Quantitative investigation of the 4\textit{f} occupation in the quasikagome Kondo lattice CeRh\textsubscript{1−}\textit{x}Pd\textsubscript{\textit{x}}Sn

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CeRhSn with the Ce atoms forming a quasikagome lattice in the hexagonal plane has recently been discussed in the context of quantum criticality driven by magnetic frustration. Furthermore, it has been reported that the successive substitution of Rh by Pd leads to magnetic order. Here we have investigated the change of the 4\textit{f} occupation in the substitution series CeRh\textsubscript{1−}\textit{x}Pd\textsubscript{\textit{x}}Sn for for \textit{x} = 0, 0.1, 0.3, 0.5, 0.75 by means of photoelectron spectroscopy with hard x-rays (HAXPES). The quantitative analysis of the core level spectra with a combined full multiplet and configuration interaction analysis shows a smooth decrease of the 4\textit{f} contribution with rising \textit{x} due to an increase of the effective 4\textit{f} binding energy \textit{e}_\text{4f} and the reduction of the effective hybridization \textit{V}_{\text{eff}}. We further compare valence band data with the calculated partial density of states and find that the Pd 4\textit{d} states are about 1 eV further away from the Ce 4\textit{f} states at the Fermi energy than the Rh 4\textit{d} states. In fact, the effective binding energy \textit{e}_\text{4f} of the 4\textit{f} states in the configuration interaction analysis of the core level spectra decreases by the same amount.

I. INTRODUCTION

The physics of heavy fermion or Kondo lattice systems is driven by the hybridization of localized 4\textit{f} and conduction electrons (cf-hybridization)\textsuperscript{[1,2]}. The cf-hybridization increases with the exchange interaction \textit{J}, thus leading to a competition of the RKKY (Ruderman-Kittel-Kasuya-Yosida) interaction that favors magnetic order and the Kondo interaction that leads to a non-magnetic ground state. Kondo screening is the dominant interaction for strong cf-hybridization and with increasing \textit{J}, eventually, magnetic order is suppressed to zero Kelvin\textsuperscript{[3]} and a quantum critical point occurs\textsuperscript{[4,5]}. With further increasing cf-hybridization the \textit{f} electrons are partially delocalized so that the occupation of the 4\textit{f} shell is no longer integer. A non-integer 4\textit{f} occupation usually goes along with a large Kondo temperature \textit{T}_\text{K} and the reduction of the effective hybridization \textit{V}_{\text{eff}}. We further discuss valence band data with the calculated partial density of states and find that the Pd 4\textit{d} states are about 1 eV further away from the Ce 4\textit{f} states at the Fermi energy than the Rh 4\textit{d} states. In fact, the effective binding energy \textit{e}_\text{4f} of the 4\textit{f} states in the configuration interaction analysis of the core level spectra decreases by the same amount.

Kondo temperature \textit{T}_\text{K} of 6 K and orders antiferromagnetically below 2.7 K with only two out of three Ce ions participating in this order. In addition short-range magnetic correlations have been observed\textsuperscript{[18,19]}. Both effects are interpreted in terms of frustration. CeRhSn crystallizes in the same hexagonal structure\textsuperscript{[20]} but, in contrast to CePdAl, it is a large \textit{T}_\text{K} system\textsuperscript{[21]} (\textit{T}_\text{K} = 200 K) and remains paramagnetic down to at least 50 mK\textsuperscript{[22,23]} with indications for the proximity to a magnetic quantum critical point\textsuperscript{[24]}. The application of uniaxial stress or a magnetic field in the hexagonal plane seemingly pushes CeRhSn from a quantum critical state into a long-range ordered state\textsuperscript{[25,26]}. This is a great surprise because in cerium compounds pressure tends to suppress magnetic order (see e.g. in Refs.\textsuperscript{[27] and [28]} and references therein). The formation of the magnetic ground state upon application of uniaxial pressure in the \textit{ab}-plane has, therefore, been interpreted in terms of a stress induced reduction of geometrical frustration in the hexagonal plane.

