Single-ion Kondo Scaling of the Coherent Fermi Liquid Regime in Ce\textsubscript{1-x}La\textsubscript{x}Ni\textsubscript{2}Ge\textsubscript{2}

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Thermodynamic and transport properties of the La-diluted Kondo lattice Ce\textsubscript{Ni}Ge\textsubscript{2} were studied in a wide temperature range. The Ce-rich alloys Ce\textsubscript{1-x}La\textsubscript{x}Ni\textsubscript{2}Ge\textsubscript{2} were found to exhibit distinct features of the coherent heavy Fermi liquid. At intermediate compositions (0.7 ≤ x ≤ 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 both in the local as well as coherent regimes, with the characteristic Kondo temperature decreasing rapidly from about 30 K for the parent compound CeNi\textsubscript{2}Ge\textsubscript{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.

In the dilute regime, the magnetic ions are well separated from each other and randomly distributed in the lattice. Therefore, the Kondo effect occurs independently at each site, and physical properties of such compounds are a function of the characteristic Kondo temperature T\textsubscript{K}. 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. [1]. Based on scaling laws found for the La-diluted Kondo-lattice system CeCoIn\textsubscript{5}, they revealed a characteristic temperature T* that governs the inter-site coupling of the f shells in the coherent Kondo lattice. T* was found to be much different from the concentration-independent single-ion T\textsubscript{K}, responsible for the on-site 4f-conduction-electron hybridization. This conclusion provided the basis for the development of a phenomenological two-fluid model [5], 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\textsubscript{2}Ge\textsubscript{2}, the basic assumption of the two-fluid model, i.e. the concentration-independence of the single-ion T\textsubscript{K}, is not fulfilled. In particular, the specific heat of the Ce\textsubscript{1-x}La\textsubscript{x}Ni\textsubscript{2}Ge\textsubscript{2} alloys follows the predictions of the single-ion Kondo model in the local as well as coherent regimes, with T\textsubscript{K} decreasing by one order of magnitude with increasing the La content. The rapid reduction of T\textsubscript{K} with increasing La concentration is confirmed by electrical transport properties.

The experiments were performed on polycrystalline samples of Ce\textsubscript{1-x}La\textsubscript{x}Ni\textsubscript{2}Ge\textsubscript{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 PPMS. The heat-capacity measurements were extended to 70 mK, employing the semi-adiabatic method in a commercial Oxford Instruments 3He–4He dilution fridge with a home-made measuring setup [4].

The heavy-fermion compound CeNi\textsubscript{2}Ge\textsubscript{2} is a well-known, magnetically non-ordered and non-superconducting 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\textsubscript{1-x}La\textsubscript{x}Ni\textsubscript{2}Ge\textsubscript{2} increases linearly with increasing the La content. Instead, large and constant ∆C/T values, characteristic of a heavy Fermi liquid (FL), are observed in the La-doped samples with 0.05 ≤ x ≤ 0.40 over more than one decade of temperature. As will become clear below,
The Kondo temperature $T_K$ is the characteristic temperature of the system. The solid line represents the Kondo impurity contribution to the specific heat $\Delta C(T/T^*) = C_K(T/T_K)$ given by Eq. (1).

$$T_K$$ 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. 1). This is expected for a dense Kondo system under volume expansion $17, 18$. It is worth noting that the $C_K(T/T_K)$ 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$_x$Ni$_2$Ge$_2$ 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 this finding allows us to analyze the $4f$-contribution to the specific heat of Ce$_{1-x}$La$_x$Ni$_2$Ge$_2$ in terms of the single-ion Kondo model.

According to the Kondo resonant-level model by Schotte and Schotte $14$, the Kondo-impurity contribution $C_K$ to the total specific heat per one mole of the impurities with effective spin $S = 1/2$ is described by the formula:

$$C_K(T/T_K) = 2RT_K^2/\pi T^3 \left[ 1 - T_K^2/2\pi T \psi \left( 1/2 - T_K^2/2\pi T \right) \right].$$  (1)

$R$ is the universal gas constant, $\psi'$ 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 $\Delta_{CEF}$. Such an increase of $T_K/\Delta_{CEF}$ with decreasing $x$ is indicated by the transport properties of Ce$_{1-x}$La$_x$Ni$_2$Ge$_2$ (Fig. 3, see below).

