LETTER TO THE EDITOR

Non-Fermi-liquid behaviour close to the disappearance of ferromagnetism in $CePd_{1-x}Rh_x$

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Abstract
The orthorhombic $CePd_{1-x}Rh_x$ system exhibits a continuous evolution from ferromagnetic order in CePd ($T_C = 6.6$ K) to an intermediate-valence ground state in CeRh. Here we report low-temperature ($T \geqslant 0.08$ K) specific-heat measurements for concentrations $0.80 \leqslant x \leqslant 0.95$ close to the disappearance of magnetic order (~0.87). In contrast to $x = 0.8$, still demonstrating a smeared phase transition signature at 0.27 K, non-Fermi-liquid behaviour $\Delta C(T)/T \propto \log T$ is observed in the electronic specific-heat coefficient at $x = 0.85$. For higher Rh concentrations a weak power-law dependence $\Delta C(T)/T \propto T^{-\alpha}$ with $\alpha \approx 0.4$ is found. Upon applying magnetic fields Fermi-liquid-like behaviour $\Delta C(T)/T \sim$ const is recovered in all the different samples. The magnetic entropy as well as the concentration of unscreened magnetic moments at 2 K indicate a broad distribution of local T_K values ranging from well below 2 K to far above 50 K.

1. Introduction

Unique physical properties of quantum critical matter, which result from the competition of quantum fluctuations with classical (thermal) ones at temperatures approaching absolute zero, are at present one of the central topics in condensed matter physics [1]. The most interesting examples include a divergent specific-heat coefficient, a linear temperature dependence of the electrical resistivity, or a divergent Grüneisen parameter [2, 3]. Such commonly called non-Fermi-liquid (NFL) behaviour has been evidenced in a number of compounds close to an antiferromagnetic (AFM) quantum critical point (QCP) [4]. In contrast, the ferromagnetic

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(FM) QCP is much less experimentally studied mainly because of a lack of suitable materials (see e.g. [5]). The search for appropriate compounds is motivated by theories, which predict the physical properties to differ significantly between AFM- and FM-QCPs [6].

The system $CePd_{1-x}Rh_x$ is very suitable for studying quantum criticality in ferromagnets. It has been reported to exhibit a continuous evolution from FM order at $T_C = 6.6$ K (CePd) to an intermediate-valence (IV) ground state (CeRh) [7]. In particular, the Curie temperature was found to be suppressed by the Rh doping down to about 3 K in $CePd_{0.40}Rh_{0.60}$. Recent studies of physical properties at lower temperatures of the alloys with $x \geqslant 0.60$ showed a further decrease of T_C with increasing x, down to about 0.25 K for $x = 0.80$ [8, 9]. Specific-heat measurements have been performed down to 0.45 K [9]. Overall they show the reduction of the low-temperature specific heat with increasing x, compatible with a strong increase of the Kondo temperature. The analysis of the temperature dependence of the 4f contribution to the specific heat $\Delta C(T)/T$ suggests NFL behaviour, at least down to 0.45 K. Whereas $-\log T$ behaviour is observed below 1 K for $x = 0.8$ and 0.85, a weak power-law dependence $\Delta C(T)/T \sim T^{-\alpha}$ with $\alpha \approx 0.5$ has been found for $x = 0.87$, 0.90 and 0.95 in the temperature range $0.45\ \mathrm{K} \leqslant T \leqslant 3$ K [9].

In order to shed more light on quantum criticality and NFL behaviour in $CePd_{1-x}Rh_x$ close to the Rh concentration where ferromagnetism disappears, we have performed systematic studies of polycrystals with compositions $x = 0.80$–0.95, by means of specific-heat measurements down to very low temperatures and at high magnetic fields. Below, we prove that NFL behaviour extends down to millikelvin (mK) temperatures and can be found in an extended x-range ($0.85 \leqslant x \leqslant 0.95$). We propose that this behaviour could be related to a broad distribution of local Kondo temperatures ranging from well below 2 K to far above 50 K.

