Electronic structure and magnetism of RPdIn compounds
(R = La, Ce, Pr, Nd)

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Abstract

RPdIn (R = La–Nd) compounds were studied by means of magnetic susceptibility, specific heat and photoelectron spectroscopy measurements. The results prove that CePdIn is an antiferromagnetic Kondo lattice with T_N below 1.7 K. The Pr-based indide remains paramagnetic down to 1.7 K, and the lack of any magnetic ordering may be due to the presence of a singlet as the crystalline electric field ground state or/and strong hybridization between Pr 4f states and Pd 4d states. In turn, NdPdIn exhibits ferromagnetism below about 26 K. In contrast to CePdIn, for the Pr- and Nd-based compounds any significant enhancement of the electronic specific heat coefficient was observed.
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1. Introduction

RTX ternary compounds (R = rare earth, X = d-electron metal, X = p-electron element) that crystallize in hexagonal structures of the ZrNiAl-type exhibit intriguing physical properties, which are often governed by geometrical frustration within the R sublattice (triangular coordination). Interplay of this special topological feature with unusual electronic phenomena such as mixed valence, heavy fermion or Kondo behaviour have been attracting much attention for the last two decades [1–10].

Among the ternary rare earth palladium indides RPdIn, the compound with R = Ce has been studied most intensively [1–7,10]. It was reported to be a heavy fermion system with the characteristic Kondo temperature of 3.3 K [4] and the C_m/T ratio ranging from 700 to 1400 mJ/(mol K^2) at very low temperatures [1,4]. However, an estimation of the electronic

specific heat coefficient made within the temperature range 10–20 K yielded just $\gamma = 123$ mJ/(mol K^2) [3]. From the bulk magnetic and electrical data as well as from neutron diffraction results the compound was found to order antiferromagnetically below 1.8 K with a commensurate magnetic structure given by the propagation vector (1/4; 0; 0) [1,3,7], which is unique within the ZrNiAl-type crystal structure antiferromagnets. In the most recent studies on hydrogenation of CePdIn it was shown that with rising hydrogen content the Kondo interactions get suppressed and the Néel temperature increases up to 3 K [10].

The La-based representative has been investigated by electrical resistivity and heat capacity measurements up to 80 K only [1,2]. The latter experiments yielded $\gamma = 14$–15 mJ/(mol K^2) and the Debye temperature Θ_D of 194 K [1,3], close to $\Theta_D = 200$ K found for CePdIn [3]. Interestingly enough, LaPdIn becomes superconducting below 1.6 K [3].

In this paper we report on the magnetic properties of the RPdIn compounds with R = La, Ce, Pr and Nd.

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Table 1
Lattice parameters and free positional parameters of R and In atoms for RPdIn
(R = La, Ce, Pr, Nd) compounds

	LaPdIn	CePdIn	PrPdIn	NdPdIn
a (Å)	7.73375(33)	7.70031(37)	7.68948(32)	7.67607(31)
c (Å)	4.14356(27)	4.07411(30)	4.04081(27)	4.00693(26)
x_R	0.58759(82)	0.58292(89)	0.58554(79)	0.58629(76)
x_{In}	0.24515(91)	0.24853(93)	0.24744(90)	0.25021(88)

Complementary data concerning the magnetic susceptibility, the specific heat and the electronic structure probed by photoelectron scpectroscopy are presented and discussed in the general framework of magnetism in the RPdIn series. To the best of our knowledge, the magnetic properties of PrPdIn are reported here for the first time. According to our former neutron diffraction studies, NdPdIn exhibits ferromagnetic ordering of the Nd magnetic moments below 30 K and a spin reorientation at a temperature of about 15 K [9].

2. Experimental details

Polycrystalline samples of the RPdIn compounds (R = La, Ce, Pr, Nd) were synthesized by arc melting stoichiometric amounts of high purity elements (R — 3N; Pd and In — 5N). The syntheses were carried out on a water-cooled copper heart in purified argon atmosphere using Ti as a getter. The buttons were remelted several times to ensure good homogeneity and subsequently annealed in vacuum at 800 °C for one week.

Quality of the products was checked by X-ray powder diffraction. All the samples appeared to be single phases with the expected ZrNiAl-type crystal structure. The lattice and positional parameters refined from the X-ray diffraction data are listed in Table 1.

