# Evidence for strong *f*-*d* hybridization in the intermetallic ferromagnet CePdIn<sub>2</sub>

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We have investigated the contribution of Ce 4*f* states to the electronic structure of the intermetallic ferromagnet CePdIn<sub>2</sub> by means of x-ray absorption spectroscopy and resonant and nonresonant photoemission spectroscopy. The line shape of the Ce  $M_{5,4}$  absorption edge reveals the localized nature of the 4*f* states, and is consistent with a predominantly 3+ ionic state for Ce ions. Fitting of the Ce 3*d* core level gives a Ce 4*f* occupation number at room temperature of 0.92, which is in good agreement with the Ce effective magnetic moment of  $2.20\mu_B$  (corresponding to ~87% of the free-electron moment) as calculated from the inverse magnetic susceptibility. Moreover, the hybridization strength between 4*f* and conduction electrons is found to be ~180 meV, revealing that CePdIn<sub>2</sub> is a strongly hybridized system. This is consistent with the results from the analysis of the resonant valence band photoemission measurements at both the  $N_{5,4}$  and the  $M_5$  edges, showing that the Ce 4*f* states are composed of the features predicted by the single-impurity Anderson model, i.e., a broad 4*f*<sup>0</sup> peak centered at 1.9 eV and two 4*f*<sup>1</sup> spin-orbit states much closer to the Fermi level. The same spectra also show that the Ce 4*f* resonant spectral weight extends over a wide binding energy range, overlapping with that presumably occupied by the Pd 4*d* ligand states. This energy overlap is interpreted as a signature of the strong hybridization governing the system, which could possibly favor the emergence of long-range ferromagnetism through the indirect exchange between localized 4*f* states mediated by highly dispersive *d* electrons.

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# I. INTRODUCTION

A large proportion of research into rare-earth-based intermetallic compounds has been dominated by the study of many-body, cooperative phenomena such as new quantum states of matter, magnetic ordering, itinerant heavy fermion behavior, and unconventional superconductivity in Ce-based systems, which can be tuned by the change of the degree of hybridization between band electrons and the 4f electrons of Ce [1,2]. An important protocol for understanding this variety of observed phenomena has been established by Doniach [3], where the relative strength of the Kondo and Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions ultimately determines the ground state properties of the system.

Ternary indides of Ce and Pd in various stoichiometric configurations have provided fertile ground in which to study the consequences of the hybridization between rare-earth f electrons and highly dispersive Pd d electron bands, characterized by a large radial extent of their wave function. There are almost 20 phases known to form in the Ce-Pd-In system [4]. Reported studies of the physical properties of CePdIn [5,6], CePdIn<sub>2</sub> [7,8], CePd<sub>2</sub>In [9,10], Ce<sub>8</sub>Pd<sub>24</sub>In [11], Ce<sub>4</sub>Pd<sub>10</sub>In<sub>21</sub> [12], CePd<sub>2</sub>In<sub>4</sub> [13], CePd<sub>3</sub>In<sub>2</sub> [14], Ce<sub>2</sub>PdIn<sub>8</sub> [15–17], and Ce<sub>6</sub>Pd<sub>12</sub>In<sub>5</sub> [18] reveal a remarkable diversity of crystal structures and physical phenomena. For example, the co-occurrence of heavy fermion behavior and magnetic order is found in CePdIn [5,6], Ce<sub>8</sub>Pd<sub>24</sub>In [11], CePd<sub>3</sub>In<sub>2</sub> [14], CePd<sub>3</sub>In<sub>2</sub> [14],

and  $Ce_6Pd_{12}In_5$  [18], while the nature of the heavy fermion superconducting state of  $Ce_2PdIn_8$  is still actively pursued

Amongst this variety, CePdIn<sub>2</sub> was the first Ce-containing compound discovered to form in the orthorhombic BRe<sub>3</sub>-type structure [7]. CePdIn<sub>2</sub> has been reported to order ferromagnetically at  $T_C = 10$  K, and to have a small Kondo temperature  $T_K = 5$  K [8]. The confluence of a ferromagnetic ground state and Kondo coupling happens quite rarely in the realm of Ce-based systems, and has contributed to instill interest in this particular compound. Above  $T_C$  electrical resistivity results for CePdIn<sub>2</sub> reveal predominantly metallic behavior. The above suggests that the physical properties of this system could be understood in the framework of the RKKY interaction, where Ce 4 *f* electrons are expected to have a localized nature, and that CePdIn<sub>2</sub> could consequently be described as a local moment metallic ferromagnet.

Despite this, important features regarding the physical properties of this compound still evade a complete description consistent with all the observables. In fact, the inverse magnetic susceptibility  $\chi^{-1}$  (see Fig. 8) reveals that Curie-Weiss behavior is present from 400 K down to the ferromagnetic phase transition temperature of 10 K. However, the associated effective magnetic moment is only ~87% of the theoretical value expected for trivalent Ce ions. The specific heat  $C_P(T)$  (see Fig. 9) analyzed in terms of the three-level Schottky description offers some evidence in support of strong crystalline electric field (CEF) effects present in the system, while by contrast the magnetic susceptibility shows no evidence of CEF excitations. Furthermore,  $C_P(T)$  shows

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that CePdIn<sub>2</sub> is a model mean-field ferromagnet, implying that long-range magnetic correlations are already present at high temperature and are responsible for the establishment of an ordered magnetic state. Together with the inverse magnetic susceptibility this seems to imply a narrow critical region in the vicinity of the magnetic phase transition. The emerging of long-range magnetic order could suggest either a partial delocalization of the Ce 4*f* wave function (which is not a novel feature in the framework of *f*-electron systems [21–25]) or hint to the pivotal role played by the interaction between Ce 4*f* and band electrons in this compound.

