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Abstract

Soft x-ray resonant photoemission spectroscopy has been used as a tool to investigate the cerium 4f electronic levels of a single-crystalline sample of CeCo$_2$Ge$_2$. Temperature-dependent angle-integrated and angle-resolved results are discussed. For the lowest investigated temperatures two distinct 4f spectral features are clearly observed close to the Fermi level: the Kondo resonance and its lower lying spin–orbit partner. As the temperature is increased, the intensity of such features evolves consistently with the theoretical predictions of the single-impurity Anderson model. However, the angle-resolved results show momentum-dependent effects that require a modification of the single-impurity theory.

1. Introduction

The low-temperature resistivity minimum that appears in dilute magnetic impurity alloys, together with the enhancement of the linear coefficient of the specific heat and the reduction of the overall magnetic moment, are the three identifiers of the so-called Kondo effect [1, 2]. The effect occurs when a localized impurity level is in close proximity to the Fermi surface of a non-magnetic host. For temperatures that are lower than a characteristic temperature T_K, defined as the Kondo temperature, the magnetic moment of the impurity is compensated by the spin of the conduction electrons and the resulting magnetic moment is reduced. On the other hand, for $T > T_K$, dilute Kondo systems behave as local moment systems. Although it was originally thought that the Kondo effect was limited to dilute magnetic alloys, experiments performed on La–Ce alloys [3] soon demonstrated that such spin compensation effects also take place for high impurity concentrations. In particular, if elements like cerium (Ce), ytterbium (Yb) or uranium (U) are dissolved in simple metals, a very large number of impurity ions can be built into the metallic host without destroying the Kondo effect. Such

systems are known as concentrated Kondo systems. Over the past 40 years the extraordinary low-temperature properties of concentrated Kondo systems have strongly motivated transport and thermodynamic measurements as well as neutron scattering and electron spectroscopy investigations [4–7].

Resonant photoemission spectroscopy at the Ce 4d $\rightarrow$ 4f and 3d $\rightarrow$ 4f absorption edges is a powerful tool for probing the 4f electronic structure of Ce intermetallic compounds and a deeper understanding of the spectroscopic data has been obtained as a result of the single-impurity Anderson model (SIAM) and its numerical solutions, namely the Gunnarsson–Schönhammer approximation [8] and the non-crossing approximation [9]. From a microscopic point of view, for $T < T_K$, the hybridization between the localized impurity and the extended conduction states results in a singlet ground state whose fingerprint in the photoemission spectrum is the temperature-dependent, dispersionless, Kondo resonance that appears close to the Fermi level, E_F. The cross-over from the low-temperature ($T < T_K$) to the high-temperature ($T > T_K$) regime is associated with a decrease of the Kondo resonance's intensity. Most importantly, given the essentially localized nature of the 4f electrons, the resonance is predicted to be a momentum-independent feature for temperatures both above and below T_K. Whether or not a localized description of the Ce 4f electrons in terms of the impurity model is appropriate has been a strongly debated issue. Despite the fact that the majority of the low-energy ($h\nu \leqslant 120$ eV) photoemission results [10–13] indicate a good qualitative agreement with the theoretical predictions, some authors [14, 15] claim that the model is not necessary for the interpretation of the spectra. Added to this, the validity of the impurity model has been further put into question by the observation of momentum-dependent variations of the 4f intensity observed close to E_F for a variety of Ce compounds [16–21]. Nevertheless, the surface sensitivity of these low photon energy results may well be one of the underlying causes of the conflicting interpretations. In fact, one of the main parameters of the single-impurity model, the Kondo temperature T_K, is a bulk property of the investigated material. Therefore, when comparing photoemission data with theoretical predictions, the importance of bulk representative experimental results must not be underestimated. This is especially so in the case of Ce compounds that are well known for having different surface to bulk electronic properties [22]. Hence, 4f spectra that are more representative of the bulk are needed to settle the controversy. These can be obtained at the Ce 3d $\rightarrow$ 4f threshold where the photoelectron inelastic mean free path, λ, is as long as 15 Å [23] and $\approx$15% of the photoemitted signal comes from the surface [24], in contrast to $\lambda \leqslant 5$ Å for the low-energy measurements for which the surface contribution increases to $\approx$55%. However, because of the stringent photon flux and energy resolution requirements that are necessary to perform accurate photoemission experiments at this deeper lying absorption edge, more bulk representative results have only recently been obtained [25–27]. These suggest an agreement with the predictions of the SIAM. Accurate soft x-ray angle-resolved photoemission experiments are even more challenging than their angle-integrated counterparts. Nowadays, however, thanks to the development of dedicated photoemission beamlines, to the rapid improvement of electron analyser instrumentation, and to the availability of good-quality single-crystalline samples, measuring soft x-ray angle-resolved photoemission spectra with relatively high energy and angular resolution has become a reality [28–31].