Magnetic measurements were performed in the temperature range 1.7–400 K and in magnetic fields up to 5 T using a Quantum Design MPMS SQUID magnetometer. The specific heat was measured in the temperature range 2–300 K by quasiadiabatic method employing a Quantum Design PPMS platform. The photoelectron spectra were recorded at room temperature using a SPECS LHS 10+ spectrometer with the incident photons energy of 1253.6 eV (Mg K$_\alpha$ radiation). Surface of the specimens was cleaned using a diamond file; during each experiment high vacuum conditions were maintained ($5 \cdot 10^{-9}$ mbar).

3. Results and discussion

3.1. Magnetic behaviour

The temperature dependencies of the inverse molar magnetic susceptibility of CePdIn and PrPdIn are shown in Fig. 1. These curves were taken at applied magnetic field of 0.1 T. For CePdIn the Curie–Weiss law is fulfilled above 50 K with the effective magnetic moment μ_{eff} of 2.58(1)μ_B and the paramagnetic Curie temperature θ_p of –52.5(1) K. The value of μ_{eff} agrees with the estimates given in the literature [2, 3] and it is very close to the theoretical value for a free
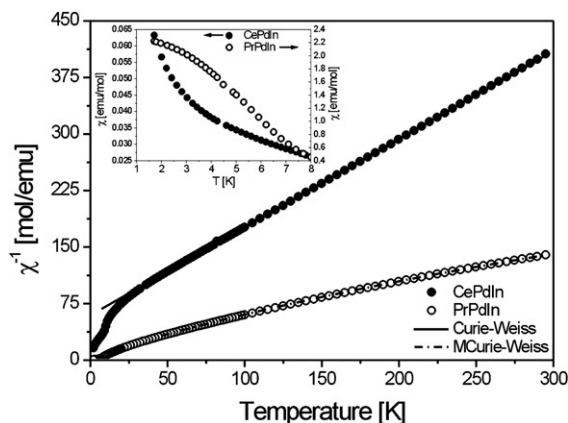

Fig. 1. Temperature dependencies of the inverse magnetic susceptibility of CePdIn and PrPdIn. The lines represent the fits discussed in the text. In the inset the low-temperature susceptibility of both compounds is shown.

Ce^{3+} ion. The negative θ_p that is much larger than the Néel temperature reported for this compound ($T_N = 1.8$ K [3]) hints at strong Kondo interactions. The inset to Fig. 1 presents the magnetic susceptibility of CePdIn measured down to 1.72 K. At the lowest temperatures it rapidly rises, yet do not show any clear hint at the antiferromagnetic phase transition. Presumably, the sample measured orders magnetically at slightly lower temperature than reported in the literature.

In contrast to the case of CePdIn, the inverse magnetic susceptibility of PrPdIn does not show any range where it is proportional to the temperature. Instead, the $\chi^{-1}(T)$ dependence may be approximated by the modified Curie–Weiss (MCW) formula containing Pauli-like contribution χ_0. The parameters obtained in the least-squares fit of the experimental data to the MCW law are as follows: $\mu_{eff} = 3.57(1)\mu_B$, $\theta_p = -8.8(1)$ K and $\chi_0 = 1.9(1) \times 10^{-3}$ emu/mol. The effective magnetic moment is very close to the theoretical value for Pr^{3+} ion. The negative paramagnetic Curie temperature implies antiferromagnetic exchange interactions, which, however, do not result in any long-range magnetic ordering. As displayed in the inset to Fig. 1, the magnetic susceptibility bends towards a plateau at the lowest temperatures, hence suggesting that the crystal field ground state is a singlet. The presence of a non-magnetic ground state (in concert with strong f–d hybridization; see below) may explain the lack of magnetic order in this compound. Worthwhile noting is the large value of the temperature independent contribution to the magnetic susceptibility that is of the order of those characteristic of strong spin fluctuators.

The results of our magnetic measurements of NdPdIn have recently been reported elsewhere [9]. This compound orders ferromagnetically below about 30 K. In the paramagnetic region the modified Curie–Weiss behaviour is observed with $\mu_{eff} = 3.59\mu_B$ and $\theta_p = 2$ K. The experimental value of μ_{eff} is close to that expected for a free Nd^{3+} ion within the LS coupling approach.