These results have inspired the electronic structure investigation reported in this study. We have probed the contribution of the Ce 4 f states to the electronic structure in CePdIn<sub>2</sub> by means of x-ray absorption spectroscopy (XAS) across the Ce  $M_{54}$  absorption edge, photoemission spectroscopy (PES) of the Ce 3d core level, and resonant photoemission spectroscopy (ResPES) at the Ce  $N_{5,4}$  and  $M_5$  edges. There are several examples in the literature where combining measurable bulk physical properties with electronic structure measurements in Ce-based intermetallic compounds has led to further unraveling of the full picture of the ground state properties of these systems (see, for example, Refs. [26-29]). The combined analysis of the Ce  $M_{5.4}$  XAS and the Ce 3d core level has revealed the localized character of the Ce 4f wave function that coexists with a strong f-d hybridization. The enhancement of the Ce 4f photoionization cross section due to the resonance process has allowed us to unambiguously identify the contribution and the location of the Ce 4f states to the valence band, giving further insights into the degree of *f*-*d* hybridization in this compound.

### **II. EXPERIMENTAL DETAILS**

Polycrystalline samples of CePdIn<sub>2</sub> were prepared from stoichiometric amounts of the constituent elements in an arc furnace under ultrahigh-purity argon atmosphere. The purity of Ce, Pd, and In (in wt. %) was 99.99, 99.99, and 99.999, respectively. The cast samples were wrapped in Ta foil and annealed at 800 °C for 14 days in an evacuated quartz ampoule. The crystalline structure and the chemical composition were checked by means of powder x-ray diffraction (XRD), scanning electron microscopy (SEM), and multispot energy dispersive spectroscopy (EDS). Figure 1 shows the experimental powder x-ray diffractogram for CePdIn<sub>2</sub> together with the simulated spectrum calculated from a full profile Rietveld refinement using GSAS [30,31]. The refined lattice parameters for the orthorhombic unit cell are (in angstroms) a = 4.6191(1), b = 10.6859(3), and c = 7.4499(2), in goodagreement with those reported by Ijiri et al. [7]. Figure 2 shows a SEM micrograph of a polished area of CePdIn<sub>2</sub>, where the lack of chemical contrast is taken to indicate a single bulk phase and a high degree of homogeneity. EDS elemental analysis revealed a stoichiometry (normalized to the at. % of Ce) of  $Ce_{1.0(2)}Pd_{1.0(2)}In_{2.0(2)}.$  No impurity phases were detected by either XRD or EDS. Taken together, these results indicate that CePdIn<sub>2</sub> formed in the desired phase and that impurity phases are absent to within the detection limits.

Photoemission and XAS measurements were acquired at the beamline BACH at Elettra [32], the Italian synchrotron



FIG. 1. (Color online) Powder x-ray diffractogram of annealed polycrystalline CePdIn<sub>2</sub> (black circles) and the simulated spectrum calculated from a full profile Rietveld refinement (red solid line). The residual spectrum is shown at the bottom of the graph (black solid line).

radiation facility in Trieste. Samples were scraped with a diamond file in ultrahigh vacuum at a base pressure of  $6 \times 10^{-10}$  mbar, and kept at room temperature for the duration of the measurements. The pressure in the measurement chamber was stable at  $5 \times 10^{-10}$  mbar throughout the experiment. Photon energies were calibrated by measuring the Au 4*f* core level on a clean gold reference sample. The cleanliness of the sample surface was ensured by checking the C 1*s* and O 1*s* photoemission core levels throughout the measurements, as well as by checking the O 2*p* contribution to the valence band around 6 eV binding energy. Valence band measurements on an aged sample surface (i.e., 16 hours after scraping, shown in



FIG. 2. SEM micrograph of a polished and carbon coated CePdIn<sub>2</sub> sample. This image has been measured at a magnification of  $647 \times$  with a view field of 535  $\mu$ m.



FIG. 3. (Color online) Ce  $M_{5,4}$  XAS spectra for (a) a clean CePdIn<sub>2</sub> sample just after scraping, (c) a contaminated CePdIn<sub>2</sub> sample (i.e., measured before scraping in UHV), and (d) an aged CePdIn<sub>2</sub> sample measured 18 hours after scraping. The features that are the signature of surface contamination are indicated with arrows in spectra (c) and (d). Spectrum (b) is the simulation of the  $M_{5,4}$  edge for the Ce<sup>3+</sup> ionic state, as explained in the main text; this is to be compared to spectrum (a) in this figure.

Fig. S1 of the Supplemental Material [33]) have shown that the effect of surface contamination is to drastically suppress the spectral weight at the Fermi level ( $E_F$ ), as well as to develop a broad peak located from 3.5 to 5 eV binding energy. In order to avoid this contribution to the valence band spectra, samples were scraped every 12 hours, and all measurements shown here [except for the XAS spectra in Figs. 3(c) and 3(d)] were acquired within 10 hours from the latest scraping.

XAS spectra were measured in total electron yield (TEY) by measuring the drain current from the sample with a photon energy resolution of 200 meV. PES spectra were measured with a Scienta R3000 electron energy analyzer. The angle between the incoming photon beam and the electron analyzer's electrostatic lens axis was fixed at  $60^{\circ}$ , and the PES spectra were acquired in normal emission. The overall (photon+analyzer) energy resolution was set to 300 meV for the Ce 3*d* core level, 80 meV for Ce  $N_{5,4}$  ResPES, and 250 meV for Ce  $M_{5,4}$  ResPES.