2. Experimental details

Polycrystalline samples of $CePd_{1-x}Rh_x$ with $x = 0.80$, 0.85, 0.87, 0.90 and 0.95 were prepared as described in [8, 9]. Additionally, the non-magnetic reference system LaRh was synthesized. The specific-heat measurements were carried out in two overlapping temperature ranges, employing different methods: a thermal relaxation technique at $0.35\ \mathrm{K} \leqslant T \leqslant 10$ K, utilizing a commercial Quantum Design PPMS system, and a compensated quasi-adiabatic heat-pulse method adapted to a dilution refrigerator at temperatures ranging from 80 mK up to 4 K [10]. The experiments were performed in applied magnetic fields up to 3 T.

3. Results

3.1. Zero field measurements

The temperature dependence of the specific heat of the non-magnetic reference system LaRh, $C_{La}(T)$ (not presented here), was found to be typical for simple metals and well describable below about 6 K by the sum of a phononic (Debye T^3-law) and linear-in-T electronic contribution. A best fit according to $C_{La}(T) = \gamma_{La}T + \beta_{La}T^3$ yields $\gamma_{La} = 1.1(1)$ mJ mol^{-1} K^{-2} and $\beta_{La} = 1.36(1)$ mJ mol^{-1} K^{-4}. The latter parameter corresponds to a Debye temperature of about 140 K.

The 4f contribution $\Delta C(T)$ to the total specific heat of $CePd_{1-x}Rh_x$ was then estimated by subtracting $C_{La}(T)$ from the raw data for each sample. The nuclear (quadrupolar) specific-heat contribution was found to be negligible at temperatures above 80 mK in all samples studied. Figure 1(a) shows zero-field data of $\Delta C(T)/T$ for all $CePd_{1-x}Rh_x$ compounds investigated. In the entire temperature range, $\Delta C(T)/T$ decreases with increasing x, compatible with the increase of the Kondo temperature with Rh content as deduced from previous studies [7–9].

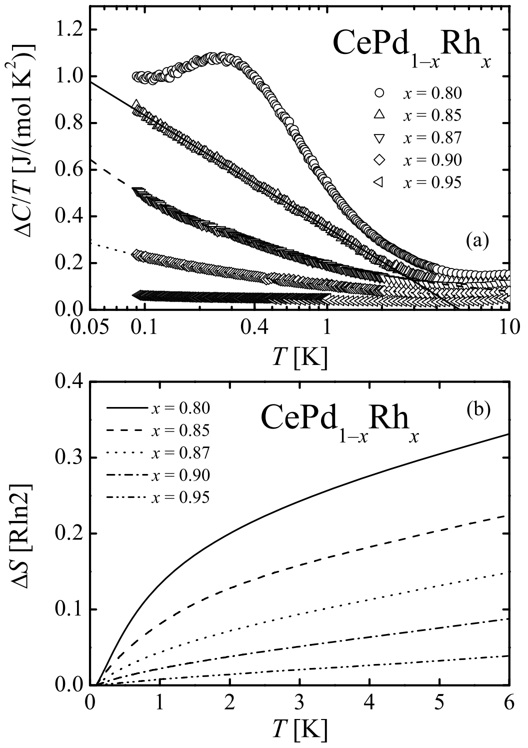

Figure 1. (a) 4f contribution to the specific heat of CePd$_{1-x}$Rh$_x$ with $x = 0.80$–0.95 as $\Delta C(T)/T$ versus temperature (on logarithmic scale). The solid and broken lines represent logarithmic and power-law behaviour, respectively; see text. (b) Corresponding entropy increment $\Delta S(T) = \int_{0.08\ \mathrm{K}}^{T} (\Delta C(T')/T)'\, \mathrm{d}T'$.

