Origin of the Smeared Ferromagnetic Quantum Phase Transition in $CePd_{1-x}Rh_x$: Evidence of a Kondo-Cluster-Glass State

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During the last four decades one of the most studied topics in condensed matter physics is the behavior of strongly-correlated-electron metals on the border between their ferro- (FM) or anti-ferromagnetically (AFM) ordered phase and the paramagnetic (PM) one at temperatures close to zero. The reason for this is the observed anomalous behavior which deviates from the standard theory of metals, the Fermi-liquid (FL) theory [1,2]. Moreover, the discovery of unconventional superconductivity [3] in this region of the magnetic phase diagram in some heavy-fermion (HF) compounds has strongly increased the number of systems that have been put under investigation: Among them, Ce- and Yb-based *f*-electron Kondo-lattice (KL) systems have shown the most drastic forms of non-Fermi-liquid (NFL) behavior [2]. In these materials, the ground state sensitively depends on the balance between two competing interactions, which are both determined by the strength of the 4*f*-conduction electron hybridization *J*: Whereas the Kondo interaction leads to a screening of the local moments below a Kondo temperature T_K, resulting in a paramagnetic ground state with itinerant 4*f*-electrons, the indirect exchange coupling (RKKY interaction) can mediate long-range magnetic ordering [4].

One of the explanations for such NFL phenomena is the presence of a quantum critical point (QCP) at a particular J_c: If the transition temperature T_C of the long-range magnetic order is continuously shifted to zero by an external parameter *x(J),* e.g. pressure, magnetic field or chemical substitution, a 2^{nd} order quantum phase transition (QPT) takes place at $x_c(J_c)$ and $T = 0$, to which a QCP is associated. Here, the typical length and time scales of order parameter fluctuations diverge when approaching the transition point. These fluctuations are believed to be responsible for the observed NFL corrections to the FL prediction for the heat capacity *C/T(T) = const.*, magnetic susceptibility $\chi(T) = const.$, electrical resistivity $\rho(T) \sim T^2$ etc. [1,2]. QCPs are not the only mechanism to provide NFL behavior. If the magnetic order changes from long-range to short-range and disorder comes into play, spatial regions (also called "*rare regions*") can show local magnetic order, although the bulk system is in a PM state [5]. The order parameter fluctuations of these regions can become strong enough to destroy the QPT and give rise to NFL behavior [6-8]. Here, the length scale of order parameter fluctuations becomes finite, while the time scale still diverges. As consequence, e. g. in the Griffiths phase scenario, power-law corrections, $C/T(T) \sim \chi(T) \sim T^{\lambda-1}$, with $\lambda < 1$, are expected in a broad region across the QCP and not only at the QCP itself. The global phase transition is then smeared, as observed in doped FM materials, as , e. g., the itinerant $Zr_{1-x}Nb_xZn_2$ [9] or the 5*f*-based HF system $URh_{1-x}Ru_xGe$ [10].

We have chosen to investigate the FM system $CePd_{1-x}Rh_x$ mainly for the following two reasons: i) There is a large number of intensively investigated AF-QCPs, while appropriate KL candidates for the study of FM-QCPs are extremely rare, and ii) the control parameter *x* in this case is a particular one: In fact, the chemical substitution of the Ce-ligand Pd with Rh induces not just a volume effect (chemical pressure), but, more importantly, it increases locally the hybridization strength *J* of the 4*f* electrons, leading to a strong enhancement of T_K. Simultaneously, disorder is introduced in the system. That makes $CePd_{1-x}Rh_x$ a unique system. Its behavior is quite different from that observed in many other disordered NFL systems, where the Ce valence remains nearly trivalent and where an exotic percolative cluster scenario has been proposed [11]. Moreover, in many Ce-based ferromagnets the increase of the Kondo interaction with pressure tends to stabilize an AF ground state before the QCP is reached [12,13] (CePt might be an exception [14]). There are also theoretical reasons: Recent studies have suggested that the suppression of itinerant ferromagnetism in clean systems, in contrast to antiferromagnetism, always ends at a classical critical point (at finite *T*), where a 1^{st}