With regard to the measurements reported in the Appendixes, the magnetic susceptibility was obtained using a SQUID-type magnetometer (MPMS, Quantum Design, San Diego) in an applied magnetic field H = 500 Oe, while the

specific heat was obtained using the relevant measurement option of a Physical Properties Measurement System (also from Quantum Design).

## **III. RESULTS AND DISCUSSION**

Figure 3(a) shows the Ce  $M_{5,4}$   $(3d_{5/2,3/2} \rightarrow 4f)$  XAS spectrum for CePdIn<sub>2</sub>. The  $M_5$  edge is formed from two low-intensity prepeaks followed by two high-intensity components located at 881.4 and 882.5 eV. The  $M_4$  edge has a more intense feature at 900 eV, with two well-defined shoulders on its low-energy side (at 896.8 and 898.6 eV, respectively) and a broad weak shoulder on its high-energy side located at about 902.8 eV. The line shape of the  $M_{5,4}$ edge resembles very well-in terms of both energy separation and intensity distribution of the various components-the calculation performed using ligand field multiplet (LFM) formalism for the  $Ce^{3+}$  valence state shown in Fig. 3(b) (which is also in very good agreement with the results presented by Thole et al. in Ref. [34]). Our LFM simulation was carried out using the CTM4XAS 5.5 package based on the original code written by Cowan [35] and further developed by de Groot [36]. For the calculation of the Ce<sup>3+</sup> spectrum, a transition from the  $3d^{10}4f^1$  initial state to the  $3d^94f^2$  final state configuration was considered, while the crystal field was not included because it is generally negligible in f systems [35]. The Slater integral F(ff) was reduced to 72%, while F(df) and G(df) were kept at 100%, and the 3d spin-orbit coupling parameter was set at 99% of the atomic Hartree-Fock values. A Gaussian broadening of 0.2 eV and Lorentzian broadenings of 0.3 and 0.5 eV were applied to  $M_5$  and  $M_4$  edges, respectively, to take into account the instrumental broadening effect. The parameters used for the calculation of the theoretical XAS spectrum of Ce(III)  $M_{5.4}$ edge of our clean sample are very similar to those applied by Loble et al. for the calculation of the XAS signal of Ce(III) in CeCl<sub>6</sub><sup>3-</sup> [37].

The good agreement between experimental and simulated spectra suggests that the ionic state for Ce ions in CePdIn<sub>2</sub> is predominantly 3+, which corresponds to a 4 *f* level occupation number  $n_f \simeq 1$ , and it solidly points to local-moment character of the 4*f* electrons in this compound. This is supported by the quantitative results of the fitting of the Ce 3*d* PES core level spectrum presented later in this section. It is also worth mentioning that the fact that the XAS line shape resembles the calculation for Ce in its ionic form serves to confirm the nearly localized character/nature of the Ce 4*f* wave function in CePdIn<sub>2</sub>.

However, at this stage the presence of a certain percentage of Ce atoms in the  $4f^0(4+)$  ionic state in the bulk of the sample cannot be completely discarded, as it is known that XAS measurements in TEY have a certain contribution from the surface of the sample, for which the  $4f^0$  spectral weight tends to be suppressed due to a reduced hybridization of the Ce 4fstates with valence electrons at the surface [38]. Nevertheless, the Ce  $M_{5,4}$  XAS spectrum constitutes a very good qualitative indication of the Ce valence.

The XAS spectrum for a contaminated CePdIn<sub>2</sub> sample is shown in Fig. 3(c) for reference purposes. The additional features (indicated by black arrows) visible in this spectrum are characteristic of the  $4f^0$  initial state—corresponding



FIG. 4. (Color online) Ce 3*d* PES spectrum for CePdIn<sub>2</sub> measured with an incident photon energy of 1060 eV. The overall fit (thick black line) is constituted by the sum of the  $4f^0$ ,  $4f^1$ , and  $4f^2$  doublets together with a Shirley-type background, and it shows an overall good agreement with the experimental data points (black dots).

to a 4+ ionic state for Ce [34]—and are a result of the surface contamination of the sample from the atmosphere. This is consistent with the fact that these features disappear in spectrum (a) for the scraped sample and appear again once the sample has aged in UHV, as shown in spectrum (d) in this figure. The appearance of similar features in the Ce  $M_{5,4}$  XAS spectra due to surface contamination has also been reported, for example, for high-temperature superconductors CeFeAsO<sub>1-x</sub>F<sub>x</sub> [39].

