Single-Ion Kondo Scaling of the Coherent Fermi Liquid Regime in $Ce_{1-x}La_xNi_2Ge_2$

Adam P. Pikul,[1,2] Ulrike Stockert,[2] Alexander Steppke,[2] Tomasz Cichorek,[1,2] Stefanie Hartmann,[2] Nubia Caroca-Canales,[2] Niels Oeschler,[2] Manuel Brando,[2] Christoph Geibel,[2] and Frank Steglich[2]

[1]*Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław, Poland*

[2]*Max Planck Institute for Chemical Physics of Solids, Dresden, Germany*

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Thermodynamic and transport properties of the La-diluted Kondo lattice $CeNi_2Ge_2$ were studied in a wide temperature range. The Ce-rich alloys $Ce_{1-x}La_xNi_2Ge_2$ were found to exhibit distinct features of the coherent heavy Fermi liquid. At intermediate compositions ($0.7 \leq x \leq 0.9$), non-Fermi liquid properties have been observed, followed by the local Fermi liquid behavior in the dilute limit. The $4f$-electron contribution to the specific heat was found to follow the predictions of the Kondo-impurity model in both the local as well as the coherent regimes, with the characteristic Kondo temperature decreasing rapidly from about 30 K for the parent compound $CeNi_2Ge_2$ to about 1 K in the most dilute samples. The specific heat does not show any evidence for the emergence of a new characteristic energy scale related to the formation of the coherent Kondo lattice.

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Strongly correlated f-electron systems, i.e., intermetallic compounds based on lanthanoids or actinoids, have been a subject of unflagging interest for more than three decades. The main reason for that is a number of novel physical phenomena and extraordinary behaviors evidenced in these materials at low temperatures, e.g., heavy quasiparticles [1], magnetically driven superconductivity [2], non-Fermi-liquid behavior [3,4], and quantum criticality [5]. The Kondo interaction between the spins of conduction electrons and the magnetic moments of the localized f shells is a common ground for all these phenomena [6].

In dilute Kondo systems, the magnetic ions are well separated from each other and randomly distributed in the lattice. Therefore, the Kondo effect occurs independently at each f site, and physical properties of such compounds are a function of the characteristic Kondo temperature T_K [6]. In Kondo-lattice systems, containing a dense, periodic sublattice of magnetic ions, the interactions between the f shells are no longer negligible. As a consequence, the behavior of a Kondo lattice is more complex than that of a dilute Kondo alloy, and to describe its properties more involved theoretical treatments are commonly required.

A novel approach to describe dense Kondo systems was proposed by Nakatsuji *et al.* [7]. Based on scaling laws found for the La-diluted Kondo-lattice system $CeCoIn_5$, they revealed a characteristic temperature T^* that governs the intersite coupling of the f shells in the coherent Kondo lattice. T^* was found to be much different from the concentration-independent single-ion T_K, responsible for the on-site $4f$-conduction-electron hybridization. This conclusion provided the basis for the development of a phenomenological two-fluid model [8], which assumes the emergence of a collective hybridization of the whole Kondo lattice, in addition to the individual hybridization, which takes place at each f site separately.

In this Letter, we show that in another La-diluted Kondo lattice, $CeNi_2Ge_2$, the basic assumption of the two-fluid model, i.e., the concentration independence of the single-ion T_K, is not fulfilled. In particular, the specific heat of the $Ce_{1-x}La_xNi_2Ge_2$ alloys follows the predictions of the single-ion Kondo model in the local *as well as* coherent regimes, with T_K decreasing by 1 order of magnitude with increasing the La content. The rapid reduction of T_K with increasing La concentration is confirmed by electrical transport properties.

The experiments were performed on polycrystalline samples of $Ce_{1-x}La_xNi_2Ge_2$, synthesized by conventional arc melting followed by high-temperature homogenization. The quality of the samples was verified by means of x-ray powder diffraction. The transport properties of the alloys were studied at temperatures ranging from room temperature down to 2 K at ambient conditions, using a commercial Quantum Design physical property measurement system. The heat-capacity measurements were extended to 70 mK, employing the semiadiabatic method in a commercial Oxford Instruments ^{3}He-^{4}He dilution fridge with a home-made measuring setup [9].