3.2. Specific heat

The temperature variations of the specific heat of the four compounds investigated are presented in Fig. 2. The
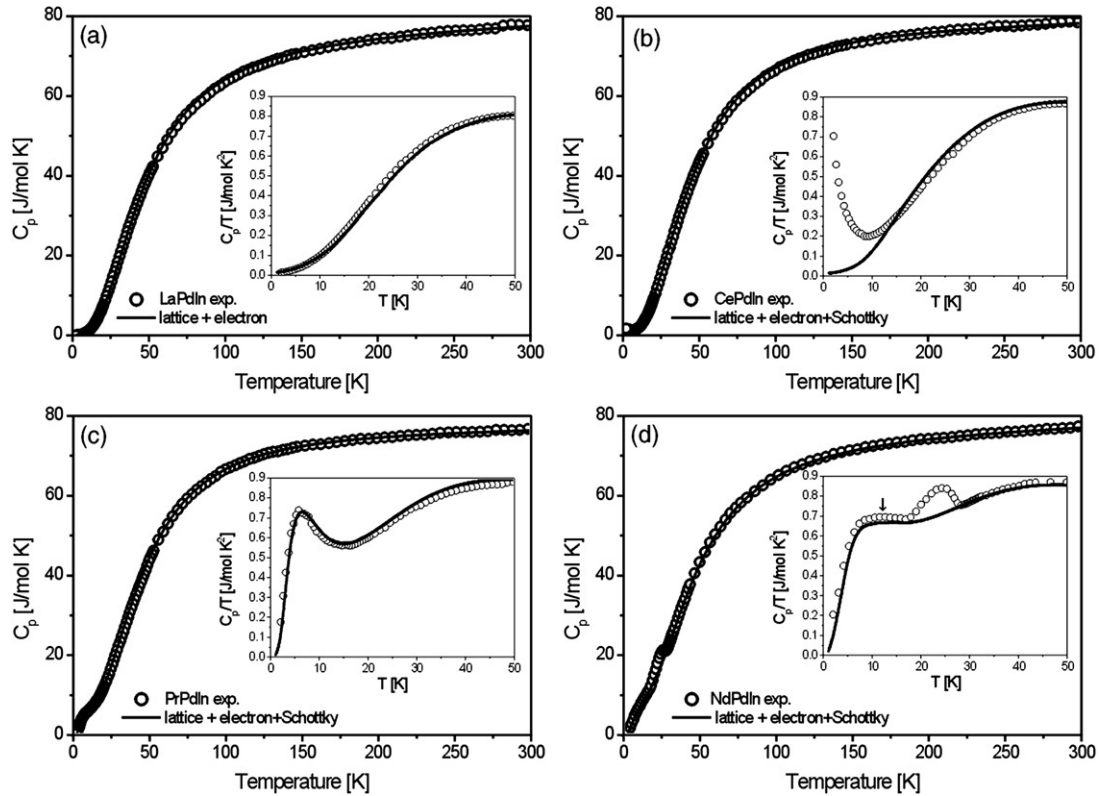
Fig. 2. Temperature variations of the specific heat for (a) LaPdIn, (b) CePdIn, (c) PrPdIn, and (d) NdPdIn. The solid lines represent the fits discussed in the text. The insets show the C/T data at low temperatures.

experimental data were analysed using the standard expression for a sum of the lattice and electronic contributions:

$$C_{ph+el} = 9nR \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\frac{\Theta_D}{T}} \frac{x^4 e^x}{(e^x - 1)^2} dx + \gamma T \tag{1}$$

where n is the number of atoms per formula unit, Θ_D is the Debye temperature, γ—Sommerfeld electronic specific heat coefficient. For the Schottky contribution due to crystalline field effect (CEF) in compounds containing magnetic R ions following formula was used:

$$C_{Schottky} = \frac{R}{T^2} \left[\frac{\sum_i E_i^2 e^{-\frac{E_i}{T}}}{\sum_i e^{-\frac{E_i}{T}}} - \left(\frac{\sum_i E_i e^{-\frac{E_i}{T}}}{\sum_i e^{-\frac{E_i}{T}}} \right)^2 \right] \tag{2}$$

where i is a label of the successive CEF level that possess an energy E_i (in Kelvins). The least-squares fits Eqs. (2) and (3) to the experimental data are shown in Fig. 2 by solid lines. The so-derived values of the Sommerfeld coefficient and the Debye temperatures are listed in Table 2, while the obtained CEF splitting schemes for the compounds with R = Ce, Pr and Nd are displayed in Fig. 3.