FIG. 1: (Color online) Temperature variation of the $4f$-electron contribution $\Delta C$ to the total specific heat of Ce$_{1-x}$La$_x$Ni$_2$Ge$_2$ with $x \leq 0.50$ (a) and $x \geq 0.50$ (b), normalized per mole of cerium and divided by temperature $T$. $\Delta C$ was obtained by subtraction of the specific heat of the isostructural phonon counterpart LaNi$_2$Ge$_2$ 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 panel (a) and (b), respectively.
of the $T/T_K$-dependence of $C_{K1}$ [Eq. 1], for all the experimental curves from 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 $C_{K1}(T/T_K)$ 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 ($\rho_{mag}$) and thermoelectric power ($S_{mag}$) of Ce$_{1-x}$La$_x$Ni$_2$Ge$_2$. $\rho_{mag}$ was calculated by subtracting the data for LaNi$_2$Ge$_2$. $S_{mag}(T)$ was determined from the Gorter-Nordheim relation $S \rho = S_{mag} \rho_{mag} + S_0 \rho_0$, where $S_0$ and $\rho_0$ are the data for the pure La system. At elevated temperatures, both $\rho_{mag}(T)$ and $S_{mag}(T)$ 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 $\rho_{mag}(T)$ and $S_{mag}(T)$ of Ce$_{1-x}$La$_x$Ni$_2$Ge$_2$ is in turn strongly dependent on the Ce content. In $\rho_{mag}(T)$ (Fig. 3(a)), the samples with large Ce concentration exhibit some broad excess below about 30 K, see inset of Fig. 3(a). With increasing the La-content, this extra contribution evolves into a maximum and moves towards lower temperatures. For $x = 0.40$ $\rho_{mag}(T)$ saturates, and in the La-rich samples $\rho_{mag}(T)$ increases as $-\ln T$ slope develops in $\rho_{mag}(T)$. Such a behavior is characteristic of Kondo systems upon dilution of the magnetic sublattice (see e.g. Ce$_2$La$_{1-x}$Cu$_6$ 21). In particular, the low-$T$ maximum observed in the dense Ce$_{1-x}$La$_x$Ni$_2$Ge$_2$ alloys results from the emergence of the coherent Kondo scattering, and the logarithmic increase in $\rho_{mag}(T)$ evidenced in the diluted region manifests the single-ion Kondo effect. The thermoelectric
power of Ce$_{1-x}$La$_x$Ni$_2$Ge$_2$ (Fig. 3(b)) exhibits a distinct low-$T$ maximum at $T_{\text{max}}$ in all the alloys studied with $T_{\text{max}}(x)$ decreasing upon increasing $x$. $S_{\text{mag}}(T)$ is proportional to $T_m$, 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., $x \approx 0.98$), the low-$T$ $S_{\text{mag}}(T)$ peak occurs at $T_{\text{max}} \approx T_K$. For a Kondo lattice ($x = 0$), where $N(E)$ develops a (partial) hybridization gap near $E_F$, $T_{\text{max}}$ refers to the coherence temperature $T_{\text{coh}}$. CeNi$_2$Ge$_2$ turns out to show $T_{\text{max}} \approx 28$ K, almost identical to $T_K$ (Fig. 4), which reflects a more fragile coherence compared to CeNi$_2$Ge$_2$. The coherent FL behavior is clearly a precursor of the anisotropic long-range antiferromagnetic order [26], while the latter turns out to show $T_{\text{coh}} \approx T_K$. CeNi$_2$Ge$_2$ becomes more fragile compared to CeNi$_2$Si$_2$ (see e.g., Ref. 24). However, the disordered Kondo-lattice system Ce$_{1-x}$La$_x$Ni$_2$Ge$_2$, 0.05 $\leq x \leq 0.5$, exhibits $T_{\text{max}}(\approx T_{\text{coh}}) < T_K$ (Fig. 4), which reflects a more fragile coherence compared to CeNi$_2$Ge$_2$. In conclusion, we have found that the La-doping does not induce any magnetic ordering in the quantum-critical heavy-fermion compound CeNi$_2$Ge$_2$, although the crystal lattice expands, and the single-ion Kondo temperature of the system rapidly decreases. Instead, the non-FL effects in CeNi$_2$Ge$_2$ 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$_2$Ge$_2$ 11, 23 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$_2$Si$_2$ 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 non-ordered in a wide concentration range 21. As shown by Rossat-Mignot et al. 27, the different responses of these two systems on the La-doping are caused by different magnitudes of the inter-site correlations, which are much stronger in CeRu$_2$Si$_2$ than in CeCu$_6$. Similar to La-doped CeCu$_6$, the inter-site correlations in Ce$_{1-x}$La$_x$Ni$_2$Ge$_2$ 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)$_{1-z}$Ce$_z$Al$_2$ alloys with moderate, fixed Ce-concentration ($z = 0.15$ and 0.06), which demonstrated a $T_K$ increase by more than two orders of magnitude on going from (La$_{1-z}$Ce$_z$)Al$_2$ to (Y$_{1-z}$Ce$_z$)Al$_2$ 28.