Here we focus on the substitution series

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{FIG1.pdf}
\caption{(Color online) ZrNiAl-type structure of CeRhSn where the Ce atoms form a quasikagome lattice with alternating planes of Ce-Rh (TM1) and Sn-Rh (TM2). Structure data from Ref.\textsuperscript{[22]}}
\end{figure}
CeRh$_{1-x}$Pd$_x$Sn. Up to $x \approx 0.8$, all compositions have the same hexagonal structure as CeRhSn. Here Pd occupies both Rh sites equally. For higher Pd concentrations the orthorhombic structure of CePdSn (TiNiSn-type) is adopted [29]. Niehaus et al. [29] characterized the substitution series in great detail and found from the expanding volume, the magnetic susceptibility, and L-III edge absorption measurements that Pd stabilizes the trivalent state. Yang et al. reported that the specific heat divided by temperature $C/T$ and the ac susceptibility develop peaks for $x \geq 0.1$ which suggests the formation of a magnetically ordered ground state [29]. The ordering temperature rises up to 2.7 K for $x = 0.75$. The static susceptibility and isothermal magnetization curves show an increase of the magnetic moment as the Pd content increases, while the Curie-Weiss temperature decreases, thus implying a decrease of the Kondo temperature $T_K$. Hence, the substitution with Pd drives CeRh$_{1-x}$Pd$_x$Sn away from the quantum critical point in CeRhSn. The question of the impact of frustration upon Pd substitution remains. It requires a detailed analysis of the putative magnetically ordered states with $\mu$SR and/or neutron diffraction [20] and the quantification of the of the $c$-$f$-hybridization as a function of the Pd substitution $x$. The present manuscript addresses the Kondo interaction.

For this purpose we present hard x-ray photoelectron spectroscopy (HAXPES) measurements of the Ce 3$d$ and Ce 3$p$ core level, and of the valence bands of CeRh$_{1-x}$Pd$_x$Sn with $x = 0, 0.1, 0.3, 0.5,$ and $0.75$ with a quantitative analysis. Weakly hybridized $4f$ states in Ce compounds are trivalent and have a $4f$ occupation of $n_f = 1$. Strong hybridization, on the other hand, leads to an intermixing of $4f$ configurations so that the valence is no longer integer. The $4f$ ground state is now a mixed state of the form $\langle \text{GS} \rangle = \alpha |f^0 \rangle + \beta |f^1 L \rangle + \gamma |f^2 L \rangle$, with $L$ and $I$ standing for the number of ligand holes. Here the amount of $f^0$ quantifies the degree of the delocalization. In core level spectroscopy, the mixed ground state of the initial state is split up into three spectral weights $|c^2 L \rangle$, $|c^1 L \rangle$, and $|c^0 \rangle$ in the final state due to the presence of the core hole $\langle \text{I} \rangle$, and the corresponding spectral weights give information about $\alpha^2$, $\beta^2$, and $\gamma^2$. The relation between these spectral weights and the respective amounts of the different configurations in the wave function is not a simple proportionality due to hybridization effects in the final state, so that configuration interaction calculation (CI) is needed to relate the measured intensities to the $f^i$ contributions, $i = 0, 1,$ and $2$ in the initial state.

II. EXPERIMENT AND SIMULATION

For the HAXPES experiments of CeRh$_{1-x}$Pd$_x$Sn, single crystalline samples were used for $x = 0$ and $0.1$, while polycrystalline samples were used for higher $x$. However, it turned out that the polycrystalline samples consisted of long grains (0.5-1.0 mm) along the hexagonal $c$ axis. For the HAXPES measurements, clean surfaces perpendicular to the $c$ axis were prepared by breaking the sample in a high vacuum. The single crystals for $x = 0$ and $0.1$ were also cut perpendicular to the $c$ axis so that we do not expect that the single or polycrystalline nature of the samples has an impact on the results. The methods of preparation and characterizations of samples are described in Ref.[25] The electron-probe microanalysis showed that the samples with $x$ up to 0.5 are homogeneous but the actual composition for the sample with the initial composition of 0.8 is approximately 0.75 due to the formation of some trivalent Ce impurity phases (alloys of CeRh$_2$Sn$_2$ and CePd$_2$Sn$_2$) [32] that amount in total to a maximum of 5% [25]. The CeRhSn sample that was used for the valence band measurements is the same as in Ref. [33].