The heavy-fermion compound $CeNi_2Ge_2$ is a well-known, magnetically nonordered and nonsuperconducting dense Kondo system with a Kondo temperature of about 30 K [10]. A number of experiments revealed that the system is very close to an antiferromagnetic quantum-critical point (see, e.g., Refs. [11,12]). However, as we briefly reported in Ref. [13], partial substitution of cerium by larger lanthanum does not induce any long-range magnetic order in the system, although the unit-cell volume of $Ce_{1-x}La_xNi_2Ge_2$ increases linearly with increasing the La content. Instead, large and constant $\Delta C/T$ values,

characteristic of a heavy Fermi liquid (FL) [1], are observed in the La-doped samples with $0.05 \leq x \leq 0.40$ over more than one decade of temperature. As will become clear below, this finding allows us to analyze the $4f$ contribution to the specific heat ΔC of $Ce_{1-x}La_xNi_2Ge_2$ in terms of the single-ion Kondo model.

According to the Kondo resonant-level model by Schotte and Schotte [14], the Kondo-impurity contribution C_{KI} to the total specific heat per 1 mol of the impurities with effective spin $S = 1/2$ is described by the formula

$$C_{KI}\left(\frac{T}{T_K}\right) = 2R\frac{T_K}{2\pi T}\left[1 - \frac{T_K}{2\pi T}\psi'\left(\frac{1}{2} - \frac{T_K}{2\pi T}\right)\right]. \quad (1)$$

R is the universal gas constant, ψ' is the first derivative of the digamma function, and T_K is the Kondo temperature defined as the width of the Lorentzian-shape Kondo resonance at the Fermi level. As can be seen in Figs. 1 and 2, this model describes surprisingly well our experimental data not only in the dilute limit ($x = 0.99$), as expected, but also for the Ce-rich alloys ($0.05 \leq x \leq 0.40$). In the latter concentration range, a slight upwards deviation from the theoretical calculations above 2 K becomes apparent with decreasing x. The behavior of this additional contribution matches nicely the predictions of Desgranges and Rasul [15,16] for the contribution of higher crystalline electric field (CEF) levels, once the Kondo scale T_K becomes larger than $1/10$ of the CEF splitting Δ_{CEF}. Such an increase of T_K/Δ_{CEF} with decreasing x is indicated by the transport properties of $Ce_{1-x}La_xNi_2Ge_2$ (Fig. 3; see below).

T_K of the lowest-lying doublet, as obtained by a least-squares fit of Eq. (1) to the data, was found to decrease with increasing the La content (cf. Fig. 4). This is expected for a dense Kondo system under volume expansion [17,18]. It is worth noting that the $C_{KI}(T/T_K)$ dependence, found by applying the phenomenological Schotte-Schotte model, is only a phenomenological approach to the density of states at the Fermi level and a $1/2$-effective spin. Although it is not the exact theory of the Kondo problem, it agrees well with the numerical (and hence less convenient in use) solution of the *s-d* model, based on the *on-site* Kondo interaction [19]. Therefore, T_K obtained from the fits of Eq. (1) appears to be a good approximation of the single-ion Kondo temperature of the $Ce_{1-x}La_xNi_2Ge_2$ alloys.

In order to find out whether some different characteristic temperature scale potentially governs the intermediate non-FL range, we plotted $\Delta C/T$ from Fig. 1 as a function of the normalized temperature T/T^*, where T^* is a scaling parameter (Fig. 2). As a consequence of the T/T_K dependence of C_{KI} [Eq. (1)], for all the experimental curves from