Fig. 2(a) presents the results obtained for LaPdIn. The $C_p(T)$ curve has a usual sigmoid shape, which can be well approximated by Eq. (1). The so-derived values of the Debye temperature and the Sommerfeld coefficient are in good agreement with the data reported previously [1,3]. The slightly

Table 2
Results of the specific heat data refinements for RPdIn (R = La, Ce, Pr, Nd) compounds

	LaPdIn	CePdIn	PrPdIn	NdPdIn
Θ_D (K)	191.2(3)	190.7(7)	190.0(5)	189.5(6)
γ (mJ/(mol K^2))	13.9(1)	13.1(3)[a]	6.8(2)	12.6(3)

Θ_D—Debye temperature, γ—Sommerfeld coefficient derived from 2 to 300 K temperature range.

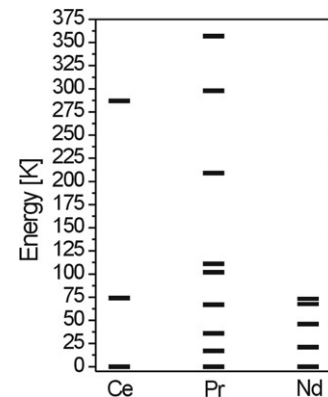[a] 70(4) mJ/(mol K^2) between 12 and 30 K.

Fig. 3. Crystal field splitting schemes for RPdIn (R = Ce, Pr, Nd). The bars represent doublets in the case of the Ce- and Nd-based compounds; and singlets in the case of the Pr-based phase.

enhanced value of γ indicates that LaPdIn cannot be treated as a simple nonmagnetic metal and some electronic correlations,

likely due to anomalous behaviour of La, have to be taken into account when describing the properties of this compound. No signal of the onset of superconductivity at 1.6 K was observed because the lowest temperature of our experiment was limited to 2 K.

The Debye temperature determined for CePdIn agrees well with that reported in Ref. [3], and it is very close to Θ_D found for the La-based compound. The $^2F_{5/2}$ ground multiplet of the Ce^{3+} ion splits into three Kramers doublets located at 0, 75 and 288 K, respectively. Both the total splitting and the energy distance of the first excited level from the ground state are similar the previous estimates [3–5]. The electronic specific heat coefficient within 12–30 K temperature range was found to be 70(4) mJ/(mol K^2); the Schottky contribution was extracted in order to avoid overestimation of γu. At lower temperatures the C/T ratio rapidly increases due to both the critical interactions in the vicinity of the magnetic phase transitions below 1.72 K and the Kondo effect [11].

The temperature variation of the specific heat of PrPdIn exhibits a hump below 15 K (see Fig. 2(c)). This anomaly may be well accounted for by considering the Schottky contribution of nine CEF singlets originating from the $^3H_4$ multiplet. The overall CEF splitting is close to 370 K, and the energy separation between the two lowest levels is about 20 K. With such a tiny distance of the excited state from the non-magnetic singlet ground state, it is possible that some induced magnetic ordering arises at low temperatures [12]. In the present case, either the CEF matrix element between these two levels is too small for efficient exchange interactions or/and another mechanism like f-ligand hybridization hampers the formation of an ordered state. The latter question will be addressed in the next section.

The specific heat data of NdPdIn (see Fig. 2(d)) confirm the previous findings [9] of the ferromagnetic ordering below about 30 K. The least-squares fitting of Eqs. (1) and (2) to the experimental results (excluding the temperature range 15–30 K) yields the overall CEF splitting of the $^4I_{9/2}$ ground multiplet of the Nd^{3+} ion into five doublets being about 75 K, i.e. notably smaller than in the other two compounds (cf. Fig. 3). Some discrepancy (marked with an arrow at the inset to the Fig. 2(d)) between fitted curve and experimental points at about 12 K seems to be connected with reorientation of Nd magnetic moments evidenced by neutron diffraction [9].

3.3. Electronic structure

Fig. 4(a) displays the 4f-electron contributions to the valence band (VB) spectra of CePdIn, PrPdIn and NdPdIn, determined by extracting from the experimental VB data the VB spectrum of LaPdIn (the latter is shown in Fig. 4(b)). Each spectrum was normalized with respect to the In 4d core levels (binding energies of 16.75 and 17.57 eV), which hardly change their positions across the RPdIn series. Moreover, it was assumed that the Pd 4d band in these compounds does not change substantially as well. As is apparent from Fig. 4(b), this level contributes to the total density of states in the form of a maximum located at about 3.5 eV below the Fermi energy.
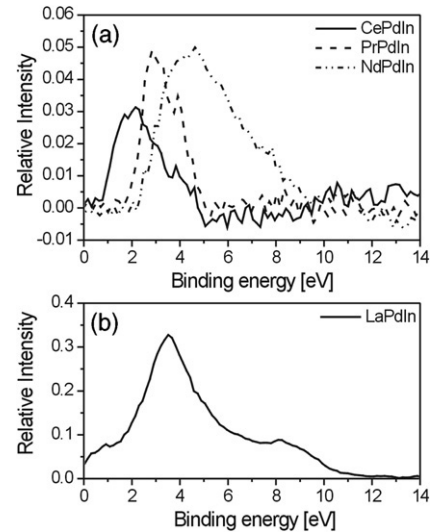