Photoelectron spectroscopy with soft x-rays (PES) has been shown to be a very valuable technique for the investigation of the electronic states of rare-earth compounds [34][35], but suffers from surface effects. PES with hard x-rays (HAXPES), on the other hand, provides the bulk sensitivity of about 80Å that is necessary to image the bulk electronic structure in these systems [37][40], especially in correlated electron systems where the degree of hybridization of the outermost surface layers can be re-
FIG. 3. (Color online) (a) Ce 3d core-level HAXPES data of CeRh$_{1-x}$Pd$_x$Sn with $x = 0, 0.1, 0.3, 0.5, 0.75$. at $T = 60 \text{K}$ after normalization to the integrated intensity before subtracting an integrated background (BG) (dashed black line), plasmons (solid black line), and the Sn 3s emission intensity (cyan line). BG and plasmons are specimen of the 30%Pd analysis. (b) Sn 3p core level of all CeRh$_{1-x}$Pd$_x$Sn samples with plasmon intensities 14 eV above the main emission lines (see red arrows). (c) Ce 3d emission lines after subtraction of BG, plasmons, and Sn 3s. The red ruler indexes the center of the respective multiplet structures of the contributing 4f configurations, $f^0$, $f^1$, and $f^2$. Insets: enlarged regions of $f^0$ and $f^2$ emission. (d) Results of the fmCl simulations for the Ce 3d emission using the CI parameters as listed in Table I.

The HAXPES data were measured at the beamline P22 at DESY/PETRA-III in Hamburg.

The experiment was performed under UHV condition of $5 \times 10^{-10} \text{mbar}$ at about $T = 60 \text{K}$ on the sample with an incident photon energy of 6 keV. The high incident energy assures that the probing depths for the Ce3d core level and valence band measurement differ only by a few percent. The Fermi edge of a Au foil was measured to convert from kinetic energy into binding energy. The instrumental resolution was about 200 meV. Just before measurements, the samples were scraped in a vacuum of $5 \times 10^{-9} \text{mbar}$ to ensure a clean surface, and the O 1s emission line at about 530 eV binding energy was monitored during the experiment to verify that the sample surfaces remained clean throughout the experiment (see Fig. 7 in Appendix).
computational aspects are manageable. This model describes the core-level spectra very well but does not give realistic numbers for e.g. the Kondo temperature. The advantages and short comings of the simplified model are discussed in great detail in Ref.47 and 48.

The valence band spectra were compared to band structure calculations. For this purpose density functional theory based calculations were performed using FPLO (v.18.00.52), making use of the LDA and including spin–orbit coupling in a full relativistic manner and weighted for the respective shell-specific photoionization cross-sections. Grids of 15 ∙ 15 ∙ 15 k points and 1 energy point every 8 meV were used for the calculation of the band structure and the density of states (DOS). The simulated valence band spectra have been obtained from the calculated cerium, transition metal and tin partial DOSs, broadened with a Gaussian lineshape with a FWHM of 0.5 eV. Takegami et al. have shown the validity of such analysis for hard x-ray valence band spectra.

III. SAMPLE CHARACTERIZATION

Figure 2a shows emission spectra of the CeRh$_{1-x}$Pd$_x$Sn (x = 0, 0.1, 0.3, 0.5, 0.75) samples covering a large energy range that confirm the high quality of the samples. The Ce and Sn emission lines precisely fall on top of each other, only the intensities of the Rh and Pd emission lines vary due to the increasing substitution of Rh by Pd. Other, unwanted contributions are not present. The blow-up of the Pd3s and Rh3s emission lines between 610 and 695 eV binding energy in Fig. 2f further confirms that the nominal composition (lines) is very much in agreement with the actual composition (dots) of the substitution series. The lines in Fig. 2b represent smoothed data of the pure Rh sample and 75% Pd sample summed to the nominal amounts.

IV. RESULTS AND ANALYSIS

Figure 3a shows the Ce3d core level of the CeRhSn and the four Pd-substituted compositions. The data are normalized to the integrated intensities across the Ce3d core level, and a systematic trend can be seen even in the raw data; namely an increase of intensity of the main emission lines at 885 and 905 eV and a decrease of the shoulder at 880, the bump at 895, and the satellite at 915 eV with rising Pd concentration.

