Superconductivity and non-Fermi-liquid behavior of La$_3$Pd$_5$Si$_4$ and Ce$_3$Pd$_5$Si$_4$

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Measurements of temperature and field dependent bulk properties have been carried out on (Ce,La)$_3$Pd$_5$Si$_4$. Rietveld refinements of x-ray powder intensity data confirm the orthorhombic $U_2Ni_4Si_4$-type structure for both compounds. While La$_3$Pd$_5$Si$_4$ exhibits superconductivity below 2 K, together with some indications of a two gap scenario, the former can be characterized as a Kondo lattice system in presence of crystalline electric field splitting. Due to the closeness of a quantum critical point, distinct non Fermi-liquid features dominate the low temperature physics of Ce$_3$Pd$_5$Si$_4$.

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I. INTRODUCTION

Intermetallic compounds with a composition of RE$_3$T$_3$X$_4$ (RE = rare earth, T = transition metal, X = Si, Ge, Sn) became the subject of intense research, partly because of the variety of magnetic structures and partly because of superconductivity occurring in four members of this series with RE = La, T = Ni, Pd, and X = Si, Ge.\(^6\)\(^-\)\(^10\) Transport and magnetic properties of the compounds containing magnetic rare earth elements are governed by the RKKY interaction in presence of strong crystalline electric field effects. While the compounds with heavy rare earth elements and X = Ge and Sn crystallize in the $U_2Ni_4Ge_4$ type of structure,\(^1\)\(^-\)\(^2\)\) Pd based ternary compounds seem not to exist for the light rare earth based metals.\(^3\)\) Sn compounds with Pr and Nd, however, do exist.\(^4\)

Ternary La-based systems with T = Pd and Ni and X = Si and Ge have been reported to crystallize in the orthorhombic $U_2Ni_4Si_4$ type of structure and superconductivity was observed for each member of this family, with $T_c$ ranging from $2.5 \text{ K}$ (La$_3$Pd$_5$Ge$_4$) to $7.6 \text{ K}$ (La$_3$Ni$_4$Ge$_4$).\(^9\) Fuji et al.\(^5\) reported type II superconductivity for La$_3$Pd$_5$Si$_4$, with $T_c = 2.15 \text{ K}$ from resistivity and magnetic susceptibility measurements. Ce$_3$Ni$_4Si_4$ and Ce$_3$Rh$_4$Si$_4$ were found to crystallize in the $U_2Ni_4Si_4$ structure, too.\(^11\)

In our previous work on the system Ce-Pd-Si,\(^12\) we reported on the existence of Ce$_3$Pd$_5$Si$_4$ with $U_2Ni_4Si_4$ type observed from both x-ray powder and single crystal diffraction data, as well as from scanning electron microscopy (SEM). The crystal structure of the compound was solved from single crystal data: space group $Ia$ $Imma$; $a = 0.41618(1)$, $b = 0.42640(1)$, $c = 2.45744(7)$ nm.\(^12\) The structure of $U_2Ni_4Si_4$ can be explained as a combination of $AlB_2$-type and $BaAl_2$-type layers.\(^13\) The unit cell and crystal structure packing of Ce$_3$Pd$_5$Si$_4$ is shown in the inset of Fig. 1. Layers of the ordered derivative from the BaAl$_2$ type, i.e., the ThCr$_2$Si$_2$ type was used as better choice for illustrating the ternary compound.

In the present paper we report on the results of field and temperature dependent electrical resistivity, magnetic susceptibility, and specific heat measurements of Ce$_3$Pd$_5$Si$_4$ at low temperatures in order to derive information about the ground state properties of this ternary compound. Data were analyzed in comparison with isostructural La$_3$Pd$_5$Si$_4$, representing the nonmagnetic background of this material, revealing clear signatures of a non-Fermi-liquid state in terms of the spin fluctuation theory by Moriya and Takimoto.\(^14\) In addition, we have studied La$_3$Pd$_5$Si$_4$ in some detail to evaluate the superconducting properties of this compound. Interestingly, the heat capacity and the upper critical magnetic field do not follow the predictions of a fully gapped s-wave state; rather, a two gap model is better suited to describe the temperature dependent specific heat, in line with a pronounced positive curvature of the upper critical magnetic field.