The Ce 3d core level spectrum for CePdIn<sub>2</sub> is shown in Fig. 4. The line shape of the core level is constituted by two sets of peaks corresponding to  $3d_{5/2}$  and  $3d_{3/2}$  spin-orbit states, whose centroids are located at binding energies of  $\approx$  884 and  $\approx$  902.5 eV, respectively, separated by a spin-orbit splitting of 18.6 eV. The composition of the Ce 3d core level in Ce-based compounds derives from the fact that the initial ground state wave function  $\psi_0$  of the 4 f electrons can be written as a linear combination of three quantummechanical states corresponding to the  $4f^0$ ,  $4f^1$ , and  $4f^2$ valence states of Ce, according to the following relation:  $\psi_0 = c_0 |4f_0\rangle + c_1 |4f_1\rangle + c_2 |4f_2\rangle$ , where  $|c_0|^2$ ,  $|c_1|^2$ , and  $|c_2|^2$ can be related to the weight of the corresponding peaks in the core level spectrum. This has been extensively studied since the beginning of the 1980s [40,41], and consequently it is very well understood. Therefore the Ce 3d line shape results from the superposition of three spin-orbit doublets ascribed to—from higher to lower binding energy—the  $4f^0$ ,  $4f^1$ , and  $4f^2$  valence states of Ce as mentioned above. These subcomponents are known to arise from the two different mechanisms with which the screening of the 3d core hole (resulting from the photoemission process) can occur for either the Ce  $4f^0$  or the  $4f^1$  states [42]. The so-called "poorly screened" channel is the one whereby the 4 f orbital is screened by other electrons within the Ce atom itself; here the Ce atom is either in the  $4f^0$  or in the  $4f^1$  configuration. The "well-screened" channel is the one whereby the screening is performed by an electron that has been transferred to the Ce 4f orbital by the ligand/conduction band states; in this case the Ce atom is either in the  $4f^1L^{-1}$  or in the  $4f^2L^{-1}$ configuration, where  $L^{-1}$  is to remind us of the hole in the ligand/conduction band states [42]. The latter mechanism is obviously favored by a larger Ce 4 f hybridization strength. It is important to underline at this point that the valence of Ce is determined by a linear combination of  $4 f^0$  and  $4 f^1$  states, i.e., it can range from 4 +to 3 +. So the existence of an  $f^2$  state is not to be attributed to a putative "2+" valence for Ce, but it is a signature of hybridization of the Ce 4 f states with the conduction electrons [42], and the more intense the  $f^2$  peak, the stronger the hybridization, i.e., the more effective is the mechanism of charge transfer described above.

Consistent with this model, the 3*d* core level PES spectrum has been fitted considering a Shirley-type background and three spin-orbit doublets representing  $4f^2$ ,  $4f^1$ , and  $4f^0$ states of Ce. The spin-orbit splitting has been kept fixed at 18.6 eV for all three subcomponents, and the branching ratio  $I(3d_{5/2})/I(3d_{3/2})$  (expected to be 1.5 for a 3*d* core level) that best fitted the data was determined to be 1.56 for all three subcomponents. Such a deviation from the expected value for the branching ratio can be explained by the fact that this parameter can have some degree of anisotropy that may depend on the photon energy and the crystal structure [43]. The subcomponents as well as the overall fit are plotted in Fig. 4, showing good agreement with the experimental data.

According to the model developed by Fuggle *et al.* [40] and Gunnarson and Schönhammer [41], two very useful parameters can be extracted from the fitting of the Ce 3*d* core level: the hybridization energy  $\Delta_{fs}$  between Ce 4*f* and conduction electrons, and the 4*f* level occupation  $n_f$ . In particular,  $\Delta_{fs}$  can be estimated from the ratio:

and

$$r = \frac{I(f^2)}{I(f^1) + I(f^2)}$$
(1)

$$n_f \simeq 1 - \frac{I(f^0)}{I(f^0) + I(f^1) + I(f^2)},$$
 (2)

where  $I(f^0)$ ,  $I(f^1)$ , and  $I(f^2)$  are the spectral intensities of the  $f^0$ ,  $f^1$ , and  $f^2$  components, respectively. The sign " $\simeq$ " in Eq. (2) is used to remind us that this relationship is valid under the assumption that the mixing of the final-state configurations can be neglected for the  $f^0$  state at least, and so the spectral weight of the  $f^0$  component is a good representation of the value of  $|c_0|^2$  described above [40]. This is acceptable if the relative spectral weight of the  $f^0$  component constitutes less than 10% of the overall spectral weight of the Ce 3d core level photoemission spectrum, as is the case here.

Considering the intensities of the two relevant components, we obtain a value of  $r \simeq 0.35$ . Making use of the relationship between r and  $\Delta_{fs}$  elucidated in Ref. [40], we obtain a value for  $\Delta_{fs} = 180 \pm 5$  meV for CePdIn<sub>2</sub>. The Ce 4f occupation number is found to be  $n_f = 0.92 \pm 0.01$ . An occupation number of 0.92 correlates well with an effective moment of 2.20 $\mu_B$  per Ce atom, as calculated from bulk magnetic measurements; this is discussed in Appendix A and the inverse magnetic susceptibility is shown in Fig. 8.  $n_f$  can be converted into an average valence of Ce ions  $v_{Ce} = 3.08 \pm 0.01$ .

Large values of  $\Delta_{fs}$  in the presence of Pd are not unusual and have been documented before [44]. This can be ascribed to the large spatial delocalization of the Pd 4*d* orbitals that would favor the overlap with the 4*f* states. The large value of  $\Delta_{fs}$  for CePdIn<sub>2</sub> is, however, amongst the largest compared to other Ce intermetallic compounds with 4*d* elements as ligand atoms [40], and hints to the important role played by it in the description of the ground state properties of this system.

It is important at this point to comment on the possible surface contribution to the line shape of the Ce 3d core level spectrum. The kinetic energy of the photoelectrons in the Ce 3d core level spectrum displayed in Fig. 4 ranges from roughly 135 to 185 eV. This energy range is very close to the minimum of the inelastic mean free path for photoelectrons reported in Refs. [45,46]. Higher bulk sensitivity in photoemission spectra can be achieved by increasing the incident photon energy to several keV. A higher bulk sensitivity is usually reflected in the Ce 3d core level photoemission spectrum as a relative increase in the spectral weight of the  $4f^0$  and  $4f^2$  components with respect to the 4  $f^1$  component [47,48]. CePdIn<sub>2</sub> can reasonably be expected to follow the same trend. Taking into account Eqs. (1) and (2), this will result in a slight increase of the value of  $\Delta_{fs}$ , corresponding to a slight decrease of the value of  $n_f$ . We can therefore conclude that, because of the enhanced surface sensitivity of our measurements, our results provide an upper limit for  $n_f$  and a lower limit for the hybridization strength  $\Delta_{fs}$ .