We report a bulk representative, temperature-dependent, resonant, angle-resolved investigation of the Ce 4f intensity close to E_F. Indeed, to the best of our knowledge, the only previously reported investigation of the kind takes advantage of the lower-lying Ce 4d $\rightarrow$ 4f absorption edge [32]. However, differing from [32] where resonant, surface-sensitive, angle-integrated spectra are presented, as a function of temperature, for three selected values of the emission angle, in the following we discuss the temperature evolution of the angle-

resolved intensity over the entire Brillouin zone. For similar investigations the use of the Ce M$_5$ absorption edge is fundamental. The counting times are long and in order to accurately compare measurements taken for different temperatures, the data must be collected from a single cleave. At low energies such a combination of temperature- and momentum-dependent measurements can be very problematic due to the degradation of the sample surface with time. Both angle-integrated and angle-resolved measurements of the valence band of CeCo$_2$Ge$_2$ will be discussed. The former display a temperature dependence that is in qualitative agreement with the SIAM, whereas the latter clearly show that an extension of the simple single-impurity model is required in order to take into account the observed directional effects. Furthermore, in agreement with [33, 34], the angle-resolved results show that, despite the intrinsic nature of the resonant process, the initial state wavevector information is not lost and actual dispersion is indeed observed.

2. Experimental details

The experiments were carried out at the ID08 soft x-ray beamline at the European Synchrotron Radiation Facility in Grenoble, France. The beamline is equipped with a Scienta SES-2002 electron analyser and when tuning the incoming photon energy to the Ce 3d $\rightarrow$ 4f absorption edge ($h\nu \approx 880$ eV) the overall energy resolution is approximately 120 and 220 meV (FWHM) for the angle-integrated and the angle-resolved measurements respectively. For the angle-resolved measurements the momentum resolution at these incoming energies is better than 0.1 Å^{-1} (FWHM). CeCo$_2$Ge$_2$ has been chosen as a weakly hybridized system whose Kondo temperature, $T_K \approx 120$ K [35], allows us to perform a detailed temperature-dependent investigation by varying T from below to above T_K. A single crystal of CeCo$_2$Ge$_2$, grown by a self-flux method out of the ternary melt [36], was cooled to $T \approx 20$ K using a continuous flow liquid He cryostat and subsequently post-cleaved. In the following, data from three different samples of the same compound will be discussed. Particular attention has been devoted to faithfully reproduce the experimental conditions during the different runs. However, because of the effect of the cleaving procedure on the samples, a one-to-one comparison between results coming from different cleaves has to be done carefully. In particular, it is observed that from cleave to cleave the general features are reproduced but the details of the spectra vary. The base pressure in the experimental chamber was kept below 5×10^{-11} mbar and the crystallographic quality, as well as the sample orientation, was checked with low-energy electron diffraction (LEED). The presence of carbon and oxygen contamination was monitored with core level photoemission and Auger spectroscopy and data were typically collected for 12 consecutive hours at which time a fresh cleave was made. For the angle-integrated measurements the Fermi level of the sample is referred to a polycrystalline Au foil mounted in electrical contact with the sample.