In PES, plasmon satellites may mislead the interpretation of the data. We therefore measured the Sn 3p emission lines of all CeRh$_{1-x}$Pd$_x$Sn compositions with good statistics (see Fig.3b), because the Sn spectrum is not affected by any configuration interaction effects. Hence, these spectra are good for searching for the presence of plasmons. And indeed, at 14 eV above the main emission lines, all spectra exhibit fairly strong plasmon signals. With the Sn 3p spectra, the plasmon lineshape and energy are determined (see Appendix Table II). These parameters are important for the plasmon correction of the Ce emission spectra, especially when the plasmons are so close in energy to hybridization induced satellites. In addition to the plasmon correction (black lines), the Ce3d spectra in Fig. 3a have to be corrected for the Shirley type background (BG) (dashed black line), and - this is special in Sn containing Ce compounds - for the intensity due to the Sn 3s emission (cyan line) at about 881 eV. Details for the correction process are given in the Appendix.

In figure 3c, that shows the corrected spectra, the shifts of spectral weights upon substitution with Pd become even more visible. Here the respective spectral weights are indexed according to their 4f occupation f$^0$, f$^1$, and f$^2$ in the initial state, and the regions of the f$^2$ spectral weight of the Ce 3d$_{5/2}$ core level and of the f$^0$ of the Ce 3d$_{3/2}$ are blown up in the insets. The strong f$^0$ intensity in CeRhSn suggests that the 4f state is almost as strongly hybridized as in intermediate valent CeIrSn.

The 10% substitution of Rh by Pd has only a minor effect on the f spectral weights. Though we expect strong hybridization for 30 and 50% substitution as well, the f$^0$ spectral weight has dropped considerably, and it has almost disappeared for 75% Pd (see insets of Figure 3c).

In Fig.3c, we model this trend with the fmCI calculation. We are able to capture the general trend of the spectral weight’s shift very well and also the overall line shape is well reproduced which is shown separately for each Pd concentration in Fig.8 in the Appendix. The resulting CI parameters are listed in Table I. Further details of the line-shape and fm calculation are provided in the Appendix. We have measured the Ce 3p core level (see Appendix) in addition to the Ce 3d because they are free of any other emission lines and, we find also that the Ce 3p spectra are well reproduced with the same CI.
FIG. 5. (Color online) (a)-(c) Calculated partial DOS of CePdSn*, CeRhSn, and CeIrSn. CePdSn* stands for a fictitious CePdSn compound with ZrNiAl structure and lattice constants of CeRh0.75Pd0.25Sn. The inset in (b) provides a blow-up at the Fermi energy for Ce f and TM d. (d)-(f) cross-section corrected and broadened calculated DOS (green lines) and partial DOS of the TM d states (orange and dark orange lines) compared to valence band data of CeRh0.75Pd0.25Sn (blue), CeRhSn (black), and CeIrSn (grey).

parameters when only adjusting the Lorentzian FWHM (see Appendix Fig. 9 and Table II).

We further present valence band (VB) spectra of the CeRh1−xPdxSn substitution series, and also of CeIrSn for comparison, in Fig. 4. The data are normalized to the Ce 4p, Sn 4d, and Sn 5s lines which agree very well. Only the Ir intensities are higher due to the much stronger cross-section of Ir 5d. Differences are visible at the valence band where we expect the Pd 4d and Rh 4d, and Ir 5d emission lines. The Ce 4f (not resolved) are expected closest to the valence band.

In Fig. 5(a-c) we show the calculated partial density of states (DOS) at the Fermi energy of CePdSn*, CeRhSn, and also CeIrSn for comparison. The asterisk in CePdSn* indicates that the DOS was calculated for a fictitious CePdSn compound with ZrNiAl structure and lattice constants of CeRh0.75Pd0.25Sn [29]. It turns out that the transition metal (TM) d states at about 3-4 eV below the Fermi edge and the 4f states at the Fermi edge are the most important contributions to the DOS in the binding energy window of 10 eV. TM1 refers to the transition metal in the Ce plane and TM2 to the ones in the Sn plane (see Fig. 1). The partial DOS of the TM1 (blue lines) and TM2 (dashed green lines) d states strongly overlap in energy reflecting that the interatomic distances d(Ce-TM1) = 3.091 Å and d(Ce-TM2) = 3.036 Å are not very different [29]. The DOS of TM2, however, is about twice as strong since there are two TM2 atoms and only one TM1 in the unit cell.