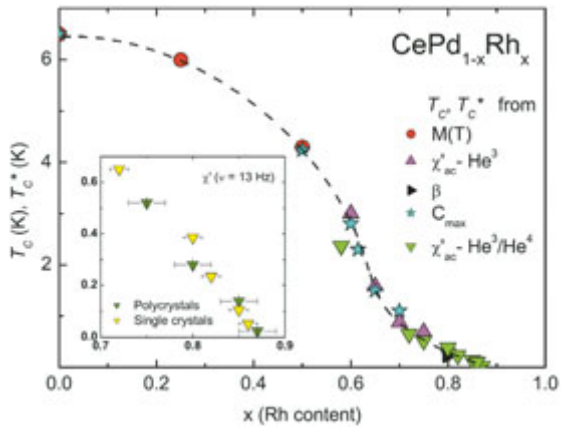

Fig. 1: Magnetic phase diagram of $CePd_{1-x}Rh_x$: Composition dependence of the ordering (freezing) temperature T_C (T_C) deduced from different measurement techniques. The inset shows the $T_C(x)$ values observed in the ac susceptibility for $x > 0.7$ in poly- and single crystals.*

order phase transition occurs [15,16]. Pure FM transition-metal compounds display indeed 1st order QPTs [17-19]. For KL systems, it is questionable whether all QCPs can be described in an itinerant scenario [20]. Thus, a detailed investigation of suitable FM systems close to their instability is highly desirable. As will be explained in the following, this choice led us to the discovery of a novel kind of ground state at the FM-QPT, the Kondo-cluster-glass state.

The growth of the $CePd_{1-x}Rh_x$ crystals and all the measurements presented here have been carried out at the MPI CPfS. Previous reports on polycrystals have shown that the system evolves from a FM ground state in CePd with $T_C = 6.6$ K to a non-magnetic intermediate-valence (IV) state in CeRh [21,22] (see also Scientific Report 2003/2005, page 153). The whole series crystallizes in the orthorhombic CrB structure. The observed decrease of T_C over more than two decades in temperature, down to 25 mK at $x = 0.87$, is presently the best known example for the continuous disappearance of FM order in any KL system (see Fig. 1). Evidence for the FM nature of the ordered state stems from the T dependence of the ac susceptibility χ_{ac}, which shows sharp maxima for all investigated samples [22]. Our new results on single crystals match very well with those on polycrystals, as shown in Fig. 1 [22-24]. The competition between FM order and, with increasing Rh content, growing Kondo screening leads to a continuous decrease of T_C. Furthermore, the smaller Rh causes a volume compression of the compounds unit cell and changes the electronic structure. Most interestingly, the curvature of the phase boundary T_C changes from negative for $x < 0.6$ to positive for $x \geq 0.6$, displaying a long tail towards higher Rh contents. In this concentration range, $T_K \approx \theta_p/2$ (θ_p: PM Weiss temperature) strongly increases with x; a similar result can be inferred from the evolution of the lattice parameters as a function of x, which change slope at $x > 0.7$ [22]. Specific-heat measurements have proved the existence of NFL behavior for concentrations close to $x_c = 0.85$ [24]. At $x = 0.85$ a logarithmic increase of the specific-heat coefficient $\gamma = \Delta C(T)/T$, down to the lowest temperature of 80 mK, was observed. Samples with higher Rh content showed a power-law T-dependence, with exponents $\lambda = 0.6$ and 0.67 for $x = 0.87$ and 0.9, respectively. For $x = 0.8$, the magnetic entropy increment ΔS is less than $0.4Rln2$ up to 6 K. With increasing Rh content this value becomes drastically reduced. Similar exponents have been found in the T-dependent ac susceptibility [25]. An analysis of the entropy and the slope of $\chi_{ac}(T)$ at 2 K revealed some fraction of still unscreened magnetic moments, even at high x where the *average* T_K is already above 50 K. Thus, a broad distribution of local T_K values with a tail down to the lowest T is realized in this system [24]. The shape of the T-x phase diagram and the evolution of T_K in $CePd_{1-x}Rh_x$ raise questions concerning the mechanism behind the suppression of FM order and the presence of a QPT at x_c.

