# Unusual Single-Ion Non-Fermi-Liquid Behavior in $Ce_{1-x}La_xNi_9Ge_4$

U. Killer,[1] E.-W. Scheidt,[1] G. Eickerling,[1] H. Michor,[2] J. Sereni,[3] Th. Pruschke,[4] and S. Kehrein[5]

[1]*CPM, Institut für Physik, Universität Augsburg, 86135 Augsburg, Germany*
[2]*Institut für Festkörperphysik, TU Wien, 1040 Wien, Austria*
[3]*Centro Atomico Bariloche, 8400 San Carlos de Bariloche, Argentina*
[4]*Institut für Theoretische Physik, Universität Göttingen, 37077 Göttingen, Germany*
[5]*TP III–EKM, Institut für Physik, Universität Augsburg, 86135 Augsburg, Germany*

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We report on specific heat, magnetic susceptibility, and resistivity measurements on the compound $Ce_{1-x}La_xNi_9Ge_4$ for various concentrations ranging from the stoichiometric system with $x = 0$ to the dilute limit $x = 0.95$. Our data reveal single-ion scaling with the Ce concentration and the largest ever recorded value of the electronic specific heat $\Delta c/T \approx 5.5\ \mathrm{J\,K^{-2}\,mol^{-1}}$ at $T = 0.08$ K for the stoichiometric compound $x = 0$ without any trace of magnetic order. While in the doped samples $\Delta c/T$ increases logarithmically below 3 K down to 50 mK, their magnetic susceptibility behaves Fermi-liquid-like below 1 K. These properties make the compound $Ce_{1-x}La_xNi_9Ge_4$ a unique system on the borderline between Fermi-liquid and non-Fermi-liquid physics.

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The investigation of metals with strong correlations among the electrons is a fundamentally important topic in modern solid state physics [1]. Landau's Fermi-liquid theory incorporates the effect of electronic interactions into a renormalized electron mass $m^*$ and is the paradigm for understanding low-temperature properties of metals. Since specific heat and magnetic susceptibility are proportional to $m^*$, a large enhancement of $m^*$ over the free electron mass $m_0$ leads to large values of the specific heat and magnetic susceptibility in the heavy fermion (HF) systems [2]. Measurements of low-temperature specific heat and susceptibility can therefore reveal whether electronic correlations renormalize the Fermi-liquid parameters or lead to non-Fermi-liquid (nFL) behavior [3,4]. The breakdown of Fermi-liquid theory and the borderline between these regimes continues to attract much interest.

In this work we report on specific heat and magnetic susceptibility measurements on the HF compound $CeNi_9Ge_4$ [5] that show pronounced nFL behavior of the specific heat over one-and-a-half decades of temperature. In fact, this Ce-$f$-electron lattice system turns out to have the largest ever recorded value of the electronic specific heat at low temperature: $\Delta c/T \approx 5.5\ \mathrm{J\,K^{-2}\,mol^{-1}}$ at 0.08 K, without showing any trace of magnetic order (only in the magnetic YbBiPt compound a higher $\Delta c/T \approx 8\ \mathrm{J\,K^{-2}\,mol^{-1}}$ is observed [6]). This Sommerfeld coefficient exceeds considerably the values observed in other nonmagnetic (e.g., $CeAl_3$, $CeCu_6$, or $CeCuIn_2$) or magnetic compounds (e.g., $CeAl_2$, $CePb_3$, or $CeAgIn_2$) with $c/T \leq 1.6\ \mathrm{J\,K^{-2}\,mol^{-1}}$ [2,7], and even the $c/T$ value of Ce systems tuned to their critical points (e.g., $CePd_3B$, with $c/T_{T\to 0} \leq 3.38\ \mathrm{J\,K^{-2}\,mol^{-1}}$ [7], $CeCu_xAl_y$, $CeCu_{6-x}Au_x$, $CePd_{1-x}Ni_x$, or $Ce_7Ni_3$ under pressure [8]).