In order to investigate the contribution of the Ce 4 f states to the valence band, we have performed ResPES measurements at both the  $N_{5,4}$  and  $M_5$  edges of Ce. This is done in order to take advantage of the enhancement of the cross section of the Ce 4 f valence band states, and it allows one to identify them amongst the other valence band states. Despite being both based upon the same resonance principle, the ResPES across the two edges are qualitatively different: the one across the  $N_{5,4}$  edges is more surface sensitive (given the photon energies involved) but it allows for the acquisition of spectra with very good energy resolution in less amount of time, while the ResPES across the  $M_5$  edge is more bulk sensitive [49] but it requires one to compromise on the energy resolution of the spectra to allow for data acquisition in a reasonable amount of time. Despite these side effects, the information gathered from both techniques can be harmoniously combined in order to obtain a more general picture.

Let us then analyze the  $N_{5,4}$  ResPES data first. Figure 5 shows the on- and off-resonance valence band spectra acquired at photon energies of 122 and 115 eV, respectively. The off-resonance spectrum shows a broad peak centered at a



FIG. 5. (Color online) Valence band spectra acquired at hv = 115 eV (thin line) and at hv = 122 eV (thick line), corresponding to just before and to the maximum of the Ce  $N_{5,4}$  resonance, respectively. The spectra have been normalized to the photon flux and offset for better clarity. The inset shows the difference between the on- and off-resonance valence bands, as well as the enlargement of the dashed region of difference spectrum in the proximity of  $E_{\rm F}$ , where the  $4f_{7/2}^1$  and  $4f_{5/2}^1$  features are visible as the crossing points of the (red) lines fitting the various slopes of the spectrum.

binding energy of  $\sim 10 \,\text{eV}$ , followed by a broad feature ranging from 7.5 to 3 eV (with maxima at 6 and 4 eV), another feature at  $\sim$  1.9 eV, and a broad structure located just before the Fermi energy cutoff. The line shape of the on-resonance spectrum resembles fairly well the off-resonance one, except for the very intense resonance in the spectral region within 3 eV from  $E_{\rm F}$ . This is clearly visible in the inset of Fig. 5, which represents the 4f resonance spectral weight (RSW), i.e., the on-off resonance difference spectrum. Here we can see that the major part of the Ce 4f RSW extends over a wide region that goes from  $E_{\rm F}$  down to about 3 eV binding energy. In particular, the RSW shows an intense feature centered at 1.92 eV, which can be attributed to the  $4f^0$  states, while the spectral weight closer to  $E_{\rm F}$  is due to the  $4f^1$  states, and specifically to the  $4f_{5/2}^1$  peak (also referred to as the tail of the Kondo resonance peak) located just below  $E_{\rm F}$  and its spin-orbit counterpart  $4f_{7/2}^1$ . These features, as predicted by the single-impurity Anderson model [41] and shown in our results, are consistent with the ResPES studies on many other Ce-based compounds [28,47,49–54]. Their spin-orbit splitting  $\Delta_{SO} \simeq 240$  meV is also qualitatively in good agreement with the values reported for other Ce-based compounds [49,55–59].

A closer look at the inset of Fig. 5 reveals that the RSW is not limited to the region from 3 eV binding energy to  $E_F$ , but



FIG. 6. (Color online) (a) Ce  $3d_{5/2}$ -4*f* ResPES series acquired with incident photon energies marked as circles on the corresponding XAS spectrum shown in (b) and labeled from 1 to 10. All spectra have been normalized to the incident flux and a Shirley background has been subtracted from each of them. The inset shows the valence band spectrum measured at hv = 867 eV (hereafter referred to as the "off-resonance" valence band) before (solid line) and after (dashed line) subtraction of a Shirley background. The on-resonance spectrum corresponds to photon energy 7 in (b). (c) Resonant valence band spectral weight obtained by subtracting the background-subtracted off-resonance spectrum [dashed line in the inset of panel (a)] from each valence band spectrum in (a). (d) Comparison between the Ce 4*f* resonant spectral weight obtained as the difference between on- and off-resonance spectra for the ResPES at both Ce  $M_5$  and  $N_{5,4}$  edges.

it extends up to 7.5 eV from  $E_{\rm F}$ . We are going to resume this issue later and to discuss it together with the results from the  $M_5$  ResPES series presented below.

ResPES across the  $M_5$  edge was performed in order to increase the bulk sensitivity to the measurements. Figure 6(a)shows valence band spectra (after subtraction of a Shirley background) acquired across the  $3d_{5/2} - 4f$  ( $M_5$ ) threshold. The photon energies used are labeled from 1 to 10 and are indicated as open circles in the XAS spectrum (b). All spectra have been normalized to the incident photon flux. The inset shows what will be referred to as the "off-resonance" valence band spectrum measured at 867 eV. This spectrum shows a broad intense peak at  $\sim 3.3$  eV binding energy with a lower-intensity shoulder centered at about 6 eV, and a constant density of states from  $\sim 1.4 \text{ eV}$  to  $E_{\rm F}$ . A qualitative comparison with the density of states calculations performed for other Ce compounds containing Pd (i.e., CePd<sub>2</sub> [38], CePd<sub>3</sub> [38,44], and  $CePd_2Si_2$  [60]) allows us to state that these states can be ascribed mostly to the Pd 4d bands, although the presence of In states cannot be ruled out as no electronic structure calculations for CePdIn<sub>2</sub> are available to date. More specifically, the calculations presented in the above-cited articles consistently locate the majority of the Pd 4d states in the binding energy region above 2 eV, which agrees well with the location of the broad and more intense feature seen in the off-resonance valence band presented in the inset.