To study the dynamic processes in the region close to x_c, the low-T χ_{ac} was measured down to 20 mK at various frequencies in the range $0.6 \leq x \leq 0.9$. Poly- and single crystals show the same behavior. The $x = 0.6$ sample clearly shows a FM phase transition at $T_C = 2.4$ K; the $x = 0.9$ one does not show any ordering down to 20 mK. The pronounced $\chi_{ac}(T)$ maxima of samples with concentrations in between exhibit a frequency dependence similar to that observed in spin-glass freezing: e. g., the $\chi_{ac}(T)$ signal of a single crystal with $x = 0.8$ shows a pronounced cusp in its real part $\chi'(T)$ and a corresponding inflection point in the imaginary part $\chi''(T)$ (Fig. 2). Both signals display a clear frequency dependence at the temperature of the χ' cusp, labeled T_C*, in order to distinguish it from the Curie temperature T_C found at lower x. Another indication for spin-glass-like behavior is the extreme sensitivity of $\chi'(T_C^*)$ to a

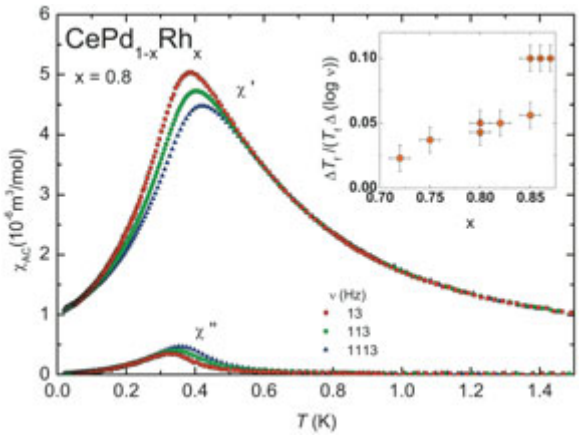

Fig. 2: Ac susceptibility of a single crystal (x = 0.8) for 3 selected frequencies in a modulation field of 11 μT. Inset: Relative temperature shift of the maximum in χ'(T) per frequency decade as function of x.

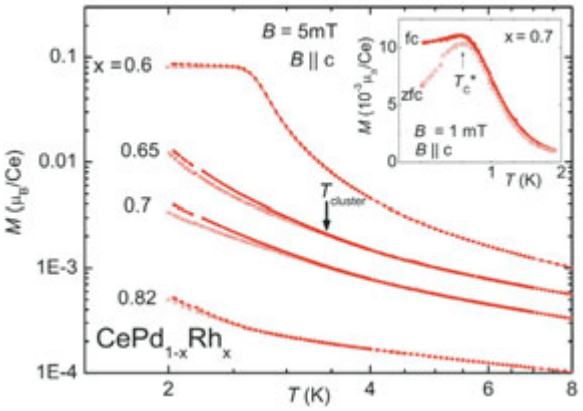

Fig. 3: Dc magnetization M vs. T in a constant field of 5 mT. FC and ZFC data on single crystals with 0.6 ≤ x ≤ 0.82 are show. The onset of the clusters formation is marked by the arrow. Inset: low-T data for x = 0.7 at B = 1 mT; the arrow indicates the clusters freezing at T_C.*

superposed static magnetic field. Only 15 mT are sufficient to suppress the absolute value to 3/5 of the signal in zero field. However, examining the relative temperature shift per decade in frequency vs. x (inset of Fig. 2), we find that this shift of about 3 to 10% per decade is considerably larger than in canonical metallic spin glasses which exhibit only 1 to 2%. It is similar in magnitude to the one observed in insulating spin glasses, but well below the value of about 28 % observed in a superparamagnet [26]. Remarkably, the maximum expected in the specific heat $C(T)$ at a temperature somewhat higher than T_C* has been observed for x = 0.8 at $T \approx T_C$*, but not for $x \geq 0.85$, where C/T diverges without any sign of transition [24].

The frequency dependence of $\chi_{ac}(T)$ provides evidence for the existence of clusters in the system. The change of the magnitude of the shift suggests that the properties of the clusters, e. g., their size and/or coupling strength, vary with the Rh content. In fact, in this regime of the phase diagram a rapid change of T_K was observed [22]. Very likely, the random distribution of Rh and Pd ligands creates regions with different local T_K values, due to differences in J: While Pd nearest neighbors tend to stabilize the Ce-moment, Rh ligands seem to screen it. The strength of the Kondo screening on a given Ce site thus depends on the local environment. This is in agreement with the analysis of $C(T)$ [24]. Since the Kondo interaction is rather extended across the lattice, this effect has to be interpreted in a different way than percolation effects caused by the dilution of magnetic moments. For $0.8 \leq x \leq 0.87$, the dimensionless Sommerfeld-Wilson ratio $R_W = (\chi_a/\chi_0) / (\gamma_a/\gamma_0)$ gives values between 20 and 30, the square root of which is an estimation of the typical number of spins in each cluster [27]: We have about 5 spins per cluster, in agreement with the small entropy at low temperatures [24].

