) multiplet mixing is not sufficient to explain the reduced magnetic moments. The interpretation of the temperature dependence of the crystal-field level scheme and the comparison with the level scheme of the RKKY-system CeRh\(_3\)Si\(_2\) shows that the dominant interaction is along the Ce-Ce chains along \( c \), and that a contribution of the Rh 4d electrons to the ground state is unimportant. We further find some Kondo induced mixing of the Ce 4f/\( \pm \frac{5}{2} \) into the ground state. The experimental findings are used to focus on the relevant projections in the DFT calculations of the uncorrelated conduction bands and the computation of the hybridization functions of the lowest three Kramer’s doublets. The calculations also show that the Rh 4d electrons are not responsible for the ferromagnetic state and that they are of lesser importance for the Kondo interaction. We conclude that the inter-atomic hybridization of the Ce 4f/\( \pm \frac{5}{2} \) and Ce 5d states in combination with intra-atomic 4f–5d exchange set up the ferromagnetic state, while hybridization of the Ce 4f/\( \pm \frac{3}{2} \) and the B sp in
the \( ab \)-plane trigger the Kondo interaction that strongly reduces the magnetic moment. The co-existence of high Curie temperature and high Kondo temperature can thus be traced back to the presence of two different \( Ce 4f \) orbitals, i.e. the \( \frac{3}{2}, \pm \frac{1}{2} \) and \( \frac{5}{2}, \pm \frac{3}{2} \), each having their own unique coupling to the different bands in \( CeRh_3B_2 \).

VI. APPENDIX

A. Crystal growth

The single crystals of \( CeRh_3B_2 \) were grown by Czochralski in a tri-arcs furnace under high quality argon atmosphere and annealed under ultra high vacuum at 950°C for 10 days. The crystals come from the same lab as the samples used in Ref. [34, 35, 59]. Single-crystallinity and orientation were verified with a Laue camera prior to all experiments, XAS and RIXS.

B. Experimental set-up

1. XAS

The \( M \)-edge (\( 3d^{10}4f^1 \rightarrow 3d^{9}4f^2 \)) XAS experiments on \( CeRh_3B_2 \) were performed at the Dragon (bending magnet) beamline at the NSRRC (National Synchrotron Radiation Research Center) in Hsinchu, Taiwan. Measurements were performed with the electric-field vector being \( \vec{E} \parallel c \) and \( \vec{E} \perp c \). This was achieved by using a rotatable sample holder. For all measurements the sample was rotated four times by 90°, so that for each polarization two equivalent positions were measured. The comparison of these spectra ensured a proper orientation of the sample with respect to the polarization vector. The spectra were recorded with the total electron yield (TEY) method and normalized to the incoming flux that was measured on a gold mesh. The energy resolution was set to 0.4 eV and the degree of linear polarization was \( \approx 98\% \) [40].

2. RIXS

The \( M \)-edge RIXS process encounters the absorption process \( 3d^{10}4f^1 \rightarrow 3d^{9}4f^2 \), immediately followed by the corresponding \( 4f \rightarrow 3d \) resonant emission. After this two photon process, an excitation can be left in the sample in the final state. For example, the electron in the \( 4f \) shell of the \( Ce^{3+} \) ion can occupy an excited crystal-field state, and the corresponding excitation energy will be detectable as an energy loss of the scattered photon. Each peak in the energy loss spectrum will therefore correspond to a crystal-field excitation with that energy. The RIXS cross section dependence on the incident photon energy (across the \( \approx 2 \) eV-wide range of the \( M_5 \) edge) and on the scattering geometry provides the possibility to enhance or suppress excitations. Horizontal incident polarization (\( \pi \)) was used to minimize the contribution of elastic scattering around 0 eV. The incident energies \( h\nu \) were chosen at the centre of the \( M_5 \)-edge (\( h\nu = E_{cen} \)) or 1 eV above (\( E_{cen} + 1 \) eV), the analyzer was positioned at 120° away from forward scattering, and the sample was turned either perpendicular (90°) to the incoming beam or to 105° (see insets in Fig. 4).