As can be inferred from figure 1(a), the electronic specific-heat coefficient, $\Delta C(T)/T$, of CePd$_{0.20}$Rh$_{0.80}$ increases upon cooling, passes a broad maximum at 0.27 K, and saturates at a large value of about 1 J mol^{-1} K^{-2} below 0.15 K. Note that previous specific-heat measurements on the same sample, performed above 0.4 K, did not show this anomaly [9]. The fact that the position of this maximum (i.e. $T_{\mathrm{max}} \approx 0.27$ K) almost coincides with that of a maximum in the magnetic ac-susceptibility ($\approx$0.25 K) [9] strongly suggests that the specific-heat anomaly is related to the low-temperature FM phase transition. In contrast to CePd$_{0.20}$Rh$_{0.80}$, $\Delta C(T)/T$ for $x = 0.85$ does not exhibit any anomaly down to 0.08 K (cf figure 1(a)). Below about 2 K and down to the lowest temperatures, i.e. over more than one decade of temperatures, $\Delta C(T)/T$ of CePd$_{0.15}$Rh$_{0.85}$ shows $-\log T$-behaviour, characteristic of the NFL systems [4]. Least-squares fitting of the formula $\Delta C(T)/T = -\log T/T^*$ to the experimental data (see the solid line in figure 1(a)) yields $A = 0.481(1)$ J mol^{-1} K^{-2} and $T^* = 5.38(3)$ K. Similar behaviour has previously been found in the temperature range 0.4–2 K [9].

Interestingly, an anomaly observed at about 0.13 K in the temperature dependence of magnetic ac-susceptibility of CePd$_{0.15}$Rh$_{0.85}$ [9] seems to be not detectable by means of specific-heat measurements (figure 1(a)). It is worth noting that our experiments were carried out exactly on the same samples as the ac-susceptibility measurements. Therefore, slight deviation from the nominal stoichiometry, which is often observed for different parts of polycrystalline arc-melted pellets, can be excluded as a reason of the absence of an anomaly in $\Delta C(T)/T$. A possible oxidation and/or decomposition of the sample (or any other ageing effects) can be also safely excluded, since all specific-heat measurements presented in this letter were performed twice, before and after the ac-susceptibility studies, yielding identical results.

The temperature dependence of the electronic specific-heat coefficient for $x = 0.87$ can be described by $\Delta C(T)/T = AT^{-\alpha}$ with $A = 194(6)$ mJ mol^{-1} K$^{-2+\alpha}$ and $\alpha = 0.40(1)$ (see dashed line in figure 1(a)). A power-law divergence is also found for $x = 0.9$ with $A = 105(1)$ mJ mol^{-1} K$^{-2+\alpha}$ and $\alpha = 0.33(1)$. Thus, our low-T measurements confirm the previous specific-heat measurements above 0.4 K, which have revealed similar behaviour, yet in a narrower temperature range [9].

Figure 1(b) displays the temperature dependence of the entropy increment, $\Delta S(T)$, for $\mathrm{CePd}_{1-x}\mathrm{Rh}_x$, obtained from integration of the electronic specific-heat coefficient data displayed in figure 1(a). With increasing Rh content, the entropy gain at constant temperature becomes drastically reduced, indicative of a strong increase of the Kondo temperature with increasing x, in agreement with previous specific-heat results [9] and compatible with the evolution with Rh substitution from a dense Kondo-system towards an IV system.

3.2. Measurements under magnetic field

Figure 2 displays the electronic specific-heat coefficient of $\mathrm{CePd}_{1-x}\mathrm{Rh}_x$ with $x = 0.80$–0.90, at different magnetic fields. At low temperatures, $\Delta C(T)/T$ measured for each sample decreases rapidly upon applying external magnetic fields. As is seen, there is also a flattening in $\Delta C(T)/T$ that resembles a Fermi-liquid behaviour, though further low-temperature electrical-resistivity and magnetic-susceptibility measurements are required to confirm that possibility. In addition, the temperature range in which $\Delta C(T)/T \sim$ const increases with field. Such a field-induced recovery of FL behaviour has also been observed in other NFL systems (cf [4]). The field strength required to induce a FL state is quite similar to that found in Ce systems close to an AFM-QCP. Thus, in the proximity of a QCP, switching from dominant antiferromagnetic intersite exchange to ferromagnetic intersite exchange does not seem to have a strong influence on the thermodynamic properties. This suggests that these thermodynamic properties are mainly governed by the intrasite Kondo exchange.