Fig. 4. (a) Contributions of rare earths 4f levels to the valence band spectra of CePdIn, PrPdIn and NdPdIn. (b) Valence band spectrum for LaPdIn.

Table 3
Electronic structure details and hybridization matrix parameters for RPdIn (R = Ce, Pr, Nd) compounds

	CePdIn	PrPdIn	NdPdIn
δ_{4d-4f} (eV)	1.4	0.3	1.8
Δ (meV)	177	149	137
V_{df} (meV)	162	141	126

δ_{4d-4f}—energetic separation between Pd 4d and rare earth 4f levels, Δ—Gunnarsson–Schönhammer hybridization parameter, V_{df}— f–d hybridization matrix element.

Then, the structures observed in Fig. 4(a) may be associated with the R 4f levels situated at 2.1, 3.2 and 5.3 eV below E_F for CePdIn, PrPdIn and NdPdIn, respectively. The energy separation δ_{4d-4f} of these features from the Pd 4d band is listed in Table 3. Interestingly, δ_{4d-4f} is the smallest not for the Ce-based indide, as could be supposed from the heavy fermion character of this compound, but for the Pr-based one. In PrPdIn the 4f and 4d levels strongly overlap and this interaction may be responsible for the absence of any magnetic ordering at low temperatures as well as for the non Curie–Weiss behaviour of its magnetic susceptibility up to room temperature.

According to the Gunnarsson–Schönhammer theory some vital information on the nature of the rare earth 4f electrons can be derived from the photoelectron spectra of the rare earth 3d core levels [13]. Applying the standard procedure described in Ref. [13], the hybridization parameter Δ was estimated for Ce-, Pr- and Nd-based compounds to be 177, 149 and 137 meV, respectively. These values clearly reflect weakening of the f-ligand hybridization on going along the series.

Similar conclusion may be formulated on the basis of the phenomenological Harrison–Straub (HS) model [14,15]. Within this approach the hybridization matrix element $V_{ll'm}$, which quantifies an overlap of the orbitals of two neighbouring atoms, can be expressed as

$$V_{ll'm} = \eta_{ll'm} \frac{\hbar^2}{m_e} \frac{\sqrt{r_l^{2l-1} r_{l'}^{2l'-1}}}{d^{l+l'+1}} \qquad (3)$$

where m_e is the free electron mass, r_l and $r_{l'}$ are the atomic radii of interacting atoms, d stands for the distance between these atoms, whereas l and l' represent the respective angular momentum and m labels the bond symmetry ($m = 0, 1, 2$ and 3 for $\sigma, \pi; \delta$ and ϕ bonds, respectively). The coefficient $\eta_{ll'm}$ in the above expression is defined as [16]

$$\eta_{ll'm} = \frac{(-1)^{l'+1}(-1)^m}{6\pi} \frac{(l+l')!(2l)!(2l')!}{2^{l+l'}l!l'!}$$
$$\times \sqrt{\frac{(2l+1)(2l'+1)}{(l+m)!(l-m)!(l'+m)!(l'-m)!}}. \qquad (4)$$

The parameters V_{df} corresponding the f–d hybridization in the RPdIn compounds, calculated from Eqs. (3) and (4), are listed in Table 3. Apparently, the values of V_{df} gradually decrease on going from CePdIn to PrPdIn to NdPdIn, in accord with the behaviour of the hybridization parameter Δ, thus reflecting an increase in the level of the localization of the rare earth 4f electrons.

The Gunnarsson–Schönhammer hybridization parameter Δ is related to the hybridization matrix element V_{df} in the following manner $\Delta \propto \rho_{max} V_{df}^2$, where ρ_{max} stands for the maximum density of states of the conduction band. This scaling is indeed almost obeyed for the studied RPdIn compounds. Some deviation from this relation may arise because of neglecting in the analysis performed the hybridization of the R 4f states with the 5p states of In.

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