Remarkably, our experiments reveal that the nFL-like logarithmic increase of the electronic specific heat $\Delta c/T$ in $CeNi_9Ge_4$ ($0.3\ \mathrm{K} < T < 1.5\ \mathrm{K}$) is proportional to the Ce concentration in La-substituted samples $Ce_{1-x}La_xNi_9Ge_4$, which suggests that a single-ion effect due to the Ce ions is responsible for the exceptional low-temperature properties of the doped compounds. While these observations preclude collective effects like the vicinity to a quantum phase transition as the cause of this nFL behavior, the low-temperature behavior of $Ce_{1-x}La_xNi_9Ge_4$ also poses a theoretical challenge in the framework of single-ion models: It is difficult to theoretically reconcile the observed nFL behavior in the electronic specific heat with a Fermi-liquid-like behavior of the magnetic susceptibility. The exceptional properties of the compound $Ce_{1-x}La_xNi_9Ge_4$ are therefore not only remarkable from a material science point of view, but also make it an interesting testing ground for theories of strongly correlated electronic systems.

All polycrystalline samples $Ce_{1-x}La_xNi_9Ge_4$ presented in this work were prepared by arc melting of pure elements (Ce, 4N; La, 4N; Ni, 4N7; Ge, 6N) under a highly purified argon atmosphere. To obtain the highest possible homogeneity, the samples were flipped over 4 times and remelted. Subsequently the samples were annealed in an evacuated quartz glass tube for seven days at 1000 °C. Powdered samples were investigated by standard x-ray techniques using Cu $K_\alpha$ radiation. $CeNi_9Ge_4$ crystallizes in a tetragonal structure with space group $I4/mcm$ and lattice parameters $a = 7.9701(1)$ Å and $c = 11.7842(3)$ Å [5]. The coordination of the Ce atoms is depicted in Fig. 1. Each Ce atom has the same threefold tetragonal antiprismatic environment formed by 16 Ni and 8 Ge neighbors. Replacement of the Ce atoms by La leads to a slight volume expansion of about 0.6%. Both lattice parameters follow Vegard's law.

The dc-susceptibility measurements were performed with a commercial SQUID magnetometer for temperatures $1.8\ \mathrm{K} < T < 400\ \mathrm{K}$ and were completed in the low-

  

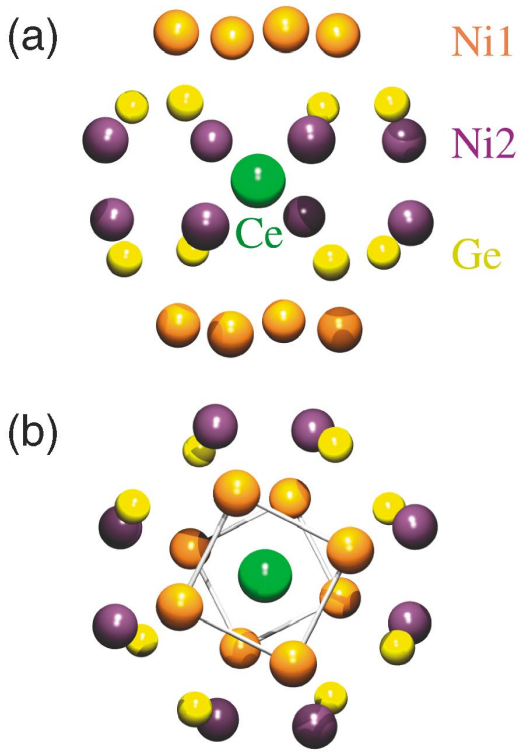


FIG. 1 (color). A simplified representation of the threefold tetragonal antiprismatic environment of Ce: (a) view along the crystallographic $a$ axis; (b) view along the $c$ axis. In (b) the tetragonal faces of the antiprism formed by the eight Ni1 located at the 16$k$ sites are indicated by squares which are rotated against each other by approximately 35°. Notice that the Ni2 and Ge reside at places with the same site symmetry (16$l$) [5].