To confirm the existence of freezing clusters, dc magnetization was measured as a function of temperature on single crystals. The inset of Fig. 3 shows the results of field-cooled (FC) and zero-field-cooled (ZFC) measurements for x = 0.7 and B = 1 mT. Below the freezing temperature, a clear deviation is observed between FC and ZFC: while the FC curve saturates below T_C*, the ZFC one exhibits a cusp at T_C*. This demonstrates the irreversibility of the freezing process in agreement with our $\chi_{ac}(T)$ results. Remarkably, a small difference between the FC and ZFC curves exists also at much higher temperatures (cf. the main part of Fig. 3). We associate the temperature below which this irreversibility is observed with $T_{cluster}$, i. e., the characteristic temperature for the formation of short-range order in clusters. With increasing x, the low-T magnetization decreases by several orders of magnitude, indicative of a drastic reduction of the average moment per Ce-site and consistent with the strong reduction of the magnetic entropy at low temperatures [24].

As discussed in the introduction, there is a fundamental difference between the NFL behavior given by long-range and short-range order fluctuations. The presence of clusters and the power-law

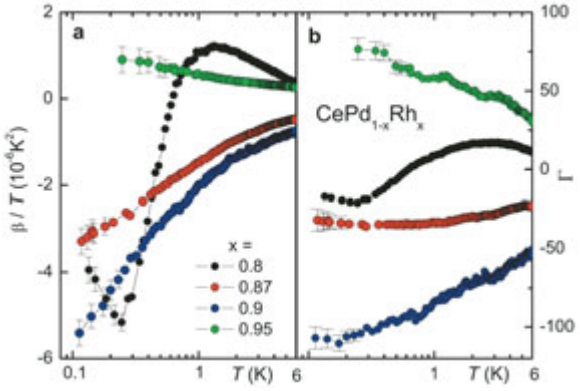

Fig. 4: a) Volume thermal expansion $\beta(T)$ of $CePd_{1-x}Rh_x$ polycrystals plotted as β/T vs. logT. a) Dimensionless Grüneisen ratio $\Gamma = V_m\beta/k_T C$ vs. logT [30].

corrections to the heat capacity [24] and susceptibility [25,28] indicate that the expected QPT at x_c is replaced by disordered phases, possibly like the Griffiths one.

The coefficient of volume thermal expansion, $\beta(T) = V^{-1}(dV/dT)$ (V: sample volume), is a highly sensitive probe of quantum critical behavior in HF systems, since it is more singular than the specific heat $C(T)$ when approaching a QCP [29,30]. Consequently, the Grüneisen ratio $\Gamma \sim \beta / C$ must diverge as T goes to zero at any HF QCP, as recently found for several KL systems exhibiting an AFM QCP [20]. Furthermore, the critical exponent in $\Gamma(T)$ provides important information on the nature of the underlying QCP [29]. Fig. 4a shows $\beta(T)$ of polycrystalline $CePd_{1-x}Rh_x$ with $0.8 \leq x \leq 0.95$ plotted as $\beta(T)/T$ vs. log T [30]. In agreement with $C(T)/T$ and $\chi_{ac}(T)$ results the minimum at $T \approx 0.25$ K in $\beta(T)/T$ marks the magnetic transition for $x = 0.8$. With increasing x, $\beta(T)/T$ shows no sign of phase transitions for $x = 0.87$ and 0.9, but rather diverges on cooling to 0.1 K. Note that for these concentrations $\beta(T)$ is negative and that for $x = 0.9$ the divergence is even larger than for $x = 0.87$, with absolute values comparable to those found in HF metals close to a QCP [20]. For the $x = 0.95$ sample, $\beta(T)/T$ is always positive, as expected for paramagnetic Ce systems, with smaller absolute values. These results are in contrast to those of $C(T)$ measurements for $0.8 \leq x \leq 0.95$, which clearly show a continuous decrease of the $C(T)/T$ values with increasing x, as expected when approaching the IV regime [24]. Analyzing the dimensionless Grüneisen ratio, defined as $\Gamma = V_m\beta/k_T C$, where V_m and k_T denote the molar volume and isothermal compressibility, respectively, we find a striking deviation from the predicted scaling results for a QCP [29]: At $x = 0.87$, i.e., very close to the Rh-concentration for which the anomaly in $\chi_{ac}(T)$ disappears, a nearly equal power-law behavior has been found for $C(T)/T$ and $\beta(T)/T$, leaving a virtually temperature independent Grüneisen ratio (see Fig. 4b). Thus, a QCP scenario can be discarded. Interestingly, in the paramagnetic regime, $x \geq 0.9$, $|\Gamma(T)|$ strongly increases on cooling in an almost logarithmic fashion but seems to saturate at the lowest temperatures.