3. Results and discussion

The resonant nature of the process we are considering allows us to identify the 4f spectral features in no uncertain terms. In fact, by tuning the photon energy to the Ce M$_5$ absorption edge, the 4f contribution to the photoemitted intensity in the near-Fermi region, if compared to the equivalent off-resonance contribution, is enhanced by more than one order of magnitude. This is shown in the inset of figure 1, where both on-resonance ($h\nu \approx 881$ eV) and off-resonance ($h\nu \approx 840$ eV) reference measurements of the $T = 20$ K valence band of CeCo$_2$Ge$_2$ are shown. On resonance, the occupied part of the Kondo resonance is clearly visible close to
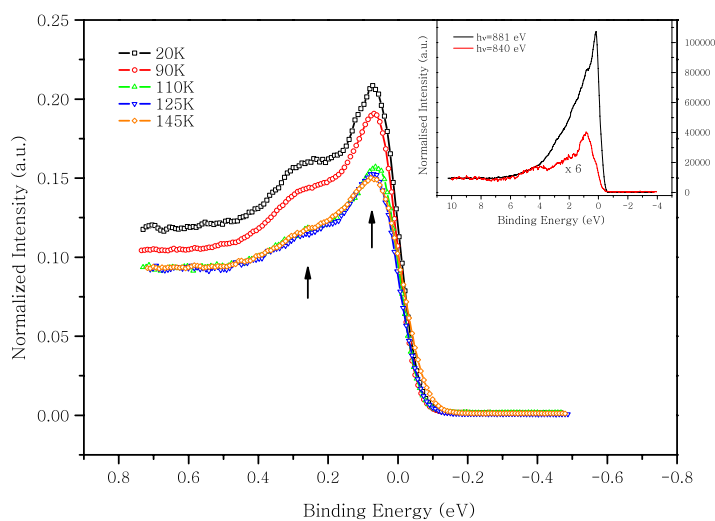
Figure 1. Temperature-dependent, resonant, angle-integrated valence band spectra. □ = 20 K, ○ = 90 K, △ = 110 K, ▽ = 125 K and ◇ = 145 K. The arrows indicate the position of the Kondo resonance and of the spin–orbit partner respectively. Their energy separation is ≈200 meV. The energy resolution is $\Delta E \approx 120$ meV. The inset shows two reference spectra measured at the Ce M_5 edge ($h\nu \approx 881$ eV) and under off-resonant conditions ($h\nu \approx 840$ eV) respectively. The energy resolution in this case is $\Delta E \approx 220$ meV. The intensity of the off-resonant spectrum has been multiplied by a factor 6.

the Fermi level, whereas only a small change in the slope is observed for $h\nu \approx 840$ eV. A weak shoulder also appears at approximately 800 meV binding energy and becomes a more prominent peak for $h\nu \approx 840$ eV. From photoionization cross-section considerations it follows that this feature arises from the hybridization between the Co 3d and the Ce 4f electrons. Figure 1 shows the 3d → 4f resonant valence band measured at several temperatures ranging from $T = 20$ to 145 K. For each temperature change, the position of the sample with respect to the photon beam and the electron analyser has been carefully adjusted to compensate for the thermal expansion of the sample manipulator. The samples were cleaved at $T = 20$ K and the spectra were recorded starting from $T = 20$ K, subsequently increasing to higher temperatures. In order to ensure a correct normalization, for each temperature the data are normalized to the area of the signal photoemitted by the Ge 3p core levels. Despite the fact that the 4f photoemitted intensity is clearly strongest at 20 K, the shape of the two low-temperature spectra is very similar. Because of the higher energy resolution with respect to the reference spectra discussed above, for the two lowest temperatures two spectral features are clearly observed: the most intense and closest to the Fermi level, found at approximately 70 meV binding energy, is the Kondo resonance, whereas the other, positioned at approximately 270 meV, is ascribed to the deeper-lying spin–orbit partner. As the temperature is raised from 90 to 110 K a decrease of the overall 4f intensity, together with a smearing out of the spin–orbit partner, is observed. By increasing the temperature further, the signal below ≈350 meV remains unchanged in both shape and intensity whereas the intensity of the Kondo resonance continues to decrease. In agreement with the predictions of the SIAM, we therefore observe a 4f intensity temperature dependence that reflects the progressive breakdown of the singlet contribution to the ground state with increasing temperature. The fact that the intensity at the Fermi level is still observable for relatively high temperatures could lead to suggest that the temperature dependence is weaker than originally predicted by the SIAM.
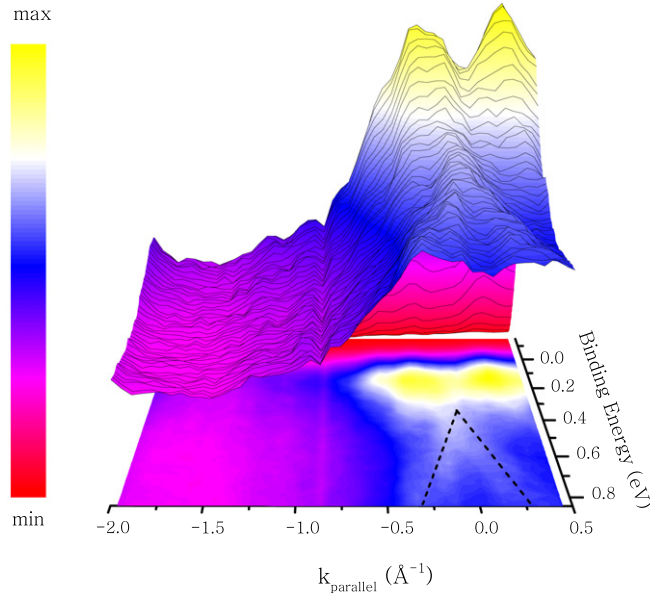
Figure 2. Resonant angle-resolved valence band spectrum measured at $T = 20$ K. At $h\nu \approx 880$ eV the zone boundary is found at $k_{par} = \pm 1.54$ Å^{-1}. The colour map indicates the intensity. Top: three-dimensional representation. The intensity modulation of the Kondo resonance is clearly symmetric with respect to $k_{par} = 0$ Å^{-1}, as is the dispersion of the deeper-lying feature. Bottom: two-dimensional projection. The dispersion of the feature at 350 meV and $k_{par} = 0$ Å^{-1} is shown by the dashed line. Since an angle-resolved energy reference spectrum has not been measured, the Fermi level is placed at the midpoint of the 4f intensity edge jump.