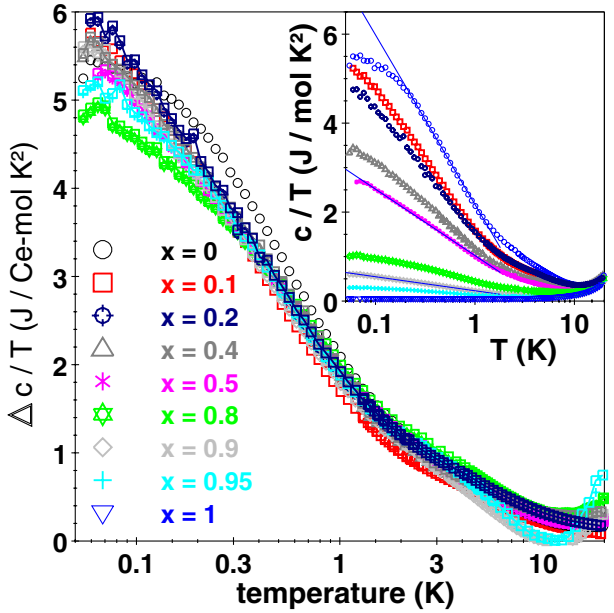


FIG. 2 (color online). The electronic contribution to the specific heat $\Delta c$ of $Ce_{1-x}La_xNi_9Ge_4$ divided by temperature and normalized per mol Ce. The inset shows the specific heat divided by the temperature of $Ce_{1-x}La_xNi_9Ge_4$. The three solid lines represent fits to the data with $c/T = \gamma_0 - a\ln T$ below 1.5 K.

temperature region ($0.03\ \mathrm{K} < T < 2.5\ \mathrm{K}$) by ac-susceptibility measurements in a $^3$He-$^4$He-dilution refrigerator. The specific heat experiments were conducted in noncommercial setups using a standard relaxation method [9] in a conventional $^4$He cryostat ($1.8\ \mathrm{K} < T < 70\ \mathrm{K}$), and in a $^3$He-$^4$He-dilution refrigerator at low temperatures ($0.05\ \mathrm{K} < T < 2.5\ \mathrm{K}$).

The specific heat divided by temperature of $Ce_{1-x}La_xNi_9Ge_4$ (with $x$ ranging between 0 and 1) is displayed in the inset of Fig. 2 in the temperature range $0.05\ \mathrm{K} < T < 20\ \mathrm{K}$. For all La-substituted samples a nearly logarithmic increase of $c/T$ below 1.5 K is observed which is characteristic of nFL physics. Only the nondiluted compound $CeNi_9Ge_4$ deviates noticeably from this logarithmic behavior below 300 mK. Notice that this polycrystalline sample reaches nearly the same value of $5.5\ \mathrm{J\,K^{-2}\,mol^{-1}}$ for the Sommerfeld coefficient at $T = 0.08$ K as observed for single crystals [5].

In order to extract the electronic contribution to the specific heat, we measured the non-$f$-electron system $LaNi_9Ge_4$ from which we derived the lattice vibration contribution. The phonon contribution can be well parametrized using a Debye term and two Einstein modes. In this calculation we fixed the number of internal degrees of freedom to $3 \times 14 = 42$, according to the 14 atoms in the unit cell. The Debye temperature $\Theta_D = 123$ K and two Einstein temperatures $\Theta_E = 187$ and 440 K were calculated with a weight distribution 3:24:15, respectively.