As the photon energy is increased across the absorption edge, we see a systematic enhancement of the spectral intensity between  $E_{\rm F}$  and  $\sim 3$  eV binding energy, reflecting to the resonance of the Ce 4f states. The maximum of the resonance occurs at hv = 879.4 eV—labeled as 7 in (b)—which corresponds to the most intense peak in the XAS spectrum. In order to make the 4f contribution to the valence band more visible, the background subtracted off-resonance valence band spectrum shown in the inset of panel (a) has been subtracted from all spectra shown in the main panel (a). The difference spectra are shown in Fig. 6(c) for the same photon energies 1–10, and represent the 4f RSW across this absorption edge. This series of spectra clearly shows (1) a strong resonance below 3 eV binding energy, characterized by two features at roughly 1.9 eV and in close proximity of  $E_{\rm F}$ , consistent with the location of the  $4f_1$  and  $4f_0$  peaks observed in the more surface sensitive N<sub>5,4</sub> ResPES; and (2) a weak RSW appearing as a broad structure between roughly 3 and 7.5 eV, again consistent with what was observed in the  $N_{5,4}$  ResPES.

Figure 6(d) shows a comparison between the RSW at the  $N_{5,4}$  and  $M_5$  edges. The spectra have been normalized to the maximum of the photoemission intensity for better

comparison. The comparison clearly shows that the  $4f^{1}/4f^{0}$  intensity ratio is enhanced in the more bulk sensitive  $M_5$  ResPES. As this ratio increases with the hybridization strength between Ce 4f and conduction states [57], this result is to be expected as the hybridization is larger in the bulk of the material with respect to the surface. This has been shown to occur in other Ce-based systems [52,61,62].

Another common feature of the  $M_5$  and the  $N_{5,4}$  ResPES is the fact that the intensity of the  $4f^0$  component is much higher than the  $4f^1$  (roughly twice as intense for the  $M_5$ resonance, and more for the  $N_{5,4}$  one). This seems to be a consistent feature in the ResPES of Ce alloys containing Pd [56,57,63,64]. In particular, the reader is invited to compare the Ce 4f RSW of CeNiSn versus CePdSn [57] and of CePd<sub>2</sub>Si<sub>2</sub> versus CeNi<sub>2</sub>Si<sub>2</sub> [63], where it is clearly visible how the  $4f^1$  peak is suppressed in the presence of Pd. Moreover, the intensity of the Kondo resonance peak is expected to increase while decreasing the temperature [58,65] and approaching the Kondo temperature of the system.

An interesting fact revealed by the RSW in Fig. 6(d) is that both ResPES series show a resonant enhancement in the binding energy region from 3 to 7.5 eV. A similar observation has been reported in CeAg<sub>2</sub>Ge<sub>2</sub> [66], even though the authors of this paper claim that the spectral weight present in this region does not show any clear resonance behavior, and it is therefore not included in their analysis.

As in most of the spectroscopic investigations of the electronic structure of Ce-based compounds the attention is generally focused on the binding energy region from  $E_{\rm F}$  to 3 eV (where the majority of the Ce 4f spectral weight is expected to be located), it is interesting to explore the behavior of the valence band states at higher binding energy across the Ce resonance. Before commenting further on this issue, we would like to provide evidence that ours is a genuine result, and not an artifact due to the contamination of the surface. For this purpose, we invite the reader to consult the material published in the Supplemental Material [33], where it is clearly shown that the effect of the surface contamination on the photoemission intensity from the valence band at binding energies higher than 3 eV is to develop some additional spectral weight in an energy region limited to the [3.5–5] eV. This is certainly not enough to justify what is seen in our analysis.

Some clarification in this regard can be sought from the evaluation of the behavior of the valence band states across the Ce  $M_5$  resonance. We have therefore divided the RSW into three energy regions, as shown in Fig. 7(a), where area 1, area 2, and area 3 represent the energy regions from 3 to 7.5 eV, from 0.5 to 3 eV (4  $f^0$  states) and from -0.5 to 0.5 eV (4  $f^1$  states), respectively. For each of them we have calculated the integral of the spectral intensity across the  $M_5$  edge and plotted them in Fig. 7(b) together with the Ce  $M_5$  XAS. This direct comparison shows that all three areas resemble quite well the features of the XAS spectrum, the only major discrepancy being the integral for area 3 showing a dip at the photon energy corresponding to the maximum absorption intensity. In the absence of density of states calculations for this compound, we can speculate that the fact that the integrated intensity for area 1 shows a trend similar to the XAS spectrum is an indication of the presence of Ce 4 f character in this energy region. The presence of 4 f density of states at binding energies higher than 3-4 eV has been



FIG. 7. (Color online) (a) Subdivision of the Ce 4f resonant spectral weight [measured with photon energy marked as 7 in Fig. 6(b)] in area 1, area 2, and area 3. Refer to the main text for further explanation. (b) Integrated intensity over areas 1, 2, and 3 plotted on top of the Ce  $M_5$  XAS for direct comparison. All three integrated intensities have been normalized to better compare to the XAS spectrum.

excluded by the electronic structure calculations performed on a number of Ce-based compounds [consider, for example, Ce<sub>2</sub>(Co/Rh)Si<sub>3</sub> [65,67], Ce(Fe/Ru/Os)<sub>2</sub>Al<sub>10</sub> [27], CeAg<sub>2</sub>Ge<sub>2</sub> [66], CeFe<sub>2</sub> [68], CeFe<sub>4</sub>P<sub>12</sub> [47], CeRhSb<sub>1-x</sub>Sn<sub>x</sub> [69], to cite a few]. For the instances where it was predicted [38,44,70], it was consistently very marginal with respect to the near- $E_F$ region, and could not justify for the RSW to correspond to almost 20% of the overall Ce 4 *f* RSW, as is found here.