The low-temperature ($T = 20$ K) 3d → 4f resonant angle-resolved valence band of CeCo₂Ge₂ is shown in figure 2 where, due to a slight misalignment of the sample, the spectrum is not centred in the image. These bulk-like angle-resolved results clearly indicate that in the low-temperature regime the nature of the 4f spectral features varies throughout the Brillouin zone. Indeed, in agreement with [17], for $T < T_K$ the 4f spectral weight is mostly concentrated within ± 0.7 Å^{-1} from the centre of the zone. Furthermore, at approximately 150 meV binding energy we observe an intensity modulation of the Kondo resonance that is symmetric with respect to $k_{par} = 0$ Å^{-1}. The different binding energy of this main feature, with respect to the data presented in figure 1, can be understood in terms of the lower energy resolution imposed by the angle-resolved measurement. Added to this, the spherical geometry of the analyser introduces an uncertainty in the exact position of the Fermi edge. Most intriguingly, for the same values of k_{par}, a weak but visible feature with a minimum binding energy of approximately 350 meV at $k_{par} = 0$ Å^{-1} is clearly seen dispersing towards higher binding energies. In the light of the resonant nature of the measurement, we assign a 4f character to both the observed features. Furthermore, for $k_{par} \approx 0$ Å^{-1} the energy separation between the two signatures is equivalent to the spin–orbit splitting deduced from the data presented in figure 1, leading us to suggest that the dispersive feature we observe may indeed be the spin–orbit partner of the Kondo resonance. However, although a 90 meV binding energy shift of the spin–orbit partner has already been documented in [17], the dispersion observed here shows an unprecedented magnitude. In particular, for the maximum value of k_{par} for which the feature is distinguished, $k_{par} \approx \pm 0.4$ Å^{-1}, the binding energy reaches approximately 750 meV. Referring to the inset of
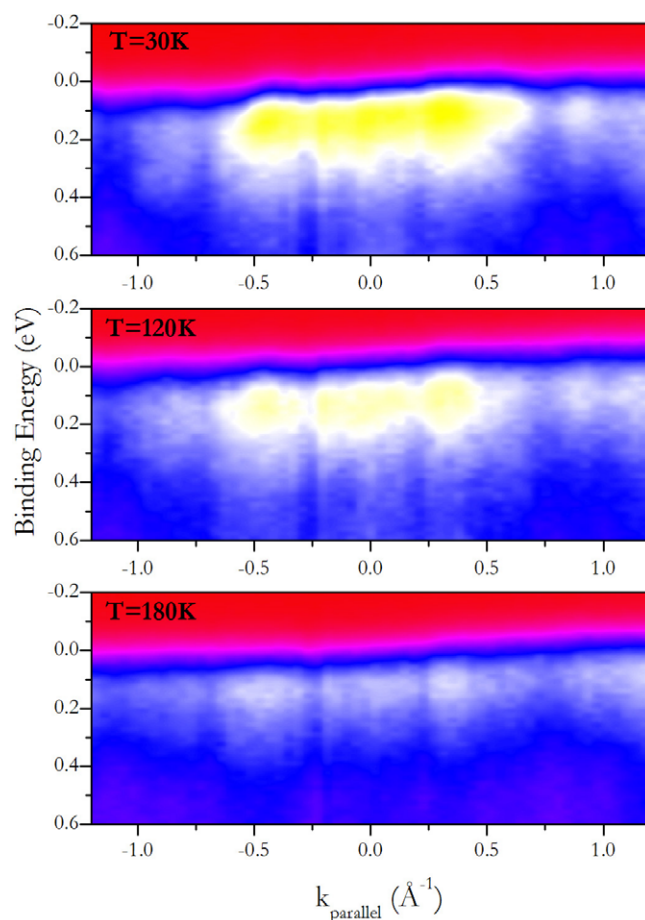
Figure 3. Angle-resolved 4f intensity as a function of temperature. From top to bottom: $T = 30$, 120 and 180 K. The colour map is the same as in figure 2.