II. EXPERIMENT

Polycrystalline samples with stoichiometric composition RE$_3$Pd$_5$Si$_4$ (RE = La, Ce), each of a weight of 1 g, were prepared by argon arc melting from high-purity elements (99.9 mass% rare-earth elements, 99.999 mass% Si, and 99.99 mass% Pd), on a water-cooled copper hearth. The melting was repeated several times with the button turned over between each melting. The weight loss was less than 0.5 mass%. After melting, the alloys were vacuum sealed in a quartz tube and annealed at 800 °C for 30 days before being quenched in cold water. Both samples were examined by x-ray powder diffraction (XRD). Data were collected at room temperature employing a STOE STADI P diffractometer with a linear PSD and CuK$_{\alpha1}$ radiation. Quantitative Rietveld refinement of the x-ray was performed with the program FULLPROF,\(^15\)\(^16\) employing internal tables for x-ray atomic form factors. Lattice parameters were calculated using program STOE-WINXPOW.\(^17\)
A superconducting quantum interference device (SQUID) magnetometer was used to study magnetic properties from 2.5 up to 300 K in fields up to 6 T using polycrystalline specimens of about 20 mg. Specific heat measurements on about 1 g of polycrystalline CePd$_3$Si$_4$ were performed at temperatures ranging from 2.5 up to 100 K by means of an adiabatic step heating method. Additionally, specific heat measurements in the temperature range between 250 mK and 20 K were carried out on La$_2$Pd$_4$Si$_4$ and CePd$_4$Si$_4$ samples with a commercial Quantum Design PPMS 3 He relaxation calorimeter in fields up to 1 T. Electrical resistivity measurements were carried out in a 3 He bath top-loading cryostat with a maximum magnetic field of 12.5 T and for temperatures from 350 mK up to 300 K. Resistivity was measured with the electrical current flowing parallel to the applied magnetic field via a four-probe technique using an ac bridge (Lakeshore 370).

III. RESULTS AND DISCUSSION

The XRD analyses indicate that RE$_2$Pd$_4$Si$_4$ phases with La and Ce as rare earth elements are present as a major phase with a minor amount of impurity phases. The XRD pattern of La$_2$Pd$_4$Si$_4$, together with the corresponding Rietveld refinement are shown in Fig. 1, revealing $a = 0.42358(1)$ nm, $b = 0.42900(1)$ nm, and $c = 2.454007(7)$. Some small XRD peaks could be indexed on the basis of a La$_2$Pd$_4$Si$_4$ phase. The content of impurities is estimated to be a few percent in each sample. In the case of CePd$_4$Si$_4$ these small impurity phases were identified as Ce$_2$Pd$_5$Si$_3$ (CeRh$_{1.5}$Ge$_{4.5}$ type) and CePd$_3$Si$_4$ (ThCe$_3$Si$_3$ type) in agreement with the Ce-Pd-Si phase diagram, where these two phases were reported as neighboring phases.

A. La$_2$Pd$_4$Si$_4$

Both resistivity and heat capacity measurements carried out on La$_2$Pd$_4$Si$_4$ evidence bulk superconductivity below 2 K. Shown in Fig. 2 is the temperature dependent electrical resistivity $\rho$ of La$_2$Pd$_4$Si$_4$ at various externally applied magnetic fields. The inset shows $\rho(T)$ of La$_2$Pd$_4$Si$_4$ at zero fields (main panel) and at various externally applied magnetic fields. Clearly visible is a superconducting transition being located slightly above 2 K. This transition temperature is in good coincidence with data reported in Refs. 6 and 7 derived from measurements of the electrical resistivity and magnetic susceptibility. Metallic behavior and the importance of s-d scattering in La$_2$Pd$_4$Si$_4$ is quantitatively revealed from the applicability of the Bloch-Wilson model, i.e.,

$$\rho(T) = A \left( \frac{T}{\theta_D} \right)^5 \int_0^{\theta_D/T} \frac{z^5 dz}{[\exp(z) - 1][1 - \exp(-z)]} + B \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{z^3 dz}{[\exp(z) - 1][1 - \exp(-z)]} - kT^3. $$