Most interestingly, the coherent FL behavior is clearly visible in the Ce-rich alloys of Ce$_{1-x}$La$_x$Ni$_2$Ge$_2$ over a wide $x$-range, and can be described 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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1. N. Grewe and F. Steglich, in Handbook on the Physics and Chemistry of Rare Earths, vol. 14, edited by K. A. Gschneidner Jr. and L. Eyring (Elsevier, Amsterdam, 1991).
2. P. Monthoux, D. Pines, and G. G. Lonzarich, Nature 450, 1177 (2007).
3. G. R. Stewart, Rev. Mod. Phys. 73, 797 (2001).
4. G. R. Stewart, Rev. Mod. Phys. 78, 743 (2006).
5. H. von Löhneysen, A. Rosch, M. Vojta, and P. Wölfle, Rev. Mod. Phys. 79, 1015 (2007).
6. A. C. Hewson, The Kondo Problem to Heavy Fermion (Cambridge University Press, Cambridge, 1993).
7. S. Nakatsuji et al., Phys. Rev. Lett. 89, 106402 (2002).
8. S. Nakatsuji, D. Pines, and Z. Fisk, Phys. Rev. Lett. 92, 016401 (2004).
9. H. Wilhelm, T. Lüthmann, T. Rus, and F. Steglich, Rev. Sci. Instrum. 75, 2700 (2004).
10. G. Knopp et al., J. Magn. Magn. Matter. 74, 341 (1988).
11. G. Knebel et al., Phys. Rev. B 59, 12390 (1999).
12. P. Gegenwart et al., J. Low Temp. Phys. 133, 3 (2003).
13. A. P. Pikul et al., Phys. Stat. Sol. (b) 247, 691 (2010).
14. K. D. Schotte and U. Schotte, Phys. Lett. 55A, 38 (1975).
15. H.-U. Desgranges and J. W. Rasul, Phys. Rev. B 32, 6100 (1985).
16. H.-U. Desgranges and J. W. Rasul, Phys. Rev. B 36, 328 (1987).
17. S. Doniach, Physica B 91, 231 (1977).
18. M. Lavagna, C. Lacroix, , and M. Cyrot, J. Phys. F: Met. Phys. 13, 1007 (1983).
19. H.-U. Desgranges and K. D. Schotte, Phys. Lett. 91A, 240 (1982).
20. V. Zlatič et al., Phys. Rev. B 68, 104432 (2003).
21. Y. Ōnuki and T. Komatsubara, J. Magn. Magn. Mater. 63–64, 381 (1987).
22. R. M. Martin, Phys. Rev. Lett. 48, 362 (1982).
23. U. Köhler, Dissertation, Technische Universität Dresden, 2007.
24. O. Stockert et al., Nature Phys. 7, 119 (2007).
25. N. Büttgen, H.-A. Krug von Nidda, and A. Loidl, Physica B 230, 590 (1997).
26. S. Quezel et al., J. Magn. Magn. Mater. 76–77, 403 (1988).
27. J. Rossat-Mignod et al., J. Magn. Magn. Mater. 76&77, 376 (1988).
28. F. Steglich, J. Phys. Soc. Jpn. 74, 167 (2005).