The electronic contribution to the specific heat $\Delta c/T$ was then obtained by subtracting this phonon contribution from the measured $c/T$. The resulting curves $(\Delta c/T)/(1-x)$ normalized per Ce concentration are displayed in Fig. 2. The record value of the electronic Sommerfeld coefficient of nearly $5.5\ \mathrm{J\,K^{-2}\,mol^{-1}}$ is found to be almost Ce-concentration independent. Even the slightly lower values below 0.2 K for $x = 0.8$ and 0.95 are consistent with this value in spite of the large error introduced by dividing the experimental data by the small number $1 - x$. The curves in Fig. 2 provide compelling evidence for scaling behavior with the Ce concentration; only the nondilute compound with $x = 0$ deviates systematically (probably due to collective interactions). This strongly suggests that the low-temperature physics in $Ce_{1-x}La_xNi_9Ge_4$ is governed by single-ion behavior due to the Ce ions.

The logarithmic increase of the Sommerfeld coefficient flattens off and crosses over into Fermi-liquid like behavior in an external magnetic field: such measurements of the specific heat for the compounds with $x = 0$, 0.5, and 0.9 in various applied magnetic fields are depicted in Fig. 3. This confirms a single-ion Kondo-like

scenario with strong electronic correlations due to the magnetic moment of the $Ce^{3+}$ ions.

Measurements of the magnetic susceptibility for various values of the Ce concentration are presented in Fig. 4(b). Similar to the specific heat analysis, we have subtracted the magnetic susceptibility of $LaNi_9Ge_4$; the resulting curves again exhibit single-ion scaling with respect to the Ce concentration. Like the electronic contribution to the specific heat, the local magnetic susceptibility presented in Fig. 4 also shows a large enhancement over the free electron value with a magnitude comparable to the specific heat data. In particular, $\Delta\chi$ also increases logarithmically for temperatures $2\ \mathrm{K} < T < 10\ \mathrm{K}$. However, in marked contrast to the specific heat the local susceptibility $\Delta\chi$ flattens off and becomes constant below 1 K [Fig. 4(a)], while $\Delta c/T$ continues to grow for at least another one-and-a-half decades down to 50 mK [compare, e.g., Fig. 3(c) for $B = 0$]. This discrepancy between the nFL-like behavior of the Sommerfeld coefficient and the Fermi-liquid-like behavior of the magnetic susceptibility is one of the key observations of our work and leads to a strongly temperature-dependent Wilson ratio below 1 K.

Resistivity measurements were performed over four decades at temperatures below 300 K for selected samples (Fig. 5). $LaNi_9Ge_4$ exhibits normal metallic behavior with a residual resistivity of 7 $\mu\Omega$ cm. With increasing Ce concentration a Kondo-like resistivity minimum is formed out, leading to a very high residual resistivity at 30 mK (e.g., 50 $\mu\Omega$ cm for $x = 0.1$). This residual resistivity can be reduced in an external magnetic field (see Fig. 5), which indicates "Kondoesque" magnetic correlations. The electrical resistivity of all the La-substituted samples exhibits single-ion local nFL-like behavior with $\rho(T) - \rho(0) \propto T^c$, $c = 0.8 \pm 0.2$ below 2 K.

The above experimental observations effectively rule out two of the three theoretical routes that are typically invoked for describing nFL-like behavior: vicinity to a quantum phase transition [10] and/or a disorder distribution of Kondo temperatures [11]. (i) A quantum phase transition scenario with collective magnetic excitations does not lead to the observed single-ion scaling in the dilute limit, rather the collective excitations should disappear and the nFL behavior vanish in the dilute limit $x \to 1$. (ii) A Kondo disorder description would imply that the disorder distribution in our compound is essentially unaffected by the dilution, which is physically unrealistic. Also, Kondo disorder models lead to logarithmic behavior in both the Sommerfeld coefficient and the magnetic susceptibility in the same temperature range, which is different from the observations in $Ce_{1-x}La_xNi_9Ge_4$. We therefore propose a local single-ion nFL scenario, which makes $Ce_{1-x}La_xNi_9Ge_4$ with its large value of the Sommerfeld coefficient a unique testing ground for unconventional Kondo models (e.g., two-channel Kondo models) [12,13].