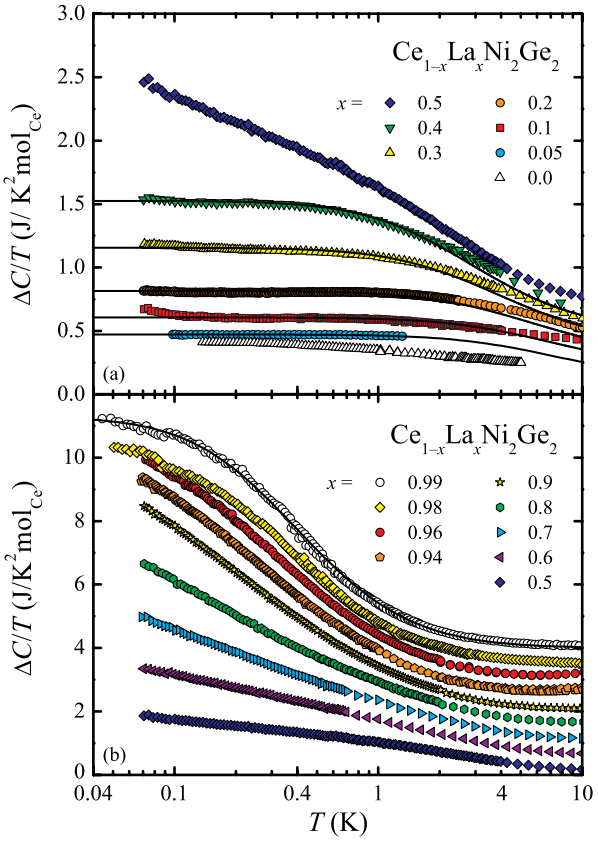

FIG. 1 (color online). Temperature variation of the $4f$-electron contribution ΔC to the total specific heat of $Ce_{1-x}La_xNi_2Ge_2$ with $x \leq 0.50$ (a) and $x \geq 0.50$ (b), normalized per mole of cerium and divided by temperature T. ΔC was obtained by subtraction of the specific heat of the isostructural phonon counterpart $LaNi_2Ge_2$ from the raw experimental curves (cf. Ref. [13]). Solid lines are fits of the Kondo resonance model [Eq. (1)]. For the sake of clarity, the curves are shifted upwards by 0.1 and 0.5 $J/K^2\,mol_{Ce}$ in (a) and (b), respectively.

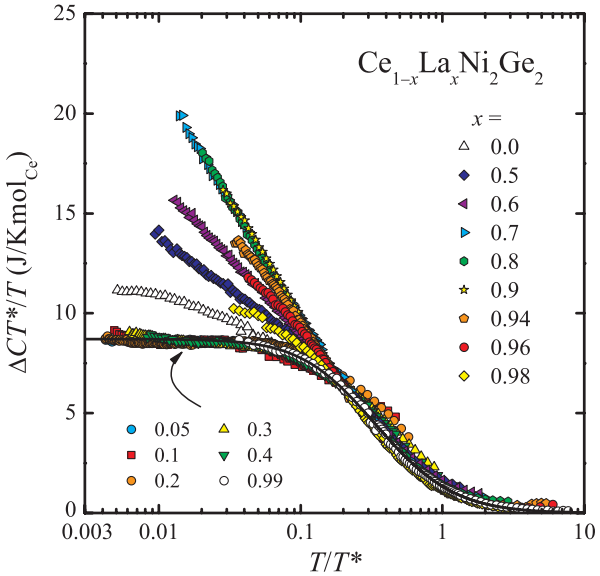

FIG. 2 (color online). $\Delta C/T$ of $Ce_{1-x}La_xNi_2Ge_2$ as a function of the normalized temperature T/T^*, where T^* is the characteristic temperature of the system. The solid line represents the Kondo-impurity contribution to the specific heat $\Delta C(T/T^*) = C_{KI}(T/T_K)$ given by Eq. (1).

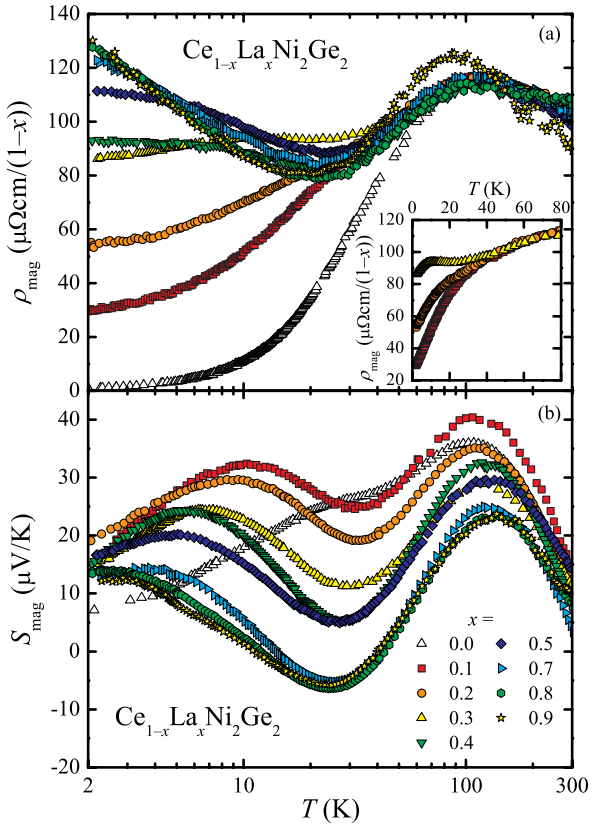

FIG. 3 (color online). Temperature variations of the magnetic contribution to the electrical resistivity (a) and thermoelectric power (b) of selected $Ce_{1-x}La_xNi_2Ge_2$ alloys.