The appearance of weak and broad maxima in $\Delta C(T)/T$ at non-zero magnetic fields (figures 2(a)–(d)) is also typical for NFL systems. Figure 3 displays the positions $T_{\max}$ of those maxima as a function of magnetic field. In the samples with $x \geqslant 0.85$, $T_{\max}(B)$ shows a linear field dependence down to the lowest fields. One can tentatively relate this maximum to a Schottky-like anomaly connected with the Zeeman splitting of the partially Kondo-screened crystal-electric-field ground-state doublet in the external magnetic field [11]. From the slope of $T_{\max}(B)$ one can then deduce a screened moment of $\approx 0.2\ \mu_{\mathrm{B}}$. On the other hand, the $T_{\max}(B)$ curve for $\mathrm{CePd}_{0.20}\mathrm{Rh}_{0.80}$ does not follow a linear dependence at low fields; instead, it saturates at a finite temperature for $B = 0$. This suggests the presence of an internal molecular field induced by (short-range) magnetic order, in accordance with the maximum in χ_{ac} observed near $T_{\max}$ [9].

4. Discussion

We have shown that the low-temperature specific heat of $\mathrm{CePd}_{1-x}\mathrm{Rh}_x$ shows signatures of NFL behaviour for a wide range of Rh concentrations x. At $x = 0.85$, the electronic specific-heat coefficient follows a $-\log T$ dependence at least down to 0.08 K. Such behaviour may result from quantum critical fluctuations close to a FM-QCP [12, 13]. However, ac-susceptibility measurements on the same crystal have found a clear cusp around 0.13 K, which proves

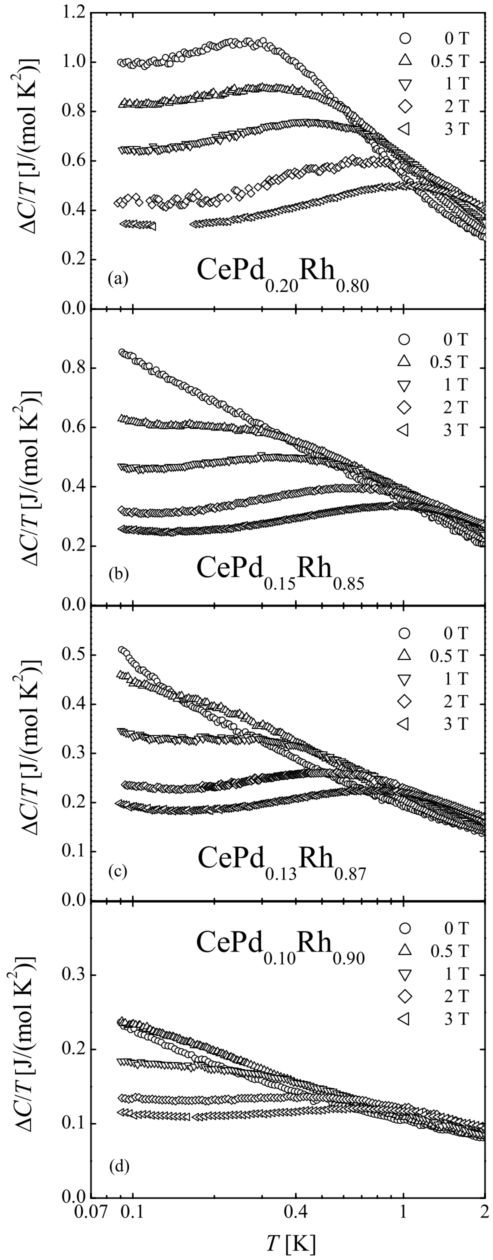

Figure 2. Semi-logarithmic plots of $\Delta C(T)/T$ of $\mathrm{CePd}_{1-x}\mathrm{Rh}_x$ with compositions $x =$ (a) 0.80, (b) 0.85, (c) 0.87, and (d) 0.90, at various magnetic fields.

that this system cannot be located directly at a QCP [6]. For $x \geqslant 0.7$, the position of the cusp in $\chi_{\mathrm{ac}}(T)$ becomes frequency dependent and shifts towards higher T with increasing frequency of the excitation field [9]. Such behaviour is characteristic of a spin-glass and indicates that beyond this Rh concentration the order is no longer of true long-range kind, but has a finite correlation length. Indeed, a tail has been observed in the T_{c} versus x phase