RIXS experiments were performed at the two state-of-the-art high resolution soft-RIXS beamlines I21 beamline at Diamond Light Source in the UK [46] and ID32 at European Synchrotron Radiation Facility (ESRF) in France [47]. At I21 data were taken at 15, 135, and 295 K, at ID32 measurements were performed with smaller temperature intervals, namely 20, 80, 165, 250, and 318 K. At both beamlines, the \( CeRh_3Si_2 \) single crystals were post-cleaved in vacuum at room temperature just prior to inserting the sample in the measurement chamber (\( P \approx 10^{-10} \) mbar). The resolution and zero energy were determined by measuring a carbon tape before and after the acquisition of the spectra. At ID21 the resolution was \( \approx 40 \) meV and at ID32 \( \approx 30 \) meV. The I21 and I32 data are presented in different ways: the data from I21 are shown with the intrinsic smoothing coming from the use of CCDs sensors for x-ray detection [60] whereas the ID32 data are presented in the so-called single photon counting algorithm where this intrinsic smoothing has been removed. The latter is necessary to achieve the highest experimental resolution of 30 meV and to extract realistic statistical error bars [61].

C. Full multiplet calculation

The XAS and RIXS data were simulated with full multiplet calculations using the QUANTY code [48]. In the calculations, the Slater integrals for the electron–electron interactions in the final (XAS) or intermediate (RIXS), respectively, 3d\(^9\)4f\(^2\) state, as well as the 3d and 4f spin-orbit parameters, were obtained from the Robert D. Cowan’s Atomic Structure Code [62]. Reduction factors take care of configuration interaction effects that are not included in the Hartree-Fock scheme. For the RIXS calculation the parameters were optimized to best reproduce the peak positions. The 4f spin-orbit parameter was reduced to about 86% of the value calculated for an isolated ion. The \( F_{ij} \) integrals for the intermediate RIXS state were scaled to 55% and the \( F_{df} \) and \( G_{df} \) integrals to 75% of their calculated value, having been tuned by fitting the isotropic XAS spectrum. The same values were used for calculating the XAS spectra of the pure \( |J, J_z\rangle \) states.

D. XAS simulation of pure \( J_z \) states

The left of Fig. 10 shows the simulations for the XAS spectra of the pure \( |J, J_z\rangle \) states. On the right, we com-
pare the simulation for a pure $|\frac{5}{2}, \pm \frac{1}{2}\rangle$ and for the multiplet mixed ground state at 20K, $\alpha \cdot |\frac{5}{2}, \pm \frac{1}{2}\rangle + \sqrt{1 - \alpha^2} \cdot |\frac{7}{2}, \mp \frac{1}{2}\rangle$ with $1 - \alpha^2 = 5\%$ that we obtain from the crystal-field analysis of the RIXS spectra at 20K (see Table I). Although the multiplet mixing does reduce the dichroism, this reduction is not sufficient to explain the XAS spectra at low $T$ (see Fig. 2).

E. RIXS data from ID32

Figure 11 shows the RIXS spectra of CeRh$_3$Si$_2$ measured on ID32 at ESRF. Data were taken at 320, 250, 165, 80, and 20 K. The data were taken with the geometry as in in Fig. 4 (left) and are extracted in the single photon algorithm (see above) so that we can give a statistical error which is here about the size of the circles representing the data points. Also here the peaks at 130, 160, and 295 meV move to higher energy transfers upon cooling, the other energies show only a minor temperature dependence. The colored dots at the top of Fig. 11 indicate the peak positions at the various temperatures between 320 K and 20 K, as estimated by Voigt fits. There is no sudden change of energies at $T_C$.

The lines in Fig. 11 are the result of crystal-field calculations (see text above) with the parameters in Table IV.

F. Finding crystal-field parameters and solutions

The $A_{0}^{3}$, $A_{0}^{5}$, and $A_{0}^{7}$ were scanned with a $41 \times 31 \times 31$ mesh in the region shown in Fig. 12. The $A_{0}^{3}$ parameter was found to have a minor effect on the crystal-field energies, and was scanned in steps of 0.15 eV between $-0.6$ eV and 0.6. The spheres in Fig. 12 represent the solutions compatible with the measured splittings (allowing for a $\pm 10$ meV error to ensure that all possible solutions
with similar splittings are found, despite the finite grid spacing used to span the parameter space).