The Mott-Jones term $kT^3$ accounts for scattering of conduction electrons on a narrow d band (e.g., Pd-4d or La-5d in La$_2$Pd$_4$Si$_4$) near to the Fermi energy and explains the negative curvature in $\rho(T)$ at higher temperatures. A least-squares fit of this model to the experimental data (solid line, Fig. 2) reveals a Debye temperature $\theta_D = 155$ K, and $\kappa \approx 10^{-7}$ $\mu$V cm K$^{-2}$ as well as a minimum photon energy $\kappa \theta_{\min} = \hbar \omega_{\min}$, with $\hbar \omega_{\min} = 98$ K. Here $\omega_{\min}$ is the frequency corresponding to the minimum $\bar{q}$ value to excite the s-d transitions.\(^{18}\) $A = 54 \mu$V cm and $B = 8.6 \mu$V cm are material dependent constants (compare Fig. 5, too).

The superconducting phase transition is relatively sharp, evidencing good sample quality. The application of magnetic fields (inset, Fig. 2) consecutively suppresses superconductivity, and magnetic fields of the order of 1 T are sufficient to entirely eliminate the superconducting state. This suppression is accompanied by a slight increase of the width of the phase transition. The Debye temperature as derived from resistivity data is significantly lower than that derived from our specific heat measurements (see below). This might be a result of
non-negligible electron-electron scattering superimposed to
electron-phonon scattering.

To prove whether superconductivity in La$_3$Pd$_4$Si$_4$ is of bulk
nature and does not refer to an impurity phase, heat capacity
measurements $C_p(T)$ have been carried out for temperatures
down to 350 mK and for magnetic fields up to 0.4 T. Results
are displayed in Fig. 3. Bulk superconductivity is obvious
from the distinct anomaly of $C_p/T$ around 2 K. An accurate
determination of the superconducting transition temperature
can be made from an idealized jump of the heat capacity
anomaly (solid line, Fig. 3) by a balance of entropy, yielding
$T_c = 1.98$ K, in good agreement with the resistivity data.
The ideal peak height of the SC anomaly would then be
27 mJ/mol K$^2$.

An estimation of the normal state Sommerfeld value $\gamma_0$
within the temperature range between 2 and 5 K, reveals
26 mJ/mol K$^2$, and, additionally, $\theta_D = 280$ K. A similar
value is obtained if field measurements (e.g., $\mu_0 H = 0.4$ T)
are considered, resulting in $\gamma_0 = 28$ mJ/mol K$^2$. The
latter, however, is derived within a much smaller range of
extrapolation.

From the jump of the specific heat $\Delta C_p(T = T_c) \approx 27$
 mJ/mol K$^2$, we calculate the parameter $\Delta C_p/(\gamma_0 T_c) \approx
1.03$, which is below the figure expected from BCS theory,
$\Delta C_p/(\gamma_0 T_c) \approx 1.45$.

Deviations from a standard BCS behavior are also evident
from the temperature dependent specific heat. Compared in
Fig. 4(a) are the experimental heat capacity data of La$_3$Pd$_4$Si$_4$
plotted in a normalized representation $C_p/(\gamma_0 T)$, together
with the heat capacity of a fully gapped $s$-wave superconductor
as tabulated by Mihlschlegel$^{29}$ (solid line, Fig. 4(a)) and
a simple power law $C_p \propto T^3$ [dashed-double-dotted line,
Fig. 4(a)]. The latter would indicate point nodes in the
superconducting gap. Obviously both models do not properly
account for the experimental data, specifically in the low
temperature range.

A further model calculation is based on a two-gap scenario
employing the so-called $\alpha$ model developed by Padamsee
et al.$^{21}$ with only one adjustable parameter $\alpha = \Delta(0)/(k_B T_c)$. 
Note, the value $\alpha = 1.764$ corresponds to the weak
coupling BCS limit. The heat capacity in the superconducting
state is then a sum of individual contributions of both
gaps $\Delta(0)$, together with the ratio $\gamma_1/\gamma_2$, with the partial
specific heat contributions $\gamma_1 + \gamma_2 = \gamma_0$. Such calculations
have been successfully applied to MgB$_2$ to borocarbide
superconductors,$^{22}$ or recently to the ternary iron-silicide
La$_2$Fe$_4$Si$_4$. Employing this model to the La$_3$Pd$_4$Si$_4$ with
$\gamma_1 = 1.95$, $\gamma_2 = 1.1$, and $\gamma_1/\gamma_2 = 0.7/0.3$ [dashed line, Fig. 4(a)]
reveals convincing agreement with the experimental data in
an extended temperature range. Such a two gap model would
also be in line with the pronounced positive curvature found
for the upper critical field of La$_3$Pd$_4$Si$_4$ (see below). The
temperature dependent difference between the experimental
data and the three theoretical models are shown in Fig. 4(b),
clearly demonstrating the superior agreement of the two gap
scenario over a fully gapped $s$-wave model or the simple
power law.