Our observation can therefore be justified as an effect occurring through the strong hybridization of the 4f states with the ligand states, which are mostly located in this higher binding energy region, as discussed earlier with regards to the inset in Fig. 6(a). These ligand states could either be the 4d electrons of Pd or the 5p electrons of In. Pd valence electrons can be reasonably expected to have a larger hybridization with the 4f states than In, as according to Ijiri *et al.* [7] Ce-Pd bond lengths are at least  $\sim 10\%$  shorter than the Ce-In ones.

We can qualitatively justify our claim by looking at the results for the detailed electronic structure calculations for CePd<sub>3</sub> in Ref. [44]. Figure 3 of this paper shows that the energy region occupied by Pd 4d states extends down to about 7 eV from  $E_{\rm F}$ , and the majority is located above 1.5 eV, while the majority of the Ce 4 f states are located from 1.5 eV to  $E_{\rm F}$ . Interestingly for us, the calculation of the f-d hybridization strength for this compound shown in Fig. 2 of the same article reveals that the hybridization strength is weak in the energy region above 1.5 eV to  $E_{\rm F}$ , while it becomes very large in the energy region occupied by the 4d states of Pd, to the point of showing two peaks corresponding to the maxima of the Pd 4d bands. In a similar study performed for CeIn<sub>3</sub> [71], the same author shows that the hybridization strength between 4 felectrons and In valence states is at least five times smaller than in the case of Pd. This might be the case for CePdIn<sub>2</sub>, even though we cannot definitively claim so based on the available information. It should, however, be noted that the shape of the off-resonance valence band shown in the inset of Fig. 6(a) is different from the shape of the resonant spectral weight shown in Fig. 6(d), even though the extension to binding energy of roughly 7.5 eV is consistent between them. The reason for the different behavior of the Pd 4d states across the Ce resonance can be only speculated about at this stage. One reason for this could be the binding energy dependence of the hybridization strength between Pd 4d and Ce 4f states, even though this should be confirmed by electronic structure calculations.

Based on the discussion above and on the large value of the hybridization strength found from the fit of the Ce 3d core level, we feel justified to attribute the 4f RSW in the binding energy region between 3 and 7.5 eV to the f-d strongly hybridized states. This suggests the fundamental role played by the indirect exchange between localized 4fstates mediated by d electrons, which could possibly favor long-range ferromagnetism at lower temperatures as well as the deviation from trivalency, consistently with the specific heat results reported later in Appendix B. Our results are consistent with the work by Batista *et al.* [72,73], where it is shown that in the strong coupling limit the hybridization between f- and d-electron bands leads to a ferromagnetic ground state possibly of itinerant nature.

#### **IV. CONCLUSIONS**

In summary, we have investigated the Ce 4f contribution to the electronic structure of CePdIn<sub>2</sub> by means of XAS at the Ce  $M_{5,4}$  edges, PES from Ce 3d core level and ResPES at the Ce  $N_{5,4}$  and  $M_{5,4}$  edges, performed on polycrystalline samples at room temperature. The Ce 4f occupation number is found to be 0.92, indicating that the vast majority (more than 90%) of the Ce ions have a 3+ charge state. This is also consistent with an effective magnetic moment of  $2.20\mu_B$ per Ce ion as found from the inverse magnetic susceptibility, that corresponds to  $\sim 87\%$  of that for a free ion, as well as with the line shape of the Ce 3d-4f XAS that shows very good agreement with that for atomic  $Ce^{3+}$  valence state. The analysis of the two ResPES series shows in a consistent manner that the Ce 4 f states are composed of the features predicted by the single-impurity Anderson model, i.e., a broad  $4f^0$  peak centered at a binding energy of 1.9 eV and two  $4 f^1$  spin-orbit states much closer to the Fermi level separated by a spinorbit coupling of roughly 240 meV. The  $4f^{1}/4f^{0}$  intensity ratio is enhanced in the more bulk sensitive  $M_5$  ResPES, as a result of the fact that the hybridization is larger in the bulk of the material with respect to the surface. Furthermore, the ResPES at both edges reveal that the 4f resonant spectral weight extends to the deeper regions of the valence band, i.e., at binding energies larger than 3 eV, that is presumably occupied by the Pd 4d ligand states. We interpret this as a signature for the strong f-d hybridization present in the system, consistent with the large value of  $\sim 180$  meV found from the analysis of the Ce 3d core level. This could possibly favor the emergence of long-range ferromagnetism through the indirect exchange between localized 4f states mediated by highly dispersive d electrons.