Finally, we compare the VB data with the broadened and cross-section corrected DOS in Fig. 5(d-f) and confirm for all three compounds the validity of the DOS calculation. The calculations reproduce the same shift of spectral weight and show that it is due to the replacement of Rh 4d states by Pd 4d upon substitution, the latter being further away from the valence band.

V. DISCUSSION

Figure 6 summarizes the findings of the the fmCI analysis of the cross-level data for CeRh1−xPdxSn. The CI parameters, the amount of n(f0), the effective magnetic moments (taken from Ref. 25 and unit cell volume [29] (not shown) all change monotonically with increasing Pd concentration x. Note, all values in Fig. 6 are normalized to the respective values of CeRhSn. The parameters U1f,4f and U4f,3d do not vary much across the CeRh1−xPdxSn series, but the hybridization Veff (red) decreases and the effective 4f binding energy ε4f (orange) increases with increasing Pd concentration. Both the smaller Veff and the larger ε4f have the effect of stabilizing the f1 configuration because it becomes energetically more expensive for the f electron to escape into the conduction band. Hence n(f0) (purple) decreases. This is very much in agreement with the recovery of the effective magnetic
TABLE I. Results from fitting the corrected 3d and 3p HAXPES spectra of CeRh$_{1-x}$Pd$_x$Sn with the fmCI model (see Fig. 3d and Fig. 9). The top rows list the respective $f^i$, $i=0,1,2$ contributions. The corresponding CI parameters are listed in the bottom rows: the $f$-Coulomb exchange $U_{4f,4f}$, the Coulomb interaction between the $f$ electron and the 3d (3p) core hole $U_{4f,3d}$ ($U_{4f,3p}$), the effective binding energy $\varepsilon_{4f}$, and the hybridization strength $V_{4f}$. The uncertainty values were estimated by varying the CI parameters independently.

| unit                      | CeRhSn   | CeRh$_{0.3}$Pd$_{0.7}$Sn | CeRh$_{0.25}$Pd$_{0.75}$Sn |
|---------------------------|----------|--------------------------|-----------------------------|
| $n(f^0)$                  | %        |                          |                             |
|                           | CeRhSn   | CeRh$_{0.3}$Pd$_{0.7}$Sn | CeRh$_{0.25}$Pd$_{0.75}$Sn |
|                           | 14.7 (20) | 12.3 (17)                | 6.8 (14)                    |
| $n(f^1)$                  | %        |                          |                             |
|                           | 82.9 (18) | 85.4 (16)                | 91.0 (14)                   |
| $n(f^2)$                  | %        |                          |                             |
|                           | 2.4 (3)   | 2.3 (3)                  | 1.9 (7)                     |
| $U_{4f,4f}$ eV            |          |                          |                             |
|                           | 9.0 (6)   | 9.3 (6)                  | 9.4 (7)                     |
| $U_{4f,3d}$ eV            |          |                          |                             |
|                           | 10.4 (4)  | 10.4 (4)                 | 10.5 (5)                    |
| $U_{4f,3p}$ eV            |          |                          |                             |
|                           | 10.75 (6) | 10.9 (6)                 | 10.9 (9)                    |
| $V_{4f}$ eV               |          |                          |                             |
|                           | 0.27 (2)  | 0.26 (2)                 | 0.23 (2)                    |
| $\varepsilon_{4f}$ eV    |          |                          |                             |
|                           | 1.6 (2)   | 1.8 (2)                  | 2.1 (3)                     |

FIG. 6. (Color online) Configuration interaction parameters as function of Pd substitution $x$ normalized to the respective values of CeRhSn. The effective magnetic moments are adapted from Ref. 25.