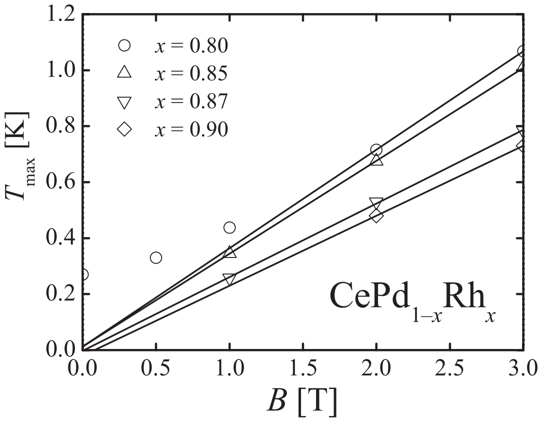

Figure 3. (a) Positions of maxima in $\Delta C(T)/T$ of $\mathrm{CePd}_{1-x}\mathrm{Rh}_x$ with $x = 0.80$–0.95 (compare figures 2(a)–(d)) as a function of magnetic field. Solid lines indicate $T_{\max} \propto B$.

diagram, which makes a (clean) FM-QCP scenario in this system rather unlikely [9]. Further on, the entropy related to the $-\log T$ behaviour in $\Delta C(T)/T$ amounts to ~20% $R \ln 2$ only, i.e. less than half of the amount typically found for systems at QCPs (cf [14]). Finally, another contradiction to the QCP scenario is that for larger Rh content ($x \geqslant 0.87$) the temperature dependence of the electronic specific-heat coefficient changes to $\Delta C(T)/T \propto T^{-\alpha}$ with $\alpha < 1$. Most likely, disorder induced by the Pd–Rh site exchange plays a crucial role in our system.

Weak power-law divergences of the electronic specific-heat coefficient have also been observed in a couple of chemically substituted U-based systems over extended ranges in composition [15] and associated with the existence of a Griffith's phase close to the magnetic instability [16]. However, for this latter scenario, the susceptibility and specific-heat coefficient have to diverge with similar exponents. For $\mathrm{CePd}_{1-x}\mathrm{Rh}_x$, with $x = 0.85$ and 0.87, on the other hand, the magnetic susceptibility shows a cusp whereas no corresponding signature is observed in the specific-heat coefficient. Similar observations have also been made for other disordered systems close to magnetic instabilities [17]. Since spin-glass effects are not explicitly treated in the model of Castro Neto *et al* [16] it remains unclear whether our observations would be compatible with the Griffith's phase scenario.

The difference between specific heat and magnetic susceptibility may indicate that the former property is mainly determined by single-ion properties, whereas the latter one is more sensitive to weak magnetic interactions. It has been shown that a distribution of (single-ion) Kondo temperatures may lead to NFL behaviour in specific heat, if such a distribution has a tail towards small T_K values [18].

For the $\mathrm{CePd}_{1-x}\mathrm{Rh}_x$ system, a dramatic increase of the (average) Kondo temperature with x has been observed for Rh concentrations beyond $x_V \approx 0.75$, where strong valence fluctuations set in. A small distribution of the local Rh concentration x around the Ce atoms may then lead to a broad distribution of (local) T_K values. The plots of $\chi_{ac}^{-1}(T)$ [9] evidence in the sample $x > 0.8$ a Curie–Weiss-like tail with a reduced moment at low temperatures, while a broad hump at higher temperatures resembles the behaviour expected in an intermediate valence system. The pronounced low-temperature Curie–Weiss tail is a direct evidence for some unscreened Ce moments. We estimated the amount of these unscreened moment by fitting the slope of the inverse susceptibility at 2 K with $\chi^{-1} = c/(T - \Theta)$ (cf figure 2 in [9]) at 2 K. Taking