The solutions are grouped in 6 regions of the phase space, which correspond to the 6 possible arrangements in energy of the three \(|J_z = \pm \frac{1}{2}\), \(|J_z = \pm \frac{3}{2}\) and \(|J_z = \pm \frac{5}{2}\) doublets of the lowest \(J = \frac{3}{2}\) multiplet. The corresponding orders of the first three \(|J_z\) states are indicated in Fig. 14 where we present the RIXS calculations for the 6 different sets of crystal-field parameters and compare them with the I21 experimental data of Fig. 13 for \(\hbar \nu = E_{cen}\). The sets of \(A_k^n\) parameters correspond to the centers of gravity of each of the 6 regions in Fig. 12. The simulations are shown only for the inelastic region because the elastic intensity in the experimental spectra may strongly depend on the surface roughness and cannot be reliably calculated. We have excluded all solutions with the exception of the red solution (top left, respectively) based on knowledge of previous findings: the ground state has to have \(\pm J_z = \pm \frac{1}{2}\) symmetry and the state at about 130 meV has to be a \(\pm J_z = \pm \frac{3}{2}\) state to be observable with inelastic neutron scattering [36]. The red simulation fits the data reasonably well (see text above).

G. Lattice data

FIG. 13. Lattice parameters of CeRh3B2 and of pseudo-hexagonal CeRh3Si2 from low \(T\) to room temperature, (top) unit cell volume, (middle) hexagonal \(c\) parameter, and (bottom) hexagonal \(a\) parameter. The data of the boron compound are adapted from Ref. [41] and of the silicon compound are calculated from the orthorhombic values given in [45].

In CeRh3Si2 the orthorhombic distortion is small so that it can be considered as pseudo-hexagonal when using the orthorhombic \(a\) axis as the hexagonal \(c\)-axis \((c_{hex})\) [45]. The comparison of the (pseudo)hexagonal lattice parameters of CeRh3B2 and CeRh3Si2 as function of temperature shows that the unit cell expands upon replacement of B by Si mainly due to expansion along the hexagonal \(c\) axis i.e. due to the larger Ce–Ce distances in the Si compound (see Fig. 13).

H. Crystal-field parameters and energies at all temperatures

Table III and IV list the crystal-field parameters and energies for all temperatures that correspond to the solution discussed in the main text. In Table IV the wave functions are labeled according to their majority \(J_z\) contribution.

TABLE III. Crystal field parameters (in meV) and spin-orbit interaction rescaling used for the RIXS simulations best fitting the data.

| Parameters      | ID32 | I21 |
|-----------------|------|-----|
| 318 K           | -85  | -80 |
| 250 K           | -76  | -73 |
| 165 K           | -70  | -69 |
| 80 K            | -69  | -60 |
| 20 K            | -13  | 113 |
| 295 K           | 150  | 150 |

\(\zeta_{SO}\) (%)

| Temperature (K) | 318 K | 250 K | 165 K | 80 K | 20 K | 295 K |
|-----------------|-------|-------|-------|------|------|-------|
| I21             |       |       |       |      |      |       |
| 318 K           | 87    | 87    | 87    | 86   | 85   | 87    |

TABLE IV. Crystal-field scheme and splitting energies (in meV) resulting from the simulations best fitting the data.

| Crystal field states | ID32 | I21 |
|---------------------|------|-----|
| \(|J, J_z|\)       | 318 K | 250 K | 165 K | 80 K | 20 K | 295 K |
| \(|\frac{5}{2}, \pm \frac{1}{2}|\) | 0     | 0     | 0     | 0    | 0    | 0     |
| \(|\frac{5}{2}, \pm \frac{3}{2}|\) | 54    | 56    | 58    | 62   | 66   | 54    |
| \(|\frac{5}{2}, \pm \frac{5}{2}|\) | 120   | 126   | 136   | 153  | 166  | 125   |
| \(|\frac{3}{2}, \pm \frac{1}{2}|\) | 262   | 263   | 266   | 267  | 270  | 263   |
| \(|\frac{3}{2}, \pm \frac{3}{2}|\) | 323   | 317   | 319   | 318  | 321  | 323   |
| \(|\frac{3}{2}, \pm \frac{5}{2}|\) | 375   | 377   | 388   | 400  | 413  | 376   |
| \(|\frac{5}{2}, \pm \frac{1}{2}|\) | 466   | 464   | 474   | 484  | 497  | 464   |
I. \textit{Ab-initio} derivation of parameters for the periodic Anderson impurity model