figure 1, this value is very close to the binding energy of the mixed 3d–4f shoulder observed in the spectrum measured at the Ce M_5 absorption edge. However, by comparing the intensities of the two reference spectra shown in the inset it follows that the 4f spectral weight of this feature is considerably more important than its 3d counterpart. We are therefore confident in assigning a strong $4f_{7/2}$ imprint to the band-like feature observed in figure 2, although a weak contribution coming from the non-4f components cannot be excluded.

A second set of resonant angle-resolved measurements was performed with the aim of investigating the momentum dependence of the 4f intensity as a function of temperature. The results obtained for $T = 30$, 120 and 180 K, i.e. below, at and above the estimated value of T_K, are shown in figure 3. In a similar way, the intensity of the Kondo resonance as a function of k_{par} is plotted in figure 4 for each investigated temperature. Although the observed momentum-dependent effects are not as marked as in figure 2, and in particular the weak dispersive feature is not observed, most probably due to a worse quality cleave, the measurements displayed in figures 3 and 4 are in qualitative agreement with the previously discussed low-temperature angle-resolved results. For $T = 30$ K the 4f intensity is mostly concentrated within ± 0.7 Å^{-1} from the zone centre and decreases when moving towards the zone boundary.
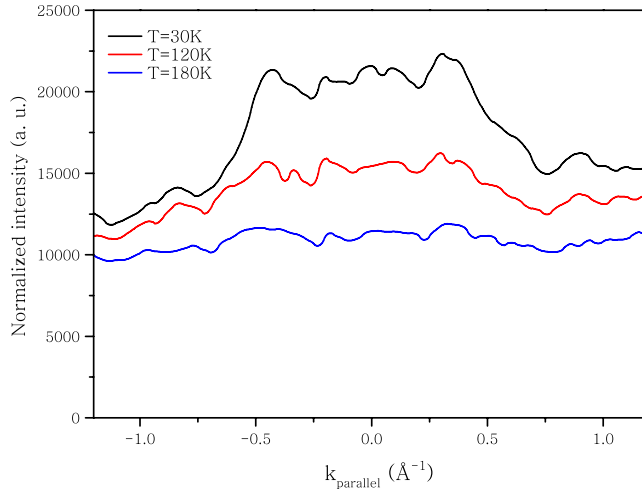
Figure 4. Intensity of the Kondo resonance as a function of k_{par}. From top to bottom: $T = 30$, 120 and 180 K. The curves are plotted after interpolation of the momentum distribution curves obtained at approximately 150 meV binding energy from the angle-resolved spectra shown in figure 3.

As the temperature is increased to the Kondo temperature, $T = 120$ K $\approx T_K$, the overall 4f intensity decreases and its momentum dependence, although still present, becomes less pronounced (see middle plot in figure 4). For $T = 180$ K the 4f intensity is close to being a constant function of k_{par}. In order to rule out effects due to the diffusion of impurities from the bulk to the surface, after having heated the sample to $T = 180$ K the low-temperature measurement at $T = 30$ K was repeated. The obtained results (not shown here) are consistent with the previous low-temperature measurements, as the intensity peaks are again close to the zone centre. We therefore observe a definite temperature dependence of the angle-resolved 4f intensity close to the Fermi level: as the temperature is increased from below to above T_K the momentum dependence decreases, suggesting that the system evolves from a band-like behaviour in the low-temperature regime to a local-moment impurity behaviour for higher temperatures. However, for $T \approx T_K$ the cross-over from the many-body ground state to a local-moment scenario, described by a momentum-independent 4f intensity, is not yet complete.