In order to better understand the local physics, we have calculated the entropy based on our specific heat data including higher temperatures. These calculations show that $R\ln 2$ per mol Ce is already reached at about 3 K,

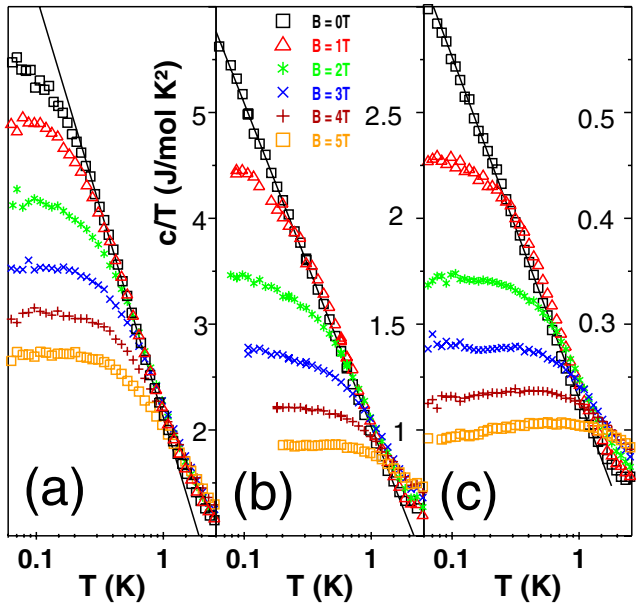


FIG. 3 (color online). The electronic specific heat divided by temperature in various magnetic fields of three particular samples: (a) $CeNi_9Ge_4$, (b) $Ce_{0.5}La_{0.5}Ni_9Ge_4$, and (c) $Ce_{0.1}La_{0.9}Ni_9Ge_4$. The solid lines are logarithmic fits to the zero-field data below 1.5 K.

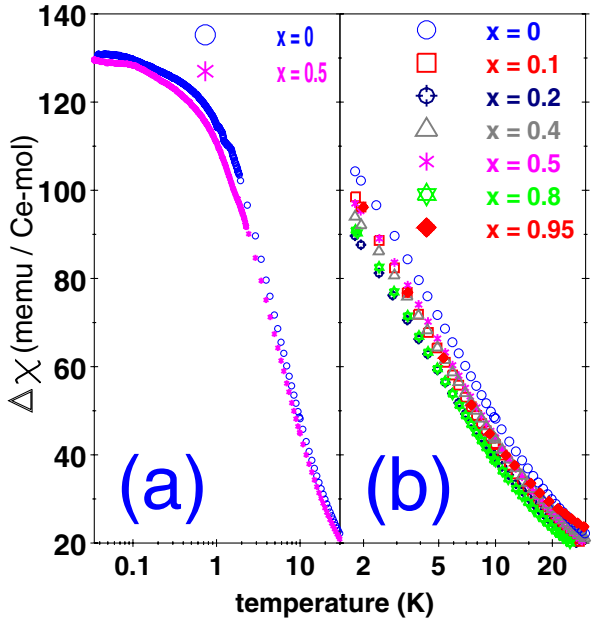


FIG. 4 (color online). The local magnetic susceptibility $\Delta\chi$ of $Ce_{1-x}La_xNi_9Ge_4$ normalized per mol Ce: (a) low-temperature data for samples $x = 0$ and $x = 0.5$ down to 0.03 K obtained by normalizing the ac-susceptibility data (magnetic <0.3 mT) to the dc-susceptibility data between 1.8 and 2.5 K. (b) dc-susceptibility data at 0.5 T for various concentrations $x$.