TABLE I. Results from fitting the corrected 3d and 3p HAXPES spectra of CeRh$_{1-x}$Pd$_x$Sn with the fmCI model (see Fig. 3d and Fig. 9). The top rows list the respective $f^i$, $i=0,1,2$ contributions. The corresponding CI parameters are listed in the bottom rows: the $f$-Coulomb exchange $U_{4f,4f}$, the Coulomb interaction between the $f$ electron and the 3d (3p) core hole $U_{4f,3d}$ ($U_{4f,3p}$), the effective binding energy $\varepsilon_{4f}$, and the hybridization strength $V_{4f}$. The uncertainty values were estimated by varying the CI parameters independently.

| unit                      | CeRhSn   | CeRh$_{0.3}$Pd$_{0.7}$Sn | CeRh$_{0.25}$Pd$_{0.75}$Sn |
|---------------------------|----------|--------------------------|-----------------------------|
| $n(f^0)$                  | %        |                          |                             |
|                           | CeRhSn   | CeRh$_{0.3}$Pd$_{0.7}$Sn | CeRh$_{0.25}$Pd$_{0.75}$Sn |
|                           | 14.7 (20) | 12.3 (17)                | 6.8 (14)                    |
| $n(f^1)$                  | %        |                          |                             |
|                           | 82.9 (18) | 85.4 (16)                | 91.0 (14)                   |
| $n(f^2)$                  | %        |                          |                             |
|                           | 2.4 (3)   | 2.3 (3)                  | 1.9 (7)                     |
| $U_{4f,4f}$ eV            |          |                          |                             |
|                           | 9.0 (6)   | 9.3 (6)                  | 9.4 (7)                     |
| $U_{4f,3d}$ eV            |          |                          |                             |
|                           | 10.4 (4)  | 10.4 (4)                 | 10.5 (5)                    |
| $U_{4f,3p}$ eV            |          |                          |                             |
|                           | 10.75 (6) | 10.9 (6)                 | 10.9 (9)                    |
| $V_{4f}$ eV               |          |                          |                             |
|                           | 0.27 (2)  | 0.26 (2)                 | 0.23 (2)                    |
| $\varepsilon_{4f}$ eV    |          |                          |                             |
|                           | 1.6 (2)   | 1.8 (2)                  | 2.1 (3)                     |

FIG. 6. (Color online) Configuration interaction parameters as function of Pd substitution $x$ normalized to the respective values of CeRhSn. The effective magnetic moments are adapted from Ref. 25.

moments (dark yellow) observed in magnetic measurements 25. The valences obtained from the present quantitative analysis differ from the numbers given in Ref. 29 because Niehaus et al. did not apply a configuration interaction calculation, hence ignoring final state effects. The PES data of CeRhSn in Ref. 55 find less $f^0$ in CeRhSn which could be due to the stronger surface sensitivity of PES with respect to HAXPES. In general, however, it is found that the Rh rich side of the phase diagram of CeRh$_{1-x}$Sn$_x$ is strongly intermediate valent ($\alpha$-Ce like). In fact, the $4f$ electrons in CeRhSn are almost as strongly hybridized as in CeIrSn 33. The Pd rich side, on the other hand, is more like a $\gamma$-type Ce compound 54.

The present valence band data as well as the calculation of the partial DOS of CeRhSn agree very well with the data and calculations by Gamza et al. 53. In addition, we find that the Pd4d states in CePdSn* are about 1 eV further away from the Fermi edge than the Rh4d and Ir5d states in CeRhSn and CeIrSn, respectively. Hence, the energy difference to the Ce4f is larger by this amount. This is very much in agreement with the CI results that find an increase of the effective binding energy of the Ce 4f electrons, $\varepsilon_{4f}$, by about the same energy when going from CeRhSn to CeRh$_{0.25}$Pd$_{0.75}$Sn (see Table I) or with respect to CeIrSn 33. Accordingly, the hybridization in the Pd rich samples is weaker than in CeRhSn and also weaker than in CeIrSn. It is amazing that these two very different approaches for data analysis, i.e. the Anderson impurity calculation for the simulation of the core level data and the band structure calculation for reproducing the valence band data yield the same shift of energy scale as function of the Pd substitution $x$. Both, however, the larger $\varepsilon_{4f}$ and the larger energy separation of TM4d and Ce4f states go along with reduced hybridization. From this we draw the conclusion that the TM 4d states are driving the hybridization with the Ce 4f states.