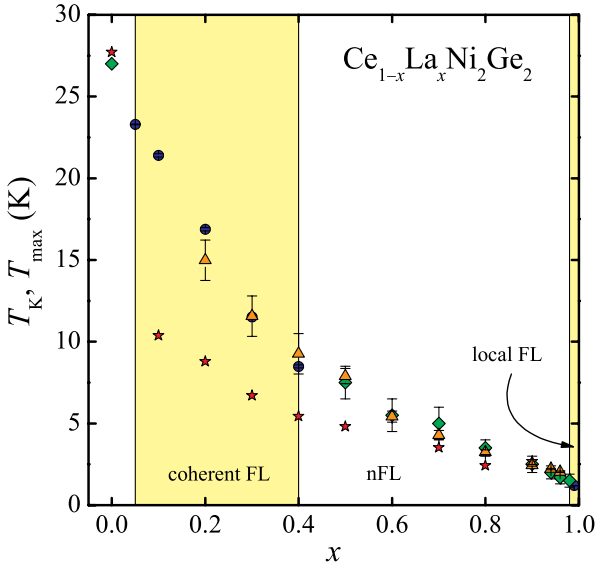

FIG. 4 (color online). Tentative phase diagram of $Ce_{1-x}La_xNi_2Ge_2$. Circles (○) mark the single-ion T_K from the fits of the Kondo resonance model applied to the specific-heat results in both the coherent and local FL regimes (Fig. 1). Diamonds (◇) are the scaling parameter T^* found for all other samples (Fig. 2). Triangles (△) are effective $T_{K,\mathrm{eff}}$ values estimated from entropy (Ref. [13]) and divided by a factor of $2\pi \times 0.103$ (cf. Ref. [19]). Additionally, positions $T_{\max}$ of the low-temperature maxima in $S_{\mathrm{mag}}(T)$ (Fig. 3) are marked by stars (★).

the two different FL regimes, a scaling relation was easily obtained with T^* being equal to T_K from the Schotte-Schotte fits. For the other curves, that do not follow Eq. (1), T^* was chosen to get as good matching as possible. As seen in Fig. 2, these curves appeared to deviate from the theoretical predictions for $T/T^* \lesssim 0.2$ but overlap with $C_{\mathrm{KI}}(T/T_K)$ at higher temperatures. Moreover, for the alloys with $0.7 \leq x \leq 0.9$, the scaling relation is obeyed in the whole temperature range studied. As inferred from Fig. 4, in the non-Fermi-liquid regime $0.5 \leq x \leq 0.98$, the scaling displayed in Fig. 2 yields T^* values which smoothly interpolate between the results for the single-ion T_K in the two adjacent FL regimes. It points out that T_K remains a dominating energy scale in the non-FL regime.

Figure 3 displays the temperature dependence of the magnetic contribution to the electrical resistivity (ρ_{mag}) and thermoelectric power (S_{mag}) of $Ce_{1-x}La_xNi_2Ge_2$. ρ_{mag} was calculated by subtracting the data for $LaNi_2Ge_2$. $S_{\mathrm{mag}}(T)$ was determined from the Gorter-Nordheim relation $S\rho = S_{\mathrm{mag}}\rho_{\mathrm{mag}} + S_0\rho_0$, where S_0 and ρ_0 are the data for the pure La system. At elevated temperatures, both $\rho_{\mathrm{mag}}(T)$ and $S_{\mathrm{mag}}(T)$ exhibit broad and nearly concentration-independent maxima just above 100 K, which can be attributed to the combined Kondo scattering of conduction electrons off the lowest-lying and excited CEF levels. Although the exact CEF scheme cannot be precisely determined from these data, one can roughly estimate the energy of the first excited CEF doublet as being of the order of room temperature (cf. Ref. [20]). The very weak dependence on x of the high-T maxima indicates that the CEF level scheme is only weakly altered by the Ce/La substitution.