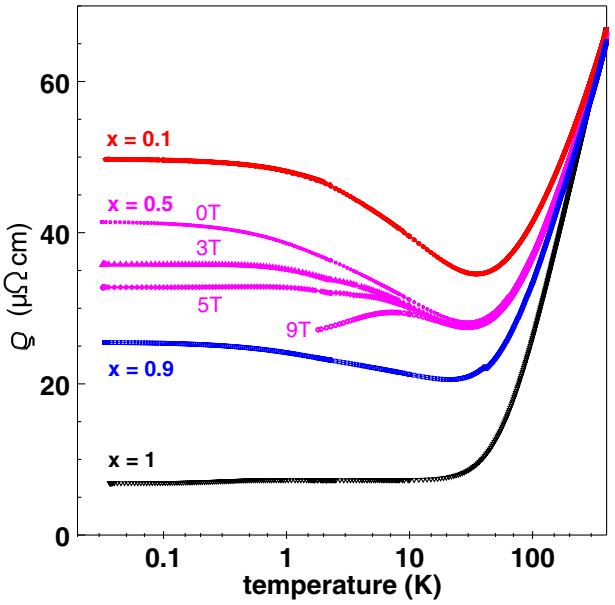


FIG. 5 (color online). The electrical resistivity $\rho(T)$ of various samples normalized to that of $LaNi_9Ge_4$ at 300 K (Vander-Pauw method). The data for $x = 0.5$ show the reduction of the residual resistivity with an external magnetic field.

which signals the participation of more than 2 degrees of freedom per Ce atom relevant for the thermodynamic behavior below $T = 15$ K. A possible origin for this is a ground state quartet of $Ce^{3+}$ that is split into two doublets by the distorted tetragonal antiprismatic crystal field around each Ce atom formed by the Ge and Ni atoms (see Fig. 1). This can lead to an interplay between the Kondo effect and the crystal field splitting on the same energy scale.

This model has been investigated theoretically by Desgranges and Rasul [14]. While the Sommerfeld coefficient always becomes finite (Fermi-liquid-like) for $T \rightarrow 0$ in this model, one can imagine that the Kondo temperature is too small in the $Ce_{1-x}La_xNi_9Ge_4$ system to observe the flattening off in the experimental data. However, the flattening off of the magnetic susceptibility curve below 1 K [Fig. 4(a)] *in contrast* with the increasing $\Delta c/T$ values [see, e.g., Fig. 3(c) for $B = 0$] is very puzzling and difficult to reconcile with a local Fermi-liquid picture: theoretically this behavior can be ruled out for large crystal fields $\Delta_{CF} \gg T_K$ where the low-energy behavior is governed by local Fermi-liquid physics due to an effective conventional spin-1/2 Kondo model. For vanishing crystal field we have performed a four-band numerical renormalization group calculation [15] and found similarly that the Desgranges-Rasul model is incompatible with the observed behavior of $\gamma$ and $\chi$. Unfortunately, no reliable theoretical data for the magnetic susceptibility is available to date for general crystal field splittings between these two limiting cases.

We conclude that while single-ion correlation models are, in general, theoretically well understood, the exceptional behavior of the $Ce_{1-x}La_xNi_9Ge_4$ system cannot easily be explained by any of them. In particular, the non-Fermi-liquid-like behavior of the specific heat in contrast with the Fermi-liquid-like behavior of the magnetic susceptibility below 1 K poses a challenge to theory and seems to rule out standard local Fermi-liquid descriptions. This suggests that the $Ce_{1-x}La_xNi_9Ge_4$ system is in a novel non-Fermi-liquid state that exhibits both non-Fermi-liquid and Fermi-liquid-like properties. A more complex theoretical model, which would incorporate local non-Fermi-liquid physics like the two-channel Kondo model [13] plus low-lying crystal field splittings, might be necessary to describe these remarkable low-temperature properties. Of particular interest are also the additional collective effects below 300 mK in the nondilute compound ($x = 0$). Further investigations of $Ce_{1-x}La_xNi_9Ge_4$ with its record value of the specific heat could be a key to gaining a better understanding of this borderline between Fermi-liquid and non-Fermi-liquid physics.

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