The negative Grüneisen ratio for $x = 0.87$ and 0.9 indicates an unusual volume dependence close to the disappearance of order. For paramagnetic Ce systems, a positive Γ, as observed for $x = 0.95$, is expected, since the Kondo interaction, being the dominant energy scale, increases under hydrostatic pressure. On the other hand, a negative sign is usually associated with magnetic ordering due to the RKKY interaction, which decreases under hydrostatic pressure. Since $\Gamma < 0$ even in the paramagnetic regime, our data suggest the presence of magnetic correlations in addition to the Kondo effect and provide evidence for the formation of frozen clusters in the region where $T_c(x)$ shows a tail.

Fig. 5 sketches different magnetic states which are passed on cooling. At temperatures high enough to overcome the Kondo screening, fluctuating magnetic moments exist on every Ce site, indicated by the small red arrows (frame a). Below the average Kondo temperature $\langle T_K \rangle$, an increasing number of f-moments becomes screened, as represented by the gray arrows (frame b). However, due to the statistical distribution of Rh dopands on the Pd site and the strong dependence of the local Kondo temperature on the number of nearest neighbors, there remain regions where the Kondo scale has not yet been reached. Inside these regions, the f-moments are still unscreened (indicated in red). At even lower temperatures, $T < T_{cluster}$, these moments form clusters with predominantly FM coupling of the moments. In frame (c), the large red arrows represent the total magnetic moment of each cluster. Within this temperature regime, the clusters are fluctuating independently. On further cooling below T_C*, random freezing of the cluster moments sets in, leaving a static spin configuration as displayed in

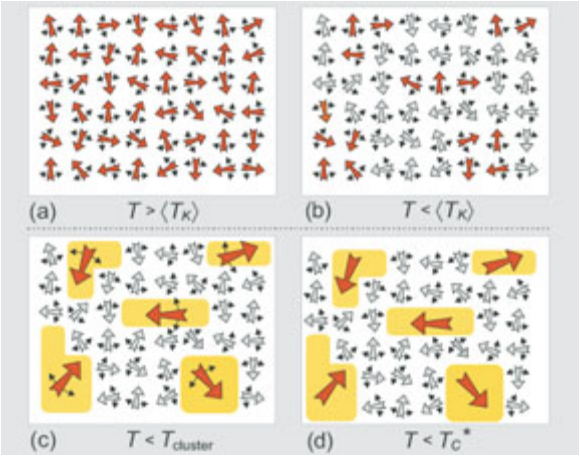

Fig. 5: Schematic representation of the formation of a Kondo-cluster glass in $CePd_{1-x}Rh_x$ as a function of T. The small red and gray arrows indicate fluctuating f-moments above and below their respective Kondo temperature, respectively; big red ones are FM clusters. The temperature decreases from frame (a) to (d) (cf. main text).

frame (d). As the broad distribution of local Kondo temperatures is responsible for the cluster formation, we propose to call the low-T state in $CePd_{1-x}Rh_x$ a "Kondo-cluster glass".

To conclude, the lack of a divergence of the Grüneisen ratio in $CePd_{1-x}Rh_x$ is incompatible with the predictions of Ref. 29 for a QCP. This raises the question about the origin of the pronounced NFL behavior found in this system. Whereas weak power-law divergences in the specific-heat coefficient may be considered as being due to a single-ion effect originating in the broad distribution of local Kondo temperatures [24], the observed negative sign of the Grüneisen ratio strongly points to a cooperative effect. The detailed investigation of magnetic properties close to the disappearance of magnetic order reveals the formation of a "Kondo-cluster-glass" state, where the clusters result from regions of low local Kondo temperatures. NFL effects in the specific heat, susceptibility and magnetization are then compatible with the quantum Griffiths phase scenario [32].

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[30] This holds true for any pressure-sensitive QCP [5]. To our knowledge, every HF QCP established so far, belongs to this category.

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