As shown in Fig. 3, both the transition temperature and the
jump of the specific heat at $T_c$ become suppressed with increasing
externally applied magnetic fields. This field dependent
lowering of $T_c$ is outlined in Fig. 4(b), where both resistivity
and heat capacity data are summarized. As it is obvious from
this figure, $T_c(\mu_0 H)$ shows a superlinear dependence, reaching
an upper critical field at zero temperature $\mu_0 H_c(0)$ of about
0.6 T. A typical BCS superconductor, however, would exhibit
a sublinear temperature dependence $\mu_0 H_c(0)$. In absence of
low temperature measurements, Fujii$^{23}$ estimated an upper
critical field $\mu_0 H_{c2} \approx 0.33$ T from a simple extrapolation of susceptibility results.

The unusual temperature dependence of the upper critical field of La$_3$Pd$_4$Si$_4$ can have different microscopic origins: (i) the existence of more than one Fermi-surface sheet with energy gaps of different magnitudes as reported, e.g., for binary MgB$_2$, or (ii) strong anisotropies of the superconducting order parameter residing on a single Fermi-surface sheet.

Positive curvatures of $\mu_0 H_{c2}(T)$ have been observed, e.g., for the nonmagnetic rare-earth nickel borocarbides RMg$_2$B$_2$C (R = Y, Lu) and were explained theoretically employing effective two-band models. Phenomenologically, $\mu_0 H_{c2}(T)$ of borocarbides and MgB$_2$ were accounted for in a wide temperature range using the expression

$$\mu_0 H_{c2} = \mu_0 H_{c2}^a (1 - T/T_c)^{\alpha + \beta},$$

where $\mu_0 H_{c2}^a$ and $\beta$ are fitting parameters. Similar to the borocarbide case and MgB$_2$, $\mu_0 H_{c2}(T)$ of La$_3$Pd$_4$Si$_4$ as displayed in Fig. 4(c), can be described on the basis of Eq. (2).

A least-squares fit is shown in Fig. 4(c) as a dashed line revealing $H_{c2}^a = 0.6$ and $\beta = 0.77$. Exponents of a similar order were derived for borocarbides and MgB$_2$, too.

Werthamer et al. derived an expression (abbreviated as WHH model) for the upper critical field $\mu_0 H_{c2}$ in terms of orbital pair breaking, including the effect of Pauli spin paramagnetism and spin-orbit scattering. The WHH model is ruled by two parameters, namely $\lambda_{so}$, the Pauli paramagnetic limitation (= Maki parameter), and $\lambda_{so}$, describing spin-orbit scattering. While the value of $\lambda_{so}$ allows enough discrimination between orbital pair breaking and Pauli limiting, $\lambda_{so}$ becomes non-negligible for heavier atoms.

The Maki parameter $\lambda_{so}$ can be estimated from the Sommerfeld value $\gamma$ and the resistivity $\rho_0$ as $\lambda_{so} = 0.25$. The reasonably low value of $\alpha$ indicates that orbital pair breaking in La$_3$Pd$_4$Si$_4$ is the essential mechanism, limiting the upper critical field. The overall temperature dependence of $\mu_0 H_{c2}$ as derived from the WHH model is displayed as a solid line in Fig. 4(b), revealing $\mu_0 H_{c2}(0) = 0.21$ T, which is more than two times smaller than the experimentally observed data.