The periodic Anderson impurity model (pAIM) contains the following terms:

\begin{equation}
\hat{H}\text{pAIM} = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} \hat{n}_{\mathbf{k}}^{\pm} + \sum_{\mathbf{i}} \varepsilon_{f_{\mathbf{i}}} \hat{n}_{f_{\mathbf{i}}}^{\pm} + \sum_{\mathbf{i}} U \hat{n}_{f_{\mathbf{i}}}^{\dagger} \hat{n}_{f_{\mathbf{i}}} + \sum_{i, \mathbf{k}} V_{J_{z,c}}(\mathbf{k})(f_{i}^\dagger c_{\mathbf{k}} + h.c.) + \mu \hat{n}_{\text{tot}}
\end{equation}

Here, $\varepsilon_{\mathbf{k}}$ is the dispersion relation of all uncorrelated conduction electrons, $\varepsilon_{f}$ stands for the on-site energy of the impurity levels (including local crystal electric field potentials), $U_{i}$ is the impurity on-site interaction, $V_{i,\mathbf{k}}$ is the coupling of impurity- and conduction orbitals and $\mu$ is the chemical potential. $\hat{n}$ are fermionic density operators, $N_{\text{tot}} = \hat{n}_{\uparrow} + \hat{n}_{\downarrow}$ is the total electron density, and $f^\dagger$ and $f$ ($c^\dagger$ and $c$) are fermionic creation and annihilation operators of impurity electrons (conduction electrons). The sum over $i$ runs over all impurity sites, the sums over $\mathbf{k}$ run over all lattice momenta $\mathbf{k}$ in the Brillouin zone.

The corresponding single particle Green function is given by:

\begin{equation}
G_{\text{full}}^{\text{pAIM}}(\omega, \mathbf{k}) = \left( \omega + i\delta + \mu \right) \mathbb{1} - \begin{pmatrix}
\varepsilon_{J_{z}} & V_{J_{z,c}}(\mathbf{k}) \\
V_{J_{z,c}}^\ast(\mathbf{k}) & \varepsilon_{c,\mathbf{k}}
\end{pmatrix}^{-1} \begin{pmatrix}
\Sigma_{J_{z}}(\omega, \mathbf{k}) & 0 \\
0 & 0
\end{pmatrix}
\end{equation}

with an implied limit of $\delta \to 0$. In the Green function, $\mu$ is the chemical potential and $\Sigma_{J_{z}}(\omega, \mathbf{k})$ is the self-energy for the $4f$-electrons which originates from the on-site interaction $U$ on the impurity sites. All quantities except for the self-energy can be extracted from the DFT calculation. Evaluating the impurity part of the Green function \cite{footnote2} leads to:

\begin{equation}
G_{J_{z,\mathbf{k}}}^{\text{imp}}(\omega, \mathbf{k}) \equiv \left[ G_{\text{full}}^{\text{pAIM}}(\omega, \mathbf{k}) \right]_{J_{z,\mathbf{k}}} = (\omega + i\delta + \mu - \varepsilon_{J_{z}} - \Sigma_{J_{z}}(\omega, \mathbf{k}) - \Delta_{J_{z}}(\omega, \mathbf{k}))^{-1}
\end{equation}

FIG. 14. RIXS calculations corresponding to the experimental spectra in Fig.4 with $E_{\text{in}} = E_{\text{cen.}}$, and $\phi = 105^\circ$ (left) and $90^\circ$ (right), respectively, using the six different sets of crystal-field parameters shown in Fig.12 For each calculation, the main $|\pm J_{z}\rangle$ character of the first three crystal-field levels is indicated.
where $\Delta_{J_z}(\omega, k)$ is the so called hybridization function

$$\Delta_{J_z}(\omega, k) \equiv \sum_c \frac{|V_{J_z,c}(k)|^2}{\omega + i\delta + \mu - \varepsilon_{c,k}} = \sum_c |V_{J_z,c}(k)|^2 \cdot G^0_c(\omega, k). \quad (4)$$

In the second line we have the Green function of the uncorrelated conduction electrons before the hybridization with the Ce 4f states: $G^0_c(\omega, k) \equiv (\omega + i\delta + \mu - \varepsilon_{c,k})^{-1}$.

A closer look reveals a deep connection between the imaginary part of the hybridization function and the Kondo temperature scale as $|V_{J_z,c}(k)|^2 \propto J$ is the effective spin coupling in the corresponding Kondo lattice model \[10\] and $-1/\pi \text{Im} G^0_c(\omega, k) = \rho^0_c(\omega, k)$ is the momentum resolved DOS of the conduction electrons. Their product determines the scale of $T_K \propto e^{-1/(\mathcal{J} \rho^0_c)}$.

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