The low-temperature behavior of $\rho_{\mathrm{mag}}(T)$ and $S_{\mathrm{mag}}(T)$ of $Ce_{1-x}La_xNi_2Ge_2$ is in turn strongly dependent on the Ce content. In $\rho_{\mathrm{mag}}(T)$ [Fig. 3(a)], the samples with large Ce concentration exhibit some broad excess below about 30 K; see the inset in Fig. 3(a). With increasing the La content, this extra contribution evolves into a maximum and moves towards lower temperatures. For $x = 0.40$ $\rho_{\mathrm{mag}}(T)$ saturates, and in the La-rich samples a $-\ln T$ slope develops in $\rho_{\mathrm{mag}}(T)$. Such a behavior is characteristic of Kondo systems upon dilution of the magnetic sublattice (see, e.g., $Ce_xLa_{1-x}Cu_6$ [21]). In particular, the low-T maximum observed in the dense $Ce_{1-x}La_xNi_2Ge_2$ alloys results from the emergence of the coherent Kondo scattering, and the logarithmic increase in $\rho_{\mathrm{mag}}(T)$ evidenced in the diluted region manifests the single-ion Kondo effect. The thermoelectric power of $Ce_{1-x}La_xNi_2Ge_2$ [Fig. 3(b)] exhibits a distinct low-T maximum at $T_{\max}$ in *all* the alloys studied with $T_{\max}(x)$ decreasing upon increasing x. $S_{\mathrm{mag}}(T)$ is proportional to Tm, where $m = \partial \ln N(E)/\partial E|_{E_F}$ and

$N(E)$ is the quasiparticle density of states. For a dilute Kondo alloy (e.g., $x \gtrsim 0.98$), the low-T $S_{\mathrm{mag}}(T)$ peak occurs at $T_{\mathrm{max}} \approx T_{\mathrm{K}}$ [20]. For a Kondo lattice ($x = 0$), where $N(E)$ develops a (partial) hybridization gap near E_{F} [22], T_{max} refers to the coherence temperature T_{coh}. $CeNi_2Ge_2$ turns out to show $T_{\mathrm{max}} \approx 28$ K [23], almost identical to T_{K} (Fig. 4). $T_{\mathrm{coh}} \approx T_{\mathrm{K}}$ was also found for isostructural $CeCu_2Si_2$ (see, e.g., Ref. [24]). However, the disordered Kondo-lattice system $Ce_{1-x}La_xNi_2Ge_2$, $0.05 \lesssim x \lesssim 0.5$, exhibits $T_{\mathrm{max}} (\approx T_{\mathrm{coh}}) < T_{\mathrm{K}}$ (Fig. 4), which reflects a more fragile coherence compared to $CeNi_2Ge_2$.

In conclusion, we have found that La doping does not induce any magnetic ordering in the quantum-critical heavy-fermion compound $CeNi_2Ge_2$, although the crystal lattice expands, and the single-ion Kondo temperature of the system rapidly decreases. Instead, the non-FL effects in $CeNi_2Ge_2$ are immediately replaced, upon doping with 5% La, by coherent FL behavior. This is indeed very surprising, as in the Pd- and Cu-doped $CeNi_2Ge_2$ [11,25] the non-FL features occur clearly as a precursor of the antiferromagnetic order, in accordance with the predictions of the Doniach phase diagram [17]. In this context, it is worth referring to studies of two other La-doped heavy-fermion compounds, namely, $CeRu_2Si_2$ and $CeCu_6$ (cf. Ref. [1]). In the former one, slight La doping (7%) induces long-range antiferromagnetic order [26], while the latter compound remains magnetically nonordered in a wide concentration range [21]. As shown by Rossat-Mignod *et al.* [27], the different responses of these two systems on the La doping are caused by different magnitudes of the intersite correlations, which are much stronger in $CeRu_2Si_2$ than in $CeCu_6$. Similar to La-doped $CeCu_6$, the intersite correlations in $Ce_{1-x}La_xNi_2Ge_2$ become weak so quickly that long-range magnetic order cannot form upon doping with La.

The values of T_{K} obtained from our specific-heat study reveal a strong increase of the single-ion Kondo scale upon decreasing average unit-cell volume. This corroborates previous studies on $(La_{1-z}Y_z)_{1-x}Ce_xAl_2$ alloys with moderate, fixed Ce concentration ($x = 0.15$ and 0.06), which demonstrated a T_{K} increase by more than 2 orders of magnitude on going from $(La_{1-x}Ce_x)Al_2$ to $(Y_{1-x}Ce_x)Al_2$ [28].

Most interestingly, the coherent FL behavior is clearly visible in the Ce-rich alloys of $Ce_{1-x}La_xNi_2Ge_2$ over a wide x range and can be described by using the single-ion Kondo temperature as the local FL regime. The coherent Kondo scattering is inferred from our transport results but not reflected in the temperature dependence of the specific heat. The two FL regimes are found to be well separated by a non-FL region ($0.5 \leq x \leq 0.98$). Whether the non-FL behavior is precursive to a low-lying magnetic phase transition remains an open question.

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