The thermodynamic critical field is calculated from the free energy difference between the superconducting and normal state, given by the expression

$$\Delta F(T) = F_s - F_n = \mu_0 H^2(T)/2 = \int f \gamma^\alpha \rho(T) d\gamma dT.$$ 

The quantity $C_p(T)$ is obtained from the zero field specific heat measurement, whereas $C_p(T)$ is obtained from the data corresponding to the $0.4$ T run. The values derived are displayed in Fig. 4(b) as a dashed-dotted line; an extrapolation to $T \to 0$ yields $\mu_0 H_{c2}(0) \approx 0.04$ T. This allows us to evaluate a value for the dimensionless Ginzburg Landau parameter $\kappa_{GL} = H_{c2}(0)/(\sqrt{2} H_c) \approx 9.8$, where the experimentally determined $H_{c2}(0) = 0.55$ T has been used. The coherence length $\xi_0$ for $T \to 0$ can be obtained from $\mu_0 H_{c2} = (\Phi_0)/(2\pi \xi_0^2)$, yielding $\xi_0 \approx 2.44 \times 10^{-8}$ m. Combining the Ginzburg Landau parameter with the coherence length, the London penetration depth can be obtained as $\lambda_s(T \to 0) \approx 2.39 \times 10^{-7}$ m.

An estimation of the electron-phonon interaction strength $\lambda_{e-ph}$ is possible in terms of the McMillan formula. Applying this model, and taking the repulsive screened Coulomb part $\mu^* \approx 0.13$, yields $\lambda_{e-ph} \approx 0.52$; this characterizes La$_3$Pd$_4$Si$_4$ as a SC in the weak coupling limit.

Similarly, an electron-phonon enhancement factor of about the same magnitude can be found if recent electronic structure calculations are considered, where the calculated density of states at the Fermi energy corresponds to a bare band value $\gamma = 19.8$ mJ/mol K$^2$. A comparison with the experimentally derived Sommerfeld value $\gamma \approx 29$ mJ/mol K$^2$ yields $\lambda_{e-ph} \approx 0.46$, supporting the weak coupling regime.

Based on the value of $\lambda_{e-ph} \approx 0.75$ we classify La$_3$Pd$_4$Si$_4$ as a weakly coupled superconductor in the dirty limit; the value of $\kappa_{GL} \approx 10$ refers to a type II superconductor.

B. Ce$_3$Pd$_4$Si$_4$

Intermetallic compounds based on Ce are known a long time for a variety of interesting ground states, primarily triggered by the Kondo effect as a result of distinct interactions between conduction electrons and the magnetic moment of the Ce ion. In the following, results derived from resistivity, heat capacity, and magnetization measurements will be obtained to obtain information on the ground state properties ofCe$_3$Pd$_4$Si$_4$.

Shown in Fig. 5 are temperature dependent resistivity measurements of Ce$_3$Pd$_4$Si$_4$ and of La$_3$Pd$_4$Si$_4$; the latter compound serves as a magnetic reference, representing the contribution to the electrical resistivity owing to the electron-phonon interaction. While $\rho(T)$ of La$_3$Pd$_4$Si$_4$ exhibits superconductivity below 2 K and a simple metallic behavior in the normal state region (see the previous section), $\rho(T)$ of Ce$_3$Pd$_4$Si$_4$ shows a much more complex temperature dependence as typical for Kondo lattice systems. The most dominant feature is a maximum in $\rho(T)$ around 8.5 K with $\rho(T)$ dropping above and below this temperature. Well above 100 K, a local minimum develops in $\rho(T)$. A comparison of the experimental data of Ce$_3$Pd$_4$Si$_4$ and La$_3$Pd$_4$Si$_4$ allows

![FIG. 5. (Color online) Temperature dependent resistivity $\rho$ of La$_3$Pd$_4$Si$_4$ and Ce$_3$Pd$_4$Si$_4$ plotted on a logarithmic temperature scale. The magnetic contribution $\rho_{mag}(T)$ of Ce$_3$Pd$_4$Si$_4$ is also shown in this plot, where the dashed line should emphasize Kondo interaction: $\rho_{mag} \approx \rho(Ce_3Pd_4Si_4) - \rho(La_3Pd_4Si_4)$. The solid line is a least squares fit as explained in Fig. 2.](image-url)
To derive the magnetic part \( \rho_{\text{mag}} \) if one assumes that the phonon contribution of both compounds is equal, \( \rho_{\text{mag}}(T) \) of \( \text{Ce}_2\text{Pd}_4\text{Si}_4 \) is included in Fig. 5, too. The logarithmic temperature dependence of \( \rho_{\text{mag}} \) at elevated temperatures evidences Kondo interaction in the presence of crystalline electric field splitting. The drop of \( \rho(T) \) at low temperatures results from the development of a coherent state owing to the Kondo lattice properties of \( \text{Ce}_2\text{Pd}_4\text{Si}_4 \). In general, such a coherent state would be concomitant with Fermi-liquid features, and a \( T^2 \) behavior of \( \rho(T) \) should become obvious. The present experimental data, however, reveal a distinctly different power law.