We can only speculate which one of the two Rh atoms in CeRhSn is most important for hybridization effects. According to the partial DOS both Rh1 and Rh2 overlap with the Ce 4f states in the vicinity of the Fermi energy (see inset in Fig. 5). Kittaka et al. suggest that a $J_z = \pm 3/2$ ground state is compatible with the strongly anisotropic non-Fermi liquid behavior that they have observed 55. Here the $J_z = \pm 3/2$ state refers to the yo-yo shaped 4f charge density, which should favor hybridization with the Rh2 atoms that are in the Sn and not in the Ce plane (see Fig. 1). We should not forget, however, that CeRhSn is strongly intermediate valent and that Kondo temperature and crystal-field splittings, based on neutron scattering data of CePtSn and CePdSn 56, are comparable. Hence, it is questionable whether these symmetry aspects can be applied to CeRhSn.

Küchler et al. and Yang et al. 28, 29 both argued that in CeRhSn signatures of local moments exist and that CeRhSn under uniaxial pressure is close to a quantum critical point, very much like CeIrSn at ambient pressure 57. Furthermore, in both compounds metamagnetic cross-overs occur under the field along the $a$ axis, and in CeIrSn antiferromagnetic correlations have
been observed at very low temperature \cite{33} thus feeding the speculation that magnetic order may be hindered by frustration despite the strong hybridization of 4f and conduction electrons. The present quantitative analysis of the 4f electronic configurations in CeRhSn shows that also CeRhSn belongs to the strongly intermediate valence regime, where, usually, magnetic order does not occur, thus, making the proximity to a quantum critical point very interesting. We believe that it is a very complex task to disentangle the impact of frustration and hybridization in such strongly hybridized compounds as CeRhSn and CeIrSn. This is very much in contrast to hybridization in such strongly hybridized compounds as CePdAl where frustration was unambiguously proven \cite{13–17} and seems to persist on substituting Pd with Ni up to the quantum critical point in CePd$_{1-x}$Ni$_x$Al at $x \approx 0.135$ \cite{18}. In the CeRh$_{1-x}$Pd$_x$Sn series, however, we found that 4f-conduction electron hybridization is still quite pronounced for $x = 0.1$ and also for $x = 0.3$ so that also here magnetic order should be hindered by the Kondo interaction. The origin of the maxima in both $C/T$ and $\chi_{ac}(T)$ remains therefore an open puzzle.

Below 100 K domains of intermediate valent Ce (80\%) and Ce$^{3+}$ are reported from $\mu$SR measurements \cite{23}. We consider this to be unlikely in view of the smooth change of the CI parameters with the Pd concentration $x$ in CeRh$_{1-x}$Pd$_x$Sn at 60 K and the good agreement of the energy scales obtained from the Anderson impurity analysis of the core level spectra and the ab initio calculation of the partial DOS that describe the valence band data, unless the same fraction of domains persists throughout the substitution series.

**VI. SUMMARY**

The substitution series of the quasikagome Kondo compounds CeRh$_{1-x}$Pd$_x$Sn with $x = 0$, 0.1, 0.3, 0.5, 0.75 has been investigated with core-level and valence band HAXPES. Both the pure Rh compound and the sample substituted with 10\% Pd belong to the intermediate valence regime. Effects of cf-hybridization are strongly suppressed for the higher Pd concentrations. The quantitative configuration interaction and full multiplet analysis show that the substitution of Pd leads to a smooth decrease of the hybridization $V_{ef}$ and an increase of the effective 4f binding energy $\varepsilon_{4f}$. We also find that the binding energy increases for the transition metal d states in the valence band data upon substitution of Pd and this increase scales with the effective binding energy of 4f electrons $\varepsilon_{4f}$. This suggests that the transition metal 4d states drive the hybridization.