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## APPENDIX A: INVERSE MAGNETIC SUSCEPTIBILITY OF CePdIn<sub>2</sub>

The inverse magnetic susceptibility  $\chi^{-1}(T)$  of CePdIn<sub>2</sub> is shown in Fig. 8, together with the magnetic susceptibility in the vicinity of  $T_C$ . The magnetic susceptibility is calculated from a field-cooled magnetization measurement using a background magnetic field of 500 Oe. Above the magnetic transition temperature the inverse magnetic susceptibility can be fitted to the modified Curie-Weiss law

$$\chi(T) = \frac{N_A}{3k} \frac{\mu_{\text{eff}}^2}{T - \Theta_p} + \chi_0, \qquad (A1)$$

where  $\mu_{\text{eff}}$  is the effective magnetic moment,  $\Theta_p$  is the paramagnetic Weiss temperature, and  $\chi_0$  accounts for possible temperature independent contributions to the magnetic susceptibility. The solid line in Fig. 8 shows the best fit of Eq. (A1) to the experimental data above 200 K. The following values were extracted from the fit:  $\Theta_p = 8.6$  K (very close to the observed value of  $T_C$ ),  $\chi_0 = -1.08 \times 10^{-9}$  m<sup>3</sup> (mol Ce)<sup>-1</sup> and  $\mu_{\text{eff}} = 2.20\mu_B$  per Ce ion. Above 200 K the average deviation between the fitted and experimental curves is  $\langle \delta_{\chi} \rangle =$  $7.30 \times 10^{-11}$  m<sup>3</sup> (mol Ce)<sup>-1</sup>. Below 200 K a slight deviation from Curie-Weiss behavior is found, possibly due to CEF effects.

A value of  $2.20\mu_B$  for the effective moment is ~87% of the expected free-ion value, which is in very good agreement



FIG. 8. (Color online) Inverse magnetic susceptibility of CePdIn<sub>2</sub> (black circles) after the subtraction of a small temperature independent contribution. Curie-Weiss behavior above 10 K is evidenced by the good agreement of the data with the fitted red solid line. Inset: Magnetic susceptibility in the vicinity of  $T_C = 10$  K.



FIG. 9. (Color online) The specific heat of CePdIn<sub>2</sub> (filled circles) together with a numerical fit (solid blue line) as described in the text. Inset: 4f electron contribution to the specific heat (filled circles). The solid lines show the magnetic configurational specific heat of a model mean-field spin-1/2 ferromagnet as well as the calculated Schottky contribution arising from the thermal population of CEF split levels as reported in the text.

with the value of 0.92 calculated for the 3d core level above. For Ce-based compounds an effective paramagnetic moment smaller than the free-ion value at high temperatures is often an indication of a departure from trivalency due to hybridization effects between the 4f and conduction electron states. This departure is accompanied by a loss of the "local moment" character of the 4f electrons.

### APPENDIX B: SPECIFIC HEAT OF CePdIn<sub>2</sub>

The specific heat  $C_P(T)$  of CePdIn<sub>2</sub> is shown in Fig. 9. With increasing temperature towards 300 K,  $C_P(T)$  approaches the classic Dulong-Petit limit (dashed line in Fig. 9) in the case of four atoms per formula unit. Below 300 K  $C_P(T)$  shows a typically phonon dominated shape, while a sharply defined anomaly emerges at  $T_C = 10$  K, consistent with magnetic ordering as reported in earlier studies [7,8]. A good fit to the data in Fig. 9 is found by considering phononic, electronic, CEF, and magnetic configurational contributions

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to  $C_P(T)$ . The fit depends on the Debye temperature  $\Theta_D$ , Sommerfeld coefficient  $\gamma$ , CEF excitation energies  $\Delta_1$  and  $\Delta_2$  (assuming a sixfold free-ion ground state degeneracy, which can be uplifted into, at most, three doublets), as well as the ferromagnetic transition temperature  $T_C$ . The Sommerfeld coefficient represents the free-electron weight at the Fermi level, and it parameterizes this contribution to the specific heat through  $C_{el} = \gamma T$ . The CEF excitation energies describe the relative position of two excited doublets above an assumed doublet 4f electron ground state. The thermal population of the CEF split energy levels produces the characteristic Schottky-type features in the specific heat (clearly shown in the inset of Fig. 9). It is important to note that in our fit  $\Delta_1$  and  $\Delta_2$  were allowed to vary between 0 and 500 K. Lastly,  $T_C$  parameterizes the purely magnetic configurational specific heat of a mean-field ferromagnet (with two assumed moment orientations). The fit was performed by means of a stochastic algorithm designed to generate random instances of the parameters described above. For every 200 000 instances the parameter set that gave the best fit to the experimental data was binned. The whole procedure was repeated 30 times, yielding the 30 best parameter sets, for which the average value was taken.

Our parametrization revealed a small electronic contribution above  $T_C$ , characterized by a Sommerfeld coefficient  $\gamma = 16 \text{ J mol}^{-1} \text{ K}^{-2}$ . This value is typically metallic and of the same order of magnitude as that reported in Ref. [8]. Furthermore, the above-mentioned procedure yields  $\Theta_D =$  $205 \pm 2$  K and  $\Delta_1/k_B = 72 \pm 10$  K, similar to the values reported in an earlier independent study [8]. We find that the second CEF excitation  $\Delta_2$  lies 438  $\pm$  30 K above the ground state. This is at odds with the value of 110 K reported in Ref. [8], where  $C_P(T)$  is only reported up to 100 K. Subtraction of the phononic and Sommerfeld contributions to the specific heat yields the data shown in the inset of Fig. 9, which we use as an estimate of the 4f electron contribution to the specific heat, i.e.,  $C_{4f}$ . As shown, the two broad maxima towards higher temperatures are well described by the CEF level dispensation proposed here. Also shown in the inset is the magnetic configurational specific heat of a mean-field ferromagnet (with two allowed moment orientations per site). At 10 K and below, the mean-field model calculation mirrors the experimental  $C_{4f}$ data extremely well, leading us to conclude that CePdIn<sub>2</sub> is a mean-field ferromagnet.

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