Although the angle-integrated results presented in figure 1 are in good qualitative agreement with the single-impurity model, the low-temperature angle-resolved 4f intensity shown in figure 2 and its evolution with increasing temperature presented in figures 3 and 4 cannot be understood within this simple approach that fails to account for the observed 4f momentum dependence. To the best of our knowledge, band structure calculations do not exist for the system investigated here. However, LDA-based calculations along a spherical path in reciprocal space that is similar to the one we experimentally investigate for CeCo$_2$Ge$_2$ with $h\nu \approx 880$ eV can be found in [37] for a closely related compound, namely CeNi$_2$Ge$_2$. Nonetheless, there is no obvious correspondence with the theoretical results discussed in [37]. In particular, the authors of [37] find bands of mainly Ni 3d character positioned within the first 1 eV below the Fermi level and no dispersing 4f contribution to the band structure is identified. In contrast, the angle-resolved results presented above emphasize the existence of momentum-dependent 4f features, demonstrating the inability of LDA-based treatments to account for these states. We therefore refer to the periodic Anderson model (PAM) [38, 39] as a model that is able to explain both the temperature dependence of the Kondo resonance's intensity and the

observed directional character of the 4f electrons. This model retains the underlying physics of the single-impurity approach, such as the existence of a singlet ground state for $T < T_K$ and its breakdown upon heating above T_K. However, in the low-temperature regime where the Kondo effect takes place, the PAM is consistent with a band-formation picture and refers to an f–d renormalized band whose f-like character exists only in a part of the Brillouin zone. Therefore, the decrease of the 4f intensity when moving away from the zone centre, as observed in the low-temperature angle-resolved spectra, can be explained as a loss of f-admixture in the renormalized band below the Fermi level with a consequent dispersion of the Kondo resonance above E_F. In a similar way, such a renormalized f–d mixing model should be able to explain the unusually large dispersion observed in figure 2. Added to this, the periodic model also predicts that the intensity of the Kondo resonance has a weaker temperature dependence than predicted by the SIAM and that a local-moment description is valid for temperatures that are higher than T_K. This, too, appears to be in agreement with our results that show a relatively slow decrease of the Kondo resonance's intensity (see figure 1) and of its momentum-dependent intensity modulations (see figures 3 and 4) with increasing temperature.

4. Conclusions

To conclude, the angle-resolved data discussed above make a strong case in favour of resonant angle-resolved photoemission spectroscopy as being an appropriate tool for investigating the electronic structure of many highly correlated systems of interest today, such as rare earth compounds, high-T_c cuprate superconductors and transition metal oxides, that display relevant absorption edges within the soft x-ray energy range. In particular, the observed momentum-dependent effects, together with the distinct $4f_{7/2}$-like dispersive feature, demonstrate that the initial-state wavevector remains a good quantum number. Dispersion coming from resonantly emitted electrons has only previously been observed for La and its compounds [33, 34]. The results presented here also contribute in a more fundamental way to our understanding of Kondo phenomena. The unmistakable 4f bulk-like character of the data allows us to relate the observed Kondo behaviour to a bulk property of the investigated system. All the momentum-resolved investigations that have addressed similar issues in the past are either highly surface-sensitive, and can therefore not be trusted to truly represent the bulk, or have been performed under non-resonant conditions giving rise to uncertainties in the assignment of the 4f photoemitted intensity. To the best of our knowledge this is the first comprehensive study that addresses the issues of temperature dependence, momentum dependence and temperature-dependent momentum dependence at the same time. The data reveal a clear 4f spectral feature whose temperature dependence is in agreement with most of the previously reported investigations and with the temperature-dependent evolution of the Kondo resonance described by the single-impurity model. The major exceptions to this scenario are given by the localization of the 4f intensity close to the centre of the Brillouin zone and the dispersion of what may be the spin–orbit partner, as observed from the low-temperature angle-resolved measurement shown in figure 2. We refer to a renormalized f–d mixing model as a possible candidate for explaining these observations. Our hope is that these results will motivate further experimental and theoretical investigations.

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