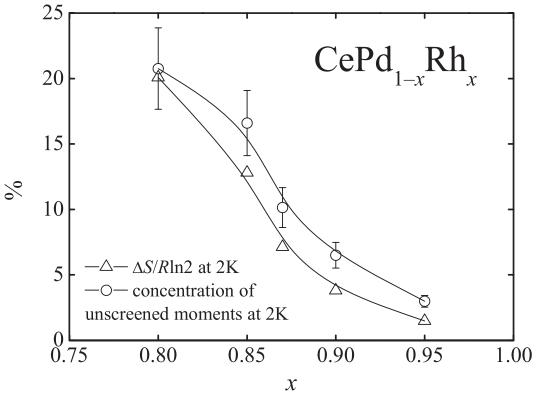

Figure 4. Concentration of unscreened moments at $T = 2$ K of CePd$_{1-x}$Rh$_x$, determined from the slope of the magnetic susceptibility (cf figure 2 in [9]) and entropy (cf figure 1(b)). See text.

$\mu_{\mathrm{eff}} = 2\mu_{\mathrm{B}}$ for 100% unscreened moments[4], corresponding to $c = 0.54$ emu K mol^{-1}, we can estimate the fraction of unscreened moments as a function of the average Rh concentration. As shown in figure 4, the so-derived fraction (plotted as circles) agrees well with the entropy fraction of $R\ln 2$ at 2 K (triangles). For $x \geqslant 0.85$, i.e. for Rh concentrations well beyond the onset of valence fluctuations, a substantial fraction of moments still remains unscreened at low temperatures. This is remarkable, since the *average* Kondo temperature, estimated from either twice the temperature at which the entropy amounts to $0.5R\ln 2$ or from the evolution of the Weiss temperature $\Theta(x)$ [9], is well above 50 K for $x \geqslant 0.85$. Thus, a broad distribution of local T_{K} values with a tail down to very low temperatures is indeed realized in our system. It has been shown within dynamical mean-field theory, that a distribution of Kondo temperatures with finite intercept $P(T_{\mathrm{K}} = 0) > 0$ leads to NFL temperature dependences for the electronic specific-heat coefficient, i.e. a logarithmic, or even weak power-law divergence, depending on the functional dependence of $P(T_{\mathrm{K}})$ which itself is a function of the disorder in the system [18]. Though we cannot determine $P(T_{\mathrm{K}})$ from specific-heat measurements alone, the distribution of single-ion Kondo temperatures may well explain the unusual NFL behaviour in this system.

5. Conclusions

CePd$_{1-x}$Rh$_x$ is a Ce-based system in which an FM transition can be continuously tuned to absolute zero temperature. In the low-temperature specific heat, we can follow the signature of the transition down to 0.25 K (at $x = 0.8$), where a broad maximum in the electronic specific-heat coefficient $\Delta C(T)/T$ is observed. For larger Rh content, no signature for this can be resolved any more, although ac-susceptibility measurements $\chi_{\mathrm{ac}}(T)$ have revealed a tail in the $T_{\mathrm{C}}(x)$ phase diagram that extends up to $x = 0.87$ [9]. We suspect that in this concentration regime the rapid increase of the Kondo temperature with x leads to a broad local variation of T_{K} related to the variation in the number of Pd and Rh first neighbours of the Ce^{3+} ions. From our analysis of the low-temperature entropy, as well as from the Curie–Weiss behaviour of the magnetic susceptibility at 2 K, we have provided evidence for a fraction of Ce moments which are still unscreened at low temperatures. On the one hand, this broad distribution of local Kondo temperatures may explain the NFL behaviour evidenced by our low-temperature specific-heat

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[4] Note: we used a reduced effective moment compared to $\mu_{\mathrm{eff}} = 2.54\ \mu_{\mathrm{B}}$ for the free Ce^{3+} ion in order to take into account the reduced moment of the (unknown) crystal-electric-field ground-state doublet.

measurements. On the other hand, it gives a natural explanation for spin-glass-like behaviour resulting from clusters of Ce atoms with low Kondo temperatures, embedded in a non-magnetic environment.

To summarize, our low-temperature specific-heat experiments provide thermodynamic evidence for NFL behaviour close to the disappearance of ferromagnetism in $\mathrm{CePd}_{1-x}\mathrm{Rh}_x$. We relate the NFL behaviour to a distribution of local Kondo temperatures, which results from the extreme sensitivity of T_{K} for each Ce site on the number of Pd and Rh neighbours.

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