A closer inspection of the low temperature resistivity data is shown in Fig. 6, where measurements at various magnetic fields are added. The low temperature maximum in \( \rho(T) \) is weakly field dependent and shifts from about 8.5 K at zero magnetic field to about 10.5 K at an externally applied field of 8 T. Such a field dependence of the electrical resistivity is typical for cerium and ytterbium based Kondo lattices. At the lowest temperatures of our study, Fermi-liquid features are absent in \( \rho(T) \). Rather, the zero field measurement can be accounted for by a simple power law \( \rho(T) = \rho_0 + A T^n \), where the exponent \( n = 1 \) reveals best agreement in the case of the 12 T run, \( n = 1.15 \). These exponents are indicative of a non-Fermi-liquid behavior, arising, most likely, from the proximity of a magnetic instability of the Ce ions.

A magnetic state of the Ce ions in \( \text{Ce}_2\text{Pd}_4\text{Si}_4 \) can be concluded from magnetic susceptibility measurements \( \chi(T) \) as shown in Fig. 7. Applying a modified Curie-Weiss law to the experimental data, i.e.,

\[ \chi = \chi_0 + \frac{C}{T - \theta_p}, \]

yields information concerning a temperature independent Pauli contribution \( \chi_0 \), the effective magnetic moment \( \mu_{\text{eff}} \) (deduced from the Curie constant \( C \)), and the paramagnetic Curie temperature \( \theta_p \). Results of a least-squares fit \( T > 50 \text{K} \)

according to Eq. (3) are shown as a solid line in Fig. 7, revealing an effective magnetic moment \( \mu_{\text{eff}} = 2.5 \mu_B \) close to that of the Ce-4f electronic configuration \( \mu_{\text{eff}}(\text{Ce}^{3+}) = 2.54 \mu_B \) and a paramagnetic Curie temperature \( \theta_p = -29 \text{K} \). The latter refers to antiferromagnetic interactions among the Ce ions. \( \chi(T) \) at low temperatures does not show any characteristic anomaly being typical for long range magnetic order. This is in line with isothermal magnetization data taken at \( T = 2 \text{K} \) (inset, Fig. 7). A smooth, slightly curvilinear \( M(H) \) dependence is observed with relatively small magnetization values at 6 T. A description of these data can be done calculating the field dependent magnetization of an effective spin 1/2 system at \( T = 2 \text{K} \). Employing a Landé factor \( g_{\text{eff}} = 0.775 \). Fairly good agreement is obtained in this way, except for the low field range, where the disagreement between the model and the experimental data appears to be in line with the Curie-like bending of the magnetic susceptibility at low temperatures. CEF effects are the primary cause for the appearance of only small magnetization values, well below \( g_{j, j} = 2.14 \mu_B \), associated with the total angular momentum of the free Ce\(^{3+} \) ion. A comparison with magnetization data of \( \text{Ce}_2\text{Pd}_4\text{Ge}_4 \) at \( T = 2 \text{K} \) shows for the latter a clear indication for a metamagnetic phase transition around 4 T, thus referring to an antiferromagnetic ground state.