**VII. APPENDIX**

In the fm part of the calculation the atomic values of the intra-atomic 4f-4f and 3d-4f (3p-4f) Coulomb and exchange interactions and the 3d (3p) and 4f spin-orbit coupling are taken from the Cowan code. Best agreement with the experimental core-level emission structure is obtained when the 4f-4f (3d-4f and 3p-4f) Coulomb interactions are reduced to 60\% (80\%) and the spin-orbit coupling of the 3d (3p) is reduced to 98\% (97.5\%).

![Diagram](image)

**FIG. 7.** (Color online) Photo-electron emission scans of CeRh$_{1-x}$Pd$_x$Sn with $x = 0$, 0.1, 0.3, 0.5, 0.75 over the energy range of O1s. The emission energies for the Pd3p and Rh3p lines were taken from Ref. 58 using the energies for Pd and Rh metals, and for the O1s using the listed energies for metal oxides.

**TABLE II. Lineshape and plasmon parameters: Lorentzian FWHM$_L$ and Gaussian full widths at half maximum FWHM$_G$, the Mahan assymetry factor $\alpha_M$ and cutoff energy $\gamma_M$, and the intensity relative to the emission line $A^{Pl}_x$ and width of the plamsons FWHM$_{Pl}^L$. Different plamsongs energies $\Delta E^{Pl}$ of 14.8, 14.7, 14.5, 14.3, 14.0 eV have been obtained form the Sn3p spectra for $x = 0$, 0.1, 0.3, 0.5, 0.75, respectively.**

| Parameter | $x = 0$ | $x = 0.1$ | $x = 0.3$ | $x = 0.5$ | $x = 0.75$ |
|-----------|---------|---------|---------|---------|---------|
| FWHM$_L$  | 1.3     | 1.3     | 1.3     | 1.3     | 1.3     |
| FWHM$_G$  | 0.3     | 0.3     | 0.3     | 0.3     | 0.3     |
| $\alpha_M$| 1       | 0.8     | 0.7     | 0.6     | 0.5     |
| $\gamma_M$| eV      | 4       | 4       | 4       | 4       |
| $A^{Pl}_x$| 1       | 1.2     | 1.4     | 1.6     | 1.8     |
| FWHM$_{Pl}^L$| eV | 6       | 6       | 6       | 6       |

Different plasmons energies $\Delta E^{Pl}$ of 14.8, 14.7, 14.5, 14.3, 14.0 eV have been obtained form the Sn3p spectra for $x = 0$, 0.1, 0.3, 0.5, 0.75, respectively.
The inset is a blow up of the 6/8 intensity ratio of the Ce 3d intensity ratio with the same CI parameters as for Ce 3d. From top to bottom, the experimental data as measured, the Ce Rh substitution, and most importantly, this trend can be captured with same parameters as for the Ce 3d. The Ce 3p1/2 and Ce 3p3/2 do not overlap with any other emission line. They are further apart in energy and broader than the Ce 3d. The f° intensities are still well separated from the f^1 spectral weights but the f^1 and f^2 spectral weights are not resolved. Nevertheless, also the Ce 3p spectra show the same shifts of spectral weights as function of Pd substitution, and most importantly, this trend can be captured with same parameters as for the Ce 3d. Only the line broadening had to be adjusted accounting for a different core-hole life time (see Table II).

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FIG. 8. (Color online) Ce 3d core-level emission lines of CeRh1−xPd_xSn with x = 0, 0.1, 0.3, 0.5, 0.75 (a–e). At the top the experimental data are shown along with the corresponding integrated background (BG) and the plasmon and Sn 3s contributions. Below, the Ce 3d emission spectra obtained from subtracting BG, plasmon, and Sn 3s from the data are shown along with the broadened full multiple (fm) configuration interaction (CI) calculation (red line). A less broadened fmCI calculation times 0.1 (green line) illustrates the underlaying multiplet lines.

FIG. 9. (Color online) Ce 3p core-level emission spectra and analysis of CeRh1−xPd_xSn with x = 0, 0.1, 0.3, 0.5, 0.75. From top to bottom, the experimental data as measured, the corrected data after BG and plasmon subtraction, and the fmCI simulations with same CI parameters as for Ce 3d are shown. The inset is a blow up of the f° region of the Ce 3p3/2.
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