To further prove the ground state of \( \text{Ce}_2\text{Pd}_4\text{Si}_4 \), heat capacity measurements \( C_p \) have been performed down to 400 mK. Results are displayed in Fig. 8 as \( C_p/T \) vs \( T \), together with those of \( \text{La}_2\text{Pd}_4\text{Si}_4 \). The most prominent feature is an almost logarithmic contribution in the range of a few Kelvin, followed by a smooth saturation of \( C_p/T \) towards zero with very large values of about 2.7 J/mol K\(^2 \), corresponding to \( \gamma = 0.9 \text{J/mol K}^2 \) per cerium ion. Considering renormalization group calculations by Oliveira and Wilkins,\(^{12} \) the Kondo temperature \( T_K \) follows from \( T_K = 0.68 \cdot R/\gamma = 6.2 \text{K} \) if a doublet is considered as ground state.
Assuming that the phonon contribution to the heat capacity of Ce$_3$Pd$_4$Si$_4$ can be represented by the specific heat of La$_3$Pd$_4$Si$_4$, the magnetic entropy $S_{mag}$ can be derived by integrating $C_{mag}/T$. Results of this evaluation are plotted in Fig. 8 as a dashed line, referring to the right axis. An entropy of $3\cdot R \ln 2$ is reached around 18 K. The slow rate of the recovery of magnetic entropy in Ce$_3$Pd$_4$Si$_4$ is a consequence of the Kondo effect present in the compound. $S_{mag}(T)$ also allows us to estimate the Kondo temperature independently from $T_K = T(S_{mag} \approx 0.45 \cdot R \ln 2) \approx 4.4$ K, in very good agreement with the estimation obtained from the Sommerfeld value. Kondo-type interaction is also supposed to be responsible for the suppression of long range magnetic order, absent in Ce$_3$Pd$_4$Si$_4$ at least down to 400 mK.

The further increase of $S_{mag}$ at higher temperatures indicates that the excited crystalline electric field levels are not well separated from the ground state; hence some hybridization between CEF levels might appear. This is seen from some deformation of the maximum of the magnetic contribution to the electrical resistivity too.

In order to test whether or not Ce$_3$Pd$_4$Si$_4$ is at or near the quantum critical point, the self-consistent renormalization (SCR) model of Moriya and Takimoto can be taken into account:

$$ C_m = 9N_0 \int_0^\infty dx x^2 \left[ u^2 - 2u \frac{d}{dt} \left( \frac{dy}{dt} \right)^2 \right] \times \left[ -\frac{1}{u} - \frac{1}{2v} + \psi(u) \right] - \frac{1}{u} - \frac{1}{2v} + \psi(u), $$

where $x^2 = u \cdot t - y$, $u = u(y)$, and $y = (y_1, y_2)$ is the reduced staggered susceptibility and $t = T/T_0$. $T_0$ is some characteristic temperature, scaling a temperature dependent physical quantity; $\gamma_1$ is a constant. The parameter $y_0$ measures the distance of the system to the magnetic instability and provides a measure of the inverse correlation length. As $y_0$ approaches zero, the system approaches the quantum critical point.

An adjustment of Eq. (4) to the experimental data is displayed in Fig. 8 as a solid line, revealing excellent agreement between the data and the model for $T_0 = 3.5$ K, $y_0 = 1.5$, and $\gamma_1 = 15$. The model reveals a constant for $T \to 0$ followed by a $T^{-3/2}$ dependence; finally, at higher temperatures, a logarithmic decrease of $C_p/T$ occurs, in accord with the experimental findings. The finite—all though small—value of $y_0$ indicates that Ce$_3$Pd$_4$Si$_4$ is not directly at the QCP; nevertheless it proves that this sample is next to a phase transition at $T = 0$.

A more stable magnetic state, however, was observed for Ce$_3$Pd$_4$Ge$_4$ where due to the increase of the unit cell volume owing to the Si/Ge substitution, a decrement of hybridization takes place; as a consequence, magnetic order occurs and the system has moved away from quantum criticality.

IV. SUMMARY

Bulk properties of RPd$_4$Si$_4$ with RE = La and Ce both with the U$_2$Ni$_4$Si$_4$-type structure were investigated by means of resistivity, specific heat, and magnetic susceptibility measurements. Nonmagnetic La$_3$Pd$_4$Si$_4$ is characterized by superconductivity below about 2 K. Disagreement from a simple, fully gapped s-wave BCS superconductor are obvious from deviations of the temperature dependent specific heat and from the positive curvature of the upper critical field $\mu_0 H_c2$. A two band and two gap model reasonably well describes the heat capacity data in the superconducting state if $\alpha_1 = 1.95$ and $\alpha_2 = 1.1$.

The isostructural Ce-based compound behaves as a Kondo lattice, exhibiting a pronounced maximum in the temperature dependent electrical resistivity as well as an extended logarithmic temperature range as a result of the Kondo effect in presence of crystalline electric field effects. At low temperatures, distinct deviations from a Fermi-liquid ground state are evident in both resistivity and heat capacity data, provoked from the proximity of a phase transition